Preparation and Characterization of Polypropylene Based Composite Films

By

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ABSTRACT

In the scope of this study, preparation of silver – natural zeolite reinforced polypropylene (PP) composite system possessing antibacterial properties via ion exchange process and characterization by means of different techniques (FTIR, TGA, DSC, mechanical tests, optical microscopy) were aimed. It has been established that zeolites are suitable for removing Ag ions from silver containing solutions and that silver zeolites are increasingly investigated as germicidal, bactericidal, antifungal, and antiseptic components in different compositions (Hagiwara 1990, Kawahara 2000, Klasen 2000).

In the present study, prior to the ion exchange studies, water sorption behavior of PP – clinoptilolite rich natural zeolite composites was investigated, since the ion exchange process was to be conducted in aqueous media. It was observed that a hydrophobic polymer, PP attained the property of water sorption due to the porous structure of the composite films. The effective diffusivity of liquid water in the PP – zeolite composites prepared by hot press and extrusion techniques varied in the range of 0.3 – 9.9 $x10^{-10}$ and 0.1 – 3.3 $x10^{-12}$ cm^2/s, respectively. Silver loading to PP - zeolite composites was provided by means of two different methods. In Method I, PP - zeolite composite films were treated with a variety of silver ion containing solutions (5 to 50 ppm $AgNO_3$ solution), whereas in Method II silver exchanged zeolite minerals (prepared with initial $AgNO_3$ concentrations of 50, 500, and 5000 ppm) were molded with PP in the presence of DOP (Dioctyl Phthalate). The amounts of Ag^+ loaded per gram of zeolite for initial $AgNO_3$ concentrations of 50, 500, and 5000 ppm were determined as 4.36, 27.85, and 183.78 mg, respectively. Antibacterial activity tests against *E.coli* indicated that the samples obtained in Method II were superior to those prepared by Method I since the penetration of silver ions to the zeolite phase was limited by the PP phase in the case of Method I. However, the discoloring effect of silver ion was readily observed for the samples prepared by Method II as indicated by the discoloration parameters. The release of Ag^+ to water was found to be negligible as reported in literature leading to long – term antibacterial activity.

The thermal characterization studies showed that the addition of the zeolite increased the crystallinity of the structure acting as a nucleating agent in PP crystallization as well as retarded the degradation temperature of PP. At low silver

concentrations, the zeolite behaved as a decelerating agent in PP, however at higher silver concentrations, the composites degraded at a faster rate than pure PP. Yet the activation energy values for the thermal decomposition reactions of Method II was considerably lower indicating that the decomposition has been accelerated by the presence of silver.

It was found that the addition of the zeolite into the PP matrix decreased the density of pure PP (0.89 g/cm^3) due to the formation of voids. However, a systematic approach was not observed with the increasing zeolite content as a consequence of the uneven zeolite distribution. On the other hand, a considerable enhancement was noticed for the tensile tested film densities changing between 0.58 – 0.78 g/cm^3, which are in a better agreement with the commercially desired range (0.6 – 0.65 g/cm^3) for packaging applications of PP composites. Mechanical tests indicated that the addition of the zeolite tended to decrease the yield stress values while a slight decrease was observed for Young moduli. The effect of silver on the Young Modulus values of the composites is not quite significant, however the yield stress values increased from 23.6 to 29.5 MPa with the increasing silver concentration.

Consequently, of all the composite films prepared by Method II, the ones loaded with 4.36 (mg Ag^+/g zeolite) containing 2, and 4 % wt zeolite were selected to be the most appropriate, considering the thermal, mechanical, and structural characteristics as well as the discoloring actions.

ÖZ

Bu çalışma kapsamında, polipropilen (PP) ile gümüş yüklü doğal zeolitten oluşan antibakteriyel kompozitlerin ekstrüzyon yöntemi ile geliştirilmesi ve farklı teknikler kullanılarak (FTIR, TGA, DSC, mekanik testler, optik mikroskop) karakterize edilmesi amaçlanmıştır. Zeolitlerin gümüş iyonu içeren çözeltilerden gümüşün uzaklaştırılmasında uygun oldukları saptanmış olup son zamanlarda gümüş formundaki zeolitlerin değişik kompozisyonlarda antifungal, bakteriyel ve antiseptik davranışları ilgiyle incelenmektedir (Hagiwara 1990, Kawahara 2000, Klasen 2000).

Bu çalışmada, iyon değişimi denemelerine öncelikle, klinoptilolitçe zengin doğal zeolit – PP kompozitlerin su sorpsiyonu davranışı incelenmiştir. İyon değişimi işlemi sulu bir ortamda gerçekleşeceğinden kompozit malzemelerin bu ortamda nasıl davrandığı gözlenmiş ve hidrofobik bir malzeme olan polipropilenin oluşan gözenekli yapıya bağlı olarak su çekme özelliği kazandığı görülmüştür. Suyun sıcak pres ve ekstrüzyon metodu ile hazırlanmış PP – zeolit kompozitlerdeki etkin difüzyon katsayısı sırasıyla $0.3 – 9.9 \times 10^{-10}$ ve $0.1 – 3.3 \times 10^{-12}$ cm^2/s aralığında değişmektedir. PP – zeolit kompozitlere gümüş yüklemesi iki metotla gerçekleştirilmiştir. Metot I de PP – zeolit kompozit filmler farklı miktarlarda gümüş iyonu içeren (5 – 50 ppm $AgNO_3$) çözeltilerle muamele edilmiş, Metot II de ise farklı gümüş derişimlerindeki (50, 500, ve 5000 ppm $AgNO_3$) çözeltilerle iyon değişimine tabi tutulmuş zeolit mineralleri DOP ortamında PP ile kalıplanmıştır. İyon değişimi prosesinde 50, 500, ve 5000 ppm Ag^+ içeren çözeltilerden gram zeolit başına yüklenen gümüş miktarı sırasıyla 4.36, 27.85, ve 183.78 mg olmuştur. *E. coli* ye karşı yapılan antibakteriyel testler Metot II ile hazırlanmış kompozitlerin Metot I e göre hazırlananlardan daha iyi sonuç verdiğini göstermiştir. Bu da Metot I ile hazırlanan kompozitlerde gümüşün zeolite ulaşmasının PP fazı tarafından engellenmesinden kaynaklanmıştır. Ancak, Metot II ile hazırlanan örneklerde gümüşün renk üzerindeki etkisi renk bozunma parametrelerinde de görüldüğü gibi gözle görülebilir seviyede olmuştur. Gümüş iyonunun suya geri salınımı ise literatürde de belirtildiği gibi ihmal edilebilir düzeydedir ki bu da antibakteriyel etkinin uzun ömürlü olmasını sağlamaktadır.

Termal karakterizasyon çalışmaları zeolitin aşı kristali gibi davranarak yapıdaki kristallik oranını arttırdığını ve PP'nin bozunmasını geciktirdiğini göstermektedir. Düşük gümüş derişimlerinde, zeolit PP içerisinde yavaşlatıcı etki yaparken yüksek

gümüş derişimlerinde ise bozunmayı hızlandırmıştır. Metot II ile hazırlanmış örneklerde termal bozunma reaksiyonlarının aktivasyon enerjilerinin Metot I'e kıyasla daha düşük olması da zeolitin ve dolayısıyla artan gümüş miktarının bozunmayı hızlandırdığını göstermektedir.

PP fazına zeolitin eklenmesi ile PP'nin 0.89 g/cm^3 olan yoğunluğunda yapıda oluşan boşluklardan dolayı azalma gözlemlenmiştir. Ancak, bu oranlar zeolitin PP fazında düzensiz dağılmış olmasından dolayı artan zeolit miktarına bağlı olarak sistematik bir değişim göstermemektedir. Gerdirilmiş filmlerde ise 0.58 ile 0.78 g/cm^3 arasında değişen yoğunlukların ticari olarak istenen aralıkla (0.6 – 0.65 g/cm^3) daha uyumlu olduğu görülmüştür. Mekanik testler, zeolitin ilavesi ile yapının akma geriliminin düştüğünü, Young modül değerlerinin ise ihmal edilebilir derecede azaldığını göstermektedir. Gümüş iyonunun ise Young modülü üzerindeki etkisi belirsiz iken akma gerilimi değerleri gümüş miktarı ile orantılı olarak 23.6 MPa dan 29.5 MPa'a artmıştır.

Sonuç olarak, Metot II ile hazırlanmış kompozitler içerisinde 4.36 (mg Ag^+/ g zeolite) ile yüklenmiş ve ağırlıkça % 2 ve 4 zeolitin içerenlerin termal, mekanik, yapısal özellikleri ve renk bozunma parametreleri göz önüne alındığında en uygun oldukları saptanmıştır.

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Chapter 1

INTRODUCTION

The development of a new science and art such as that of composites occurred at irregular intervals over a period of years, and such developments are continuing and will continue in the future.

Polymer composites are materials comprising of polymers as matrix materials, surrounding very small reinforcing fibers and or fillers. The idea behind the production of a composite material is to yield superior characteristics than that of the individual components making up the composite. That is, the individual advantages of different materials are being combined to be used in different applications.

Polymers are the most widely used matrix materials compared with ceramic or metal matrices mainly because they are easy to handle and process. Glass fibers, carbon fibers, and particulate fillers can be used as reinforcing materials. The primary advantages of polymeric composites can be listed as increase in stiffness, strength, and dimensional stability, reduced permeability to gases and liquids, and reduced cost.

Polypropylene (PP) is among the most widely exploited thermoplastic polymers and is of increasing practical importance because of its good comprehensive use, light weight (0.9 g / cc), chemical resistance, low cost, ease of processing, and recycling properties. It finds various application fields depending upon these properties such as; food packaging, medical delivery systems, carpets, fibers, protective coating, automobile, electrical and furniture industries. Some of the applications of PP appeared because no other plastic resin was capable of performing. Most applications, however, evolved over time as PP demonstrated improved economics or enhanced performance over other thermoplastic polymers, that it has become the polymer of choice. Still, some of the applications are limited to some extent due to certain drawbacks (Moore, 1996).

To improve the mechanical properties of PP such as impact toughness, strength, hardness, and the like, extensive studies on improving the mechanical properties using particulate fillers into the polymer matrices have been carried out in the last twenty years. Among the particulate fillers, talc, mica, calcium carbonate are the most used ones.

Levita et al. (1989) studied the strength and fracture properties of polypropylene filled with calcium carbonate. Untreated and surface treated (stearic acid, and titanate coupling agent) grades have been considered. The untreated filler caused a decrease of toughness whereas a maximum at ~10 % increase was observed for the treated filler.

Maiti et al. (1992) studied the tensile and impact properties of talc-filled isotactic polypropylene composites. Tensile strength and breaking strain decreased while tensile modulus increased with filler content. Surface treatment of talc with a titanate-coupling agent modified the composite properties further. Interphase interaction increased, which in turn increased the tensile modulus over the values with unmodified talc.

Liang et al. (1998) studied the effects of filler content and size on the mechanical properties such as tensile modulus, yield strength, and impact strength of glass bead – filled polypropylene composites. With the increasing filler content, elastic modulus, and impact strength increased whereas yield strength decreased non-linearly. The results showed that the stiffness, and the toughness of the composites were effectively improved by the addition of glass beads.

In recent studies, different types of zeolite minerals; either natural (clinoptilolite, mordenite, chabazite), or synthetic (A- type, X- type, Y - type) are being employed as particulate fillers. All commercial zeolites owe their value to one of the following properties: ion exchange, adsorption, and catalysis. They have unusual crystalline structures that give them unique chemical properties. For instance, in one gram of natural zeolite, the channels can provide up to several hundreds of square meters of surface area on which chemical reactions can take place. Natural zeolites can also absorb up to 30% of its dry weight of gases such as nitrogen or ammonia. Studies are reported on the removal of lead, silver, and cadmium by clinoptilolite in the presence of competing concentrations of calcium, magnesium, and sodium via ion exchange process (Semmens et al. 1979). It has been established that zeolites are suitable for removing Ag ions from silver containing solutions.

Silver zeolites are increasingly investigated as germicidal, bactericidal, antifungal, and antiseptic components in different compositions (Kawahara, 2000). Since the growth of pathogenic microorganisms and their penetration into the body is the main problem, studies were being established for an antiseptic agent to prevent invasive infection. Klasen (2000)

investigated the silver as a source of antiseptic agent. Silver salts appeared to meet the requirements to be considered as an antiseptic agent. It was thought that this antibacterial activity was caused by adsorption of silver into the microorganisms. But then it was reported that there was the case that the microorganisms loose the ability of colony forming without adsorption of silver. In this case, silver was incorporated in the inorganic compound not in the solution freely. Recently the modification of inorganic compound by the addition of silver became attractive to protect the circumstances from the diseases originating from microorganisms.

Metallic silver also finds application areas in dentistry. Ionic silver has the highest antibacterial activity among metal ions and a variety of silver compounds have been used as topically applied agents for treatment of burns and ocular infections (Kawahara, 2000).

Although an extensive amount of work has been done related with polypropylene based composite systems, most of the studies were conducted with calcium carbonate, talc, or mica and not much work is cited with zeolite as a filling material. Özmıhçı (1999) investigated the preparation and characterization of natural zeolite – polypropylene composites. In the so called study, PEG 4000 (Polyethylene Glycol) was selected as the surface modification material among different materials, which were calcium stearate, and stearic acid because in the case of PEG 4000, the agglomerates of the zeolite particles were broken into smaller particles to a higher extent than the other modification materials. Dirim (2000) studied the manufacture of a new protective polyethylene based film containing natural zeolite for food packaging. In the scope of the present study, preparation and characterization of silver- zeolite reinforced polypropylene; a composite system possessing antibacterial properties is aimed.

In this thesis, preparation and characterization of polypropylene - silver ion exchanged natural zeolite – PP composites are outlined. Chapter 2 presents general information on polymer composites and introduces the matrix and the filler to be used in this study. In Chapter 3, ion exchange process in connection with natural zeolite is discussed. Chapter 4 deals with sorption and diffusion phenomena in polymers. In Chapter 5 the characterization methodology used for the polymers is given. Chapter 6 presents information related with the microbiological aspects of this study. In Chapter 7 and 8, the experimental of this study, the materials and the methods, followed by the results and

discussions are given. Finally, Chapter 9 presents an over review of the work with the possible recommendations for future studies, highlighting the final results.

Chapter 2

POLYMER COMPOSITES

Composite materials may be defined as materials made up of two or more components and consisting of two or more phases. Such materials must be heterogeneous at least on a microscopic level.

There is no really adequate definition of a composite material, but there are three major points to be included in a definition of an acceptable composite material.

(i) It consists of two or more physically distinct and mechanically separable materials

(ii) It can be prepared by mixing the separate materials in such a way that the dispersion of one material in the other can be done in a controlled way to achieve optimum properties.

(iii) The properties are superior, and possibly unique in some specific respects, to the properties of the individual components.

Composite materials may be divided into three general categories: (1) particulate – filled materials consisting of a continuous matrix phase and a discontinuous filler phase made up of discrete particles, (2) fiber – filled composites, and (3) skeletal or interpenetrating network composites consisting of two continuous phases (Nielsen et al., 1974).

The rapid growth of the composite materials has been achieved mainly by the replacement of traditional materials, primarily metals. This suggests that, in some respects, composite materials have superior properties.

The properties of the composites are determined by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the nature of the interface between the phases (Nielsen et al., 1974). Hence, by combining the individual advantages of the components, composites with superior characteristics can be obtained.

Many commercial polymeric materials are composites, although they are often not considered as such. Examples include polyblends and ABS materials, foams, filled poly (vinyl chloride) formulations used in such applications as floor tile and wire coatings, filled rubbers, thermosetting resins containing a great variety of fillers, and glass or graphite fiber – filled plastics. The reasons for using composite materials rather than the simpler homogeneous polymers can be listed as follows: (Nielsen, 1974).

(i) Increased stiffness, strength, and dimensional stability
(ii) Increased toughness or impact strength
(iii) Increased heat distortion temperature
(iv) Reduced permeability to gases and liquids
(v) Modified electrical properties
(vi) Reduced cost.

In the present study, polypropylene was used as the matrix material while clinoptilolite; a natural zeolitic tuff was employed as the filling material.

2.1 Matrices

2.1.1 Polypropylene

Polypropylene (PP) is among the most widely used thermoplastic polymers and of increasing practical importance because of its comprehensive use, low cost, ease of processing and recycling. It has various application areas such as packaging, protective coating, automobile, electrical and furniture industries.

PP can be synthesized by the Ziegler – Natta polymerization (coordination polymerization) using metallocene catalyst.

The two most critical features of a base polypropylene are its molecular weight and its tacticity (polymer - chain configuration). Molecular weight has the strongest influence on processing characteristics, and the main effect of tacticity is to determine physical properties.

Polymers with ordered spatial distribution of chain links are called *stereoregular*, whereas those with a random spatial distribution are called *atactic*. The relative contents of the stereoregular and the atactic fraction of polypropylene, which determine to a large extent the properties of the polymer, will depend on the identity of the catalyst and on the conditions of the polymerization. Catalysts on the basis of $TiCl_3$ and alkyl aluminum halide, which contain electron-donating additives such as pyridine are highly stereospecific and yield a polypropylene, which is almost totally crystalline. If the polymerization temperature is decreased, the content of the stereoregular fraction increases.

The propylene molecule is composed of 3 C atoms and 6 H atoms and possesses one double bond. The double bond is the site for initiation of the polymerization reaction. The third carbon atom is the feature that allows the formation of the various possible chain structures.

The crystallizability of the chain is a critical factor controlling the resultant morphology. The degree of crystallinity of polypropylene homopolymer is governed primarily by the tacticity of the chain. Isotactic chains result from the head - to - tail addition of propylene monomer units, where the methyl groups always have the same configuration with respect to the polymer backbone. Syndiotactic chains result from the same head - to - tail addition of monomer units, but the methyl groups have an alternating configuration with respect to the polymer backbone. Atactic chains do not have any consistent placement of the methyl groups. Figure 2.1 shows a schematic of isotactic, syndiotactic, and atactic polypropylene chains (Moore, 1996).

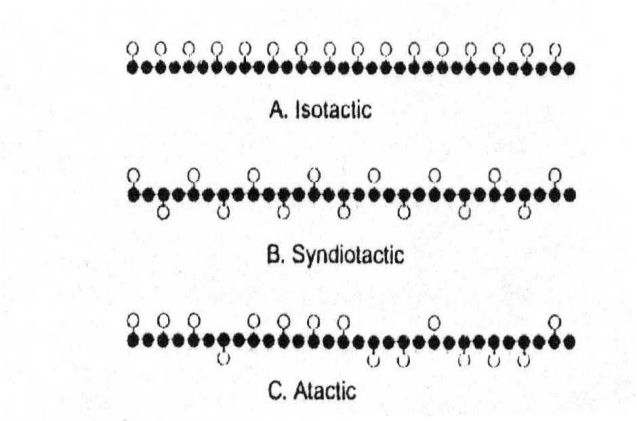


Figure 2.1.Schematic illustrations of the stereochemical configurations of PP:

A) Isotactic PP, B) syndiotactic PP, C) atactic PP

The properties of the polypropylene making it valuable can be listed as follows: (Moore, 1996).

- Fairly low physical properties
- Fairly low heat resistance
- Excellent chemical resistance
- Translucent to opaque
- Low price
- Easy to process

The nature of polypropylene is that of a high molecular weight organic material. Its semi crystalline form is enabled by the regularity of the polymer chain. It typically combines mechanical strength, stiffness, high softening point, and low density. The drawbacks of polypropylene include embrittlement at low temperatures and poor resistance to oxidants, heat and UV radiation (Moore, 1996).

Since polypropylene and its derivatives (blends and copolymers) are very susceptible to thermal and light induced oxidation, it is indispensable to stabilize any polypropylene based product in order to guarantee long – term performance. For this purpose, a variety of stabilizing additives has been developed. Processing stabilizers protect the polymer during compounding. Antioxidants and light stabilizers are added to minimize the damaging effects of heat and light in the surface.

2.2 Fillers

Fillers have been used in natural rubber, paints, and celluloid for over a century. The first large-scale use was the reinforcements of phenolic resins by attrition ground wood (wood flour) by Baekeland in the early 1900s. As in the case with Bakelite, the filler increases hardness and mechanical properties and reduces shrinkage but usually increases the specific gravity of the composite (Seymour, 1990).

The term ‘reinforcement’ is used to denote the increase in rigidity and strength achieved by dispersing inorganic fibers or particulate fillers in the polymer matrix (Mascia, 1982).

Filler particle morphology must be considered in the design of a polymeric composite since nonresinious particles obstruct resin flow. The resistance to flow is greater for composites with acicular (needle like) particles than for those with more regular shapes, such as spheres. The particle shape is related to its length to diameter or aspect ratio. The term ‘loading’ is used to describe the concentration of fillers present in a composite.

Some fillers such as carbon black, and surface-treated fillers, are actually bonded to the macromolecular chains in the matrix. Others may be considered as non-reactive fillers but they do immobilize the polymer chains as attested by an increase in glass transition temperature (Tg). However, the non-reactive fillers have less effect than most reactive fillers on modulus and heat deflection temperature of the composites.

Fillers have been classified in accordance with source, function and importance. The use of properly selected fillers extends the resin supply, and the use of coupling agents with these composites improves performance of plastics and reduces costs and energy consumption. The most widely used particulate fillers depending on the needs can be listed as follows: calcium carbonate, kaolin, silica, talc, mica, alumina, carbon black, clay, and zeolite.

Levita et al. (1989) used calcium carbonate, Rochette et al. (1988) used mica, and Alonso et al. (1997) used talc as with polypropylene for different purposes.

2.2.1 Zeolites

Zeolites are framework silicates consisting of interlocking tetrahedra of SiO_4 and AlO_4. Unlike most other framework silicates, zeolites have large vacant species in their structures that allow space for large cations such as sodium, and calcium ions to reside with water molecules. The species can be interconnected and form channels of varying sizes depending on the mineral (Dyer, 1984). Compositionally, zeolite is similar to clay minerals in that both are alumino – silicates. They differ, however, in their crystal structure. Clay

has a layered structure (similar to a deck of cards) and is subject to shrinking and swelling as water is absorbed and desorbed between the layers.

Zeolites, on the other hand, have a rigid 3 dimensional crystal structure (like a honeycomb) consisting of a network of interconnected tunnels and cages. Water can move in and out of these pores, but the zeolite framework remains rigid. The structure creates molecular sized channels, and pores that are host to loosely attached molecules of water and ions of Na, K, or Ca. The ions can be exchanged for other present ions in the environment. Uniform pore or channel sizes allow the crystal to act as a molecular sieve, admitting certain molecules of gasses or liquids into the crystal while rejecting others based upon their molecular size. Physical and chemical properties of zeolites vary among zeolite types. The differences are primarily due to differences in crystal structure, and chemical composition. Properties such as particle density, theoretical CEC (Cation exchange capacity), cation selectivity, void volume, molecular pore size, and crystal shape vary depending on the zeolite type under consideration.

Physical and chemical properties also vary for zeolites of the same type (from different sources) usually determined by the environmental conditions. One important difference between zeolites is the composition of the exchangeable cations residing in the zeolite. Exchange sites on natural zeolites are predominantly occupied by 3 major cations: K, Ca, and Na. Frequently a small amount of Mg is also present. The empirical formula of zeolite is:

$xM_{2/n}\,O.Al_2O_3.\,ySiO_2.\,zH_2O$

M- exchangeable ion

n- atomic valency of metal ion

x,y-coefficients of metal oxide and silica respectively

z-number of water of crystallization

The unusual crystalline structure of zeolites provides them unique properties. In one gram of zeolite, several hundred square meters of surface area may be present on which chemical reactions can occur. Natural zeolites can absorb up to 30% of their dry weight of gases such as nitrogen or ammonia. The schematic of the natural zeolite structure is shown in Figure 2.2. The primary-building units combine to form the secondary-building units, which the zeolite structure is comprised of.

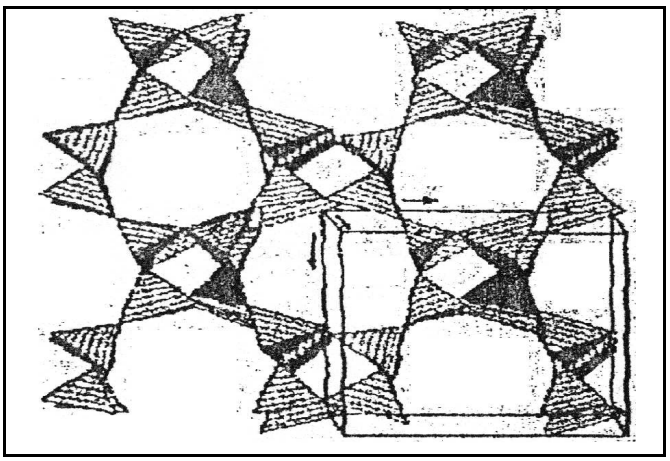


Figure 2.2. The Structure of Zeolite.

Clinoptilolite, a rare hydrothermal mineral, genesis of hydrological closed system like a saline, alkaline lake is very common and has been investigated in many times. Idealized chemical formula of clinoptilolite is $(Na, K)_6 (Al_6Si_{30}O_{72}) 20H_2O$ & Ca, K, & Mg may also be present in the clinoptilolite content. Si / Al ratio varies along 4.25 – 5.25 and the density is about 2.16 g/cc (Gottardi and Galli, 1985). Clinoptilolite containing plenty of potassium, is called as kaliclinoptilolite. It has strong ability to NH_4. Most of the components of clinoptilolite are Na, and K; the content of Ca is less than that of Na and K. Clinoptilolite is colorless or white. It is transparent to translucent.

Zeolites can be modified in many ways to become active gaseous adsorbents, to remove or concentrate gaseous pollutants, act as catalyst in chemical manufacturing, serve as fillers for composite paper, rubber, plastics or ceramics, to produce specialty low density concrete products, animal feed supplements and scores of other uses. In recent studies silver form of natural zeolites are being investigated as antibacterial agents to be used in various applications (Hagiwara 1990, Kawahara 2000, Klasen 2000, Olguin 2000).

2.3 Surface Modification

Surface modification of fillers is essential to give improved properties to plastics. A wide range of surface modifiers are offered and used commercially, ranging from the inexpensive fatty acids to silanes, titanates and zirconates. All treatments in commercial use

are chosen to bond an organic molecule chemically to the filler surface. The most common functionalities used to produce bonding with the filler surface are acids or acid precursors, and alkoxysilanes. Improvements in mechanical properties, dispersion of the filler (leading to improved properties), improved rheology and higher filling loading have all been reported to accrue from rendering the surface more hydrophobic and hence compatible with the polymer or by enabling the filler to bond covalently, through hydrogen or ionic bonds to the polymer; or by changing the physical nature of the interface so that energy absorption can occur.

It is generally accepted that besides the dimensions, shape and modulus of the reinforcement filler, the adhesion between the particle and the polymeric matrix plays a basic role on the stiffness and toughness of the material When the organic molecule is a simple hydrocarbon, then the coating will generally aid filler incorporation and dispersion, but does not form a strong bond with the polymer matrix. If strong bonding is required, then a further functionality capable of forming a covalent bond with the matrix is also incorporated into the coating molecule. These biofunctional coatings are generally known as 'coupling agents' because of their ability to chemically couple the filler to the matrix polymer (Alonso et al. 1997, Hancock et al. 1995).

Ulutan and Balköse (1997) studied the interfacial enhancement of flexible PVC – silica composites by the application of γ - aminopropyl trimethoxysilane on silica. Silane application resulted in diminishing liquid water and water vapor sorption by about 24 % and 11.9 % respectively.

Xavier and Schultz (1990) studied the influence of mica surface treatments in polypropylene composites. They used isopropyl triisostearoyl titanate (TTS) and 3 - aminopropyl triethoxysilane and investigated the effect of surface treatment on the microstructure and fracture propagation in the composites. Improved interfacial adhesion was observed in the case of silane treated mica composites.

Rochette et al. (1998) studied the rheological properties of mica filled polypropylene composites. The effect of mica concentration and of a silane-coupling agent on material functions such as the complex viscosity, the storage modulus, and the loss modulus was examined. The affinity of PP for the treated and non-treated mica was characterized. It was observed that for low mica concentrations, the composite exhibits the

classical viscoelastic behavior of a homogeneous material. For higher mica concentration, the material showed a strong heterogeneity. It was also found that the presence of a silane-coupling agent moves this critical concentration value up to 40 % by weight. Interactions between mica particles are promoted when there is no surface treatment resulting in the formation of aggregation of mica flakes. The presence of a coupling agent improves the homogeneity of the composite, its elastic modulus, and increases the affinity of PP for mica.

Alanso et al. (1997) studied the crystallization and activity of filler in surface modified talc polypropylene composites. They concluded that in injected samples the original treated talc produces a sensible effect of orientation on the matrix structure. The interaction between filler and matrix was appreciably higher when the talc has been functionalized.

Mitsuishi et al. (1995) investigated the crystallization behavior of polypropylene filled with surface- modified calcium carbonate. Alkyl dihydrogen phosphates were used to improve the affinity of the relation between $CaCO_3$ and the PP matrix.

In literature much more studies were conducted especially about the surface modified calcium carbonate polypropylene composites performed with different modifiers. For instance, Akovalı and Akman (1997) modified calcium carbonate by plasma – polymerized acetylene, Demjen and Pukanszky (1997) used eight different trialkoxy functional silane-coupling agents and the routinely used stearic acid for comparison.

2.4 Additives

In addition to the fillers, and reinforcements, used in polymer composites, there are also many functional additives used with or without fillers to improve the useful properties of polymers. Some examples to these additives can be listed as antiblocking agents, antifoaming agents, accelerators, antioxidants, antimicrobials, blowing agents, colorants, coupling agents, flame retardants, heat stabilizers, lubricants, plasticizers, odorants, and the like.

2.4.1 Antimicrobial Agents

The term ‘antimicrobial’ or ‘biocide’ includes algicides, bactericides, bacteriostats, fungicides, and germicides, etc. Nowadays, different methods for antimicrobial property are increasingly investigated. Main antimicrobial agents currently under investigation or in use include natural antibacterial agents such as chitin, chitisan, tea extracts, inorganic compounds such as titanium oxide particles, zinc oxide, silver containing zeolite, and synthetic antibacterial agents such as organic ammonium salt compounds (Barry et al. 2000, Niira et al. 1990, Kawahara et al. 2000, Olguin et al. 2000).

Natural antibacterial agents and inorganic antibacterial agents, typically silver are now attracting attention in review of their safety from toxicity.

In recent years, antibacterial goods, having an inorganic and / or antibacterial agent incorporated therein or applied are becoming available in the market; such as used in wall carpeting, rugs, antibacterial fabric and fiber production, antibacterial film and the like.

2.4.2 Plasticizers

A relatively small amount of external plasticizers is used to improve the flexibility of cellulose esters and acrylics but the major use is for the plasticization of PVC. Small amounts of plasticizers will actually increase the modulus (stiffness) of PVC and this effect is called antiplasticization (Seymour, 1990).

According to the viscosity theory, developed by Leitech in 1943, plasticizers function by modifying the rheological properties of polymers and thus, those having low temperature coefficients of viscosity have mechanical and electrical properties that are less sensitive to temperature.

According to lubricity theory, the plasticizer reduced the intermolecular friction between the polymer chains and allows the macromolecules to slide by each other. Another theory, i.e., the free volume theory, assumes that movement of polymer chains is dependent on the movement of chain segments into the free space between the molecules. The free volume is increased by the addition of plasticizers; thus, the ease of segment mobility is increased and the glass transition temperature (Tg) is reduced.

The addition of plasticizer also lowers the hardness, modulus, and tensile strength of a polymer. Thus, plasticizer efficiency may be estimated by comparing the amount of additive required to achieve a specified tensile modulus at room temperature.

Phthalates account for almost 70 % of all plasticizers used. The phthalate plasticizers include (di (2-ethyhexyl) phthalate (DOP), diisooctyl phthalate (DIOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DINP). The volatility of these phthalates decreases as the size of the alcohol group increases.

In this study, silver nitrate was used as a source of silver ion for its antimicrobial activity and dioctyl phthalate (DOP) was used as a plasticizer.

Chapter 3

ION EXCHANGE

3.1 Ion Exchange Mechanism

Ion exchange basically is a chemical reaction between ions in solution and ions in an insoluble phase. In ion exchange, certain ions are removed by the ion exchange solid, since electroneutrality must be maintained, the solid releases ions to the solution.

Ion exchangers, by common definition, are insoluble solid materials, which carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers, and carriers of anion exchangers, anion exchangers. Certain materials are capable of both cation and anion exchange. These are called amphoteric ion exchangers.

A typical cation exchange is:

$$2\,\underline{NaX} + CaCl_2\,(aq) \rightleftharpoons \underline{CaX_2} + 2Na\,Cl\,(aq)$$

A typical anion exchange is:

$$2\,\underline{XCl} + Na_2SO_4\,(aq) \rightleftharpoons \underline{X_2SO_4} + 2NaCl\,(aq)$$

X represents a structural unit of the ion exchanger; solid phases are underlined; aq indicates that the electrolyte is in aqueous solution.

Ion exchange resembles sorption in that, in both cases a dissolved species is taken up by a solid. The characteristic difference between the two phenomena is that ion exchange, in contrast to sorption, is a stoichiometric process. Each ion, which is removed from the solution, is replaced by an equivalent amount of another ionic species of the same sign. In sorption, on the other hand, a solute (an electrolyte or nonelectrolyte) is taken up

without being replaced by another species. That is, adsorption is the enrichment of one or more components in an interfacial layer (adsorbent surface + adsorption space), and it may also be used to denote the process in which adsorptive molecules are transferred to and accumulated in the interfacial layer (Helfferich, 1962).

Ion exchangers owe their characteristic properties to a peculiar feature of their structure. They consist of a framework, which is held together by chemical bonds or lattice energy. This framework carries a (+) or (-) electric surplus charge which is compensated by ions of opposite sign, the counter ions. They are free to move within the framework and can be replaced by other ions of the same sign. The counter - ion content of the ion exchanger - the so-called ion exchange capacity - is a constant, which is given solely by the magnitude of the framework charge and is independent of the nature of the counter- ion.

As a rule the pores are occupied not only by counter ions but also by solvent and solutes, which can enter the pores when the ion exchanger is in contact with a solution.

3.2 Ion Exchange in Zeolites

Various alumosilicate minerals with cation – exchange properties are known. Among the different alternative ion exchangers; zeolites have some advantages compared with the conventional organic resin types. They have a rigid 3 dimensional framework structure with cavities and channels in which the counter ions can move.

The primary features of zeolites can be listed as: (Alsoy, 1992).

1) They consist of uniform molecular sized channels and cavities through which cations diffuse in order to undergo exchange in sites, within the crystal.
2) Most zeolites do not undergo any appreciable dimensional change with ion exchange due to their 3 dimensional framework structure.
3) The aluminum content, that is the number of tetrahedrally oriented aluminum atoms per unit cell of framework, defines the maximum number of (-) charges available to cations.

4) Ion selectivity shown by specific zeolites for one cation over another is unusual and does not follow the typical rules that can be shown by other inorganic and organic exchangers.

The cation exchange behavior of zeolites depends upon:

1) Nature of cation species, cation size, and cation charge
2) Temperature
3) Concentration of cation species in solution
4) Anion species associated with the cation in solution
5) The solvent
6) The structural characteristics

The capacity of ion exchangers is defined in terms of the number of inorganic groups in the material and is usually given in milliequivalents per gram of dry H^+ form or Cl^- form of the resin, or per milliliter of swollen resin bed. The capacity, when defined in this way, is a characteristic constant of the material. The common ion - exchange resins have capacities between 2 and 10 meq. /g (Helfferich, 1962).

Ion exchangers can distinguish between different counter ions. When counter ions are exchanged, the ion exchanger usually takes up or retains counter ions in preference to others. This selectivity can arise from one or several of the following physical causes. The Donnan potential, a purely electrostatic effect, results in a preference for the counter ion of higher valence (electroselectivity), particularly when the ion – exchange capacity is high and the external solution is dilute. Specific interactions between a counter ion and the fixed ionic groups- formation of ion pairs or strong complexes – result in a preference for this ion. In resins and other gels, the tendency of the elastic matrix to contract results in a preference for the smaller ion (on a solvated equivalent – volume basis), which causes less swelling. The selectivity of zeolites, which have a regular and rather rigid lattice, is chiefly determined by lattice forces and by steric effects such as sieve action and space requirements of the (nonsolvated) counter ions.

The selectivity of ion exchangers is also affected by interactions in the external solution, particularly by complex formation of the counter ions with the co – ion. The

counter ion, which forms the weaker complex, is preferred. Thus, by addition of a complexing agent to the solution, the selectivity of a given ion exchanger can be enhanced or varied.

Ion exchange is a diffusion process. Its mechanism is a redistribution of the counter ions by diffusion. The co – ion has relatively little effect on the kinetics and the rate of ion exchange. The rate determining step in ion – exchange is interdiffusion of the exchanging counter ions either within the ion exchanger itself (particle diffusion) or in an adherent liquid, 'film' which is not affected by agitation of the solution (film diffusion).

Film diffusion control is favored by high capacity, low degree of cross linking, and small particle size of the ion exchanger; by low concentration and weak agitation of the solution; and by preference of the ion exchanger for the counter ion which is taken up from the solution. A simple criterion can be used for predicting whether particle or film diffusion will be rate – controlling under a given set of conditions.

Particle diffusion controlled exchange is more rapid when the counter ion, which is initially in the ion exchanger, is the faster one. For film diffusion controlled exchange, the opposite holds. The counter ion, which is preferred by the ion exchanger, is taken up at the higher rate and released at the lower rate. Factors which favor high rates are high counter ion mobilities, small particle size and low degree of cross linking of the ion exchanger, presence of the ion exchanger for the counter ion which is taken up, high concentration and efficient agitation of the solution, and elevated temperatures.

Ion exchange has found various application fields since 1800, where Moses used wool particles and Aristotle used silicates as ion exchangers to treat water (Akyıl, 1996). Many industries including photographic processing, metal finishing, mining and mineral processing, and oil refining industries all have problems associated with heavy metal contamination of process and runoff waters. Where metals are present in reasonably high concentrations, oxidation, reduction and precipitation processes may be used effectively for their removal. However, recovery may be difficult when the metal (s) is removed as a minor component in sludge. Where recovery is important, procedures such as solvent extraction and ion exchange may be used (Semmens, 1979).

Semmens et al. (1979) studied heavy metal removal from saline waters by clinoptilolite. Different reagents such as zinc nitrate, calcium nitrate, cadmium nitrate, lead

nitrate, silver nitrate, and magnesium nitrate were used with naturally occurring zeolite samples. The results indicate the following selectivity sequence: $Pb^{++} > Ag^{+} > Cd^{++}$. The competing cations strongly influenced the metal exchange with the zeolite. Metal removal was greatest in exchange in the order of $Mg^{++}>Ca^{++}>Na^{+}$ for silver. Silver removals were very effective at low salt concentrations.

Czaran et al. (1988) also studied Ag^{+} exchange by natural mordenite and clinoptilolite. It has been established that both zeolites are suitable for removing silver ions from silver – containing solutions. Due to the almost complete ion – exchange, the mordenite and clinoptilolite containing rocks can be advantageously used for the removal of small amounts of silver ions from the wastewaters of photochemical works. The Ag^{+} exchange was carried out with 0.15 M $AgNO_3$ solution by letting the samples stand for 24 hours in the dark for preventing the photoreduction of Ag^{+}. The amounts of Ag^{+} exchanged into the different cationic forms of clinoptilolite are as follows:

Na – Cli: 120.7 mg/g	Mg – Cli: 59.3 mg/g
K – Cli: 86.6 mg/g	Ca – Cli: 75.0 mg/g
NH_4 – Cli: 84.3 mg/g	Original rock: 74.0 mg/g

The good exchangeability of Ag ions into zeolites can be explained by the high polarizability of Ag ions.

3.3 Polymer Articles Having Antimicrobial Properties by Ion Exchange Process

It has been known that certain materials such as silver, copper, and zinc or their compounds are effective as antimicrobial agents. Silver is one of the most commonly used metal possessing the highest antimicrobial activity.

Several studies describe the antimicrobial compositions in which zeolite particles are supports for antimicrobial metal ions (Hagiwara 1990, Kawahara 2000, Matsuura 1997, Olguin 2000). By treating zeolites with solutions of metal ions, a desired antimicrobial metal ion can be substituted in the zeolite structure. Polymer articles having antimicrobial properties are made by incorporating the treated zeolites with the polymer or the zeolites

can be molded with the polymer and then treated with a solution of the desired antimicrobial metal ion. The use of zeolite particles in polymer articles was described in detail in recent years (Hagiwara et. al 1990, Matsuura 1997, Kawahara 2000, Klasen 2000, Olguin 2000).

Chapter 4

SORPTION AND DIFFUSION PHENOMENA IN POLYMERS

Owing to their favorable performances as highly efficient barrier materials, polymers have been gaining wide use in packaging and protective coatings. At ambient temperature, low molecular weight substances can easily migrate in polymer-based materials. The most important of these substances is water. In many of the applications, the coating may suffer when the material is exposed to atmospheric moisture or is in contact with liquid water for a long time. This can lead to loss of adhesive strength, production of cracks, leaching of polymer fragments, corrosion of metallic substrates and rotting of wood. This damage results from the diffusion of water molecules through out the polymer chains causing plasticization, local strain, chain rupture, and chemical degradation (Lekatou A. et al.1996, Metayer M.et al. 1999). When the composites containing ion exchanged filler, contact with water, the ions in the filler can exchange back to the water phase altering the properties of the composite materials. Therefore the knowledge of water sorption behavior in composites and in polymer matrices is recognized to be utmost importance.

The water molecule is relatively small and in the liquid and solid states is strongly associated through hydrogen bond formation. This combination of features distinguishes it from the majority of organic penetrants. Whereas the diffusion coefficient generally increases with concentration for an organic vapor, marked decreases have been observed with water in several polymers. As a result, strong localized interactions may develop between the water molecule and suitable polar groups of the polymer. In Figures 4.1 and 4.2; typical equilibrium sorption isotherms for hydrophilic and hydrophobic polymers are shown (Crank, 1968).

In order to test water permeability of polymers, various techniques can be used, which are roughly divided into sorption measurements and permeation measurements. Sorption kinetics allows the indirect assessment of permeability coefficient P, from both diffusion coefficient D and solubility coefficient K. Usually, gravimetric methods are used. These need an insulated and very sensitive microbalance for accurate measurements; this equipment is often expensive and the method is not specific to water since interferences with other volatile substances are possible (Metayer et al. 1999).

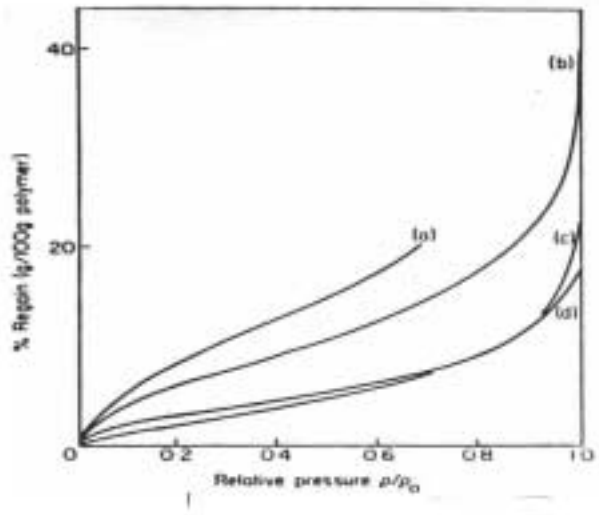


Figure 4.1. Equilibrium Sorption Isotherms for the Natural Fibres and Proteins:

(a) N.F. pectin at 29^{o}C, (b) wool, (c) cotton, (d) secondary cellulose acetate at 30^{o}C.

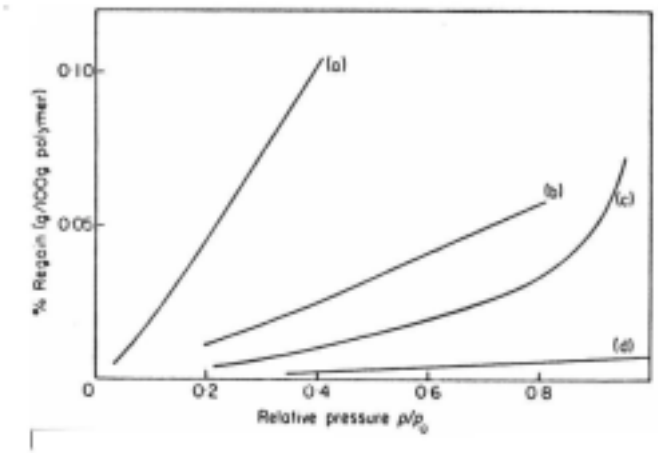


Figure 4.2. Equilibrium Sorption Isotherms of Hydrophobic Polymers:

(a) polyvinylchloride at 25^{o}C, (b) polystyrene at 25^{o}C, (c) polydimethylsiloxane at 35^{o}C, (d) polyethylene at 25^{o}C.

4.1 Sorption Kinetics

The kinetics of water penetration into polymer matrix composites has been widely studied. However, there have been very few studies of water and aqueous solution effects on heterogeneous disordered model materials, such as glass microsphe - reinforced composites. The simplified geometry of the filler and its random three – dimensional distribution in the matrix can be used for a quantitative rationalization of the degradation behavior of a whole class of engineering materials.

Water penetration into polymer matrix composites involves three mechanisms: (Lekatou et al.1996).

1) Direct diffusion of water molecules into the matrix and, to a much less extent, into the filler material
2) Flow of water molecules along the filler – matrix interface, followed by diffusion into the bulk resin
3) Transport of water by microcracks or other forms of microdamage such as pores or small channels already present in the material or generated by water attack.

Experimental studies have shown that water diffusion into polymer matrix composites initially follows the Fickian model, i.e. proportionally between mass gain and the square root of immersion time, which corresponds to the first mechanism. The latter two mechanisms result in deviations from ideal behavior. In addition, dissolution of the matrix, as well as dissolution of charged species in liquid films at the filler matrix interface, have been reported to lead deviations from Fickian behavior, the former in the form of non – attainment of equilibrium or a decrease in the mass gain after a maximum water absorption, the latter in the form of double - step sorption kinetics.

Sorption process can be modeled to determine the concentration in the sample as a function of time and position using one dimensional diffusion equation (Crank, 1968).

If by some convenient experimental arrangement, the concentrations just within the surfaces of a plane sheet of thickness, l, are maintained constant, the amount of diffusant M_t, taken up by the sheet in a time t, is given by Equation 4.1.

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{1/2}\left(\frac{1}{\Pi^{1/2}} + 2\sum_{n=0}^{\infty}(-1)^n \, ierfc\,\frac{nl}{2(Dt)^{1/2}}\right) \qquad (4.1)$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient D, and M_∞ is the equilibrium sorption attained theoretically after infinite time. Equation 4.1 with suitable interpretation of M_t and M_∞ also describes desorption from the same sheet, initially conditioned to a uniform concentration, whose surface concentrations are instantaneously brought to zero at t = 0. The value of D can then be determined by using the initial gradient of M_t / M_∞ versus ($t^{1/2}$). This observation is made easier by the fact that, for a constant diffusion coefficient, the graph for a sorption experiment is linear within the limits of the experimental errors (Crank, 1968).

Another form of the equation describing sorption and desorption is

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\Pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-\frac{D(2m+1)^2\Pi^2 t}{l^2}\right] \qquad (4.2)$$

This equation is most suitable for moderate large times, while (4.1) is best used for small times.

The more simplified form of equation 4.1 for short times can be approximated as follows:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\sqrt{\frac{Dt}{\Pi}} \qquad (4.3)$$

where,

D: diffusion coefficient

M_t: amount adsorbed at time t

M_∞: amount adsorbed at equilibrium

l: film thickness of the polymer sample or length of the transport path

t: time

By constructing a sorption curve, (M_t/ M_∞ vs $\sqrt{t}$), the diffusion coefficient can be calculated from the initial slope (s) and final equilibrium state of the curve using Equation 4.4.

$$D = \frac{\Pi}{16}(lxs)^2 \tag{4.4}$$

Lekatou et al. (1996) used silane coated glass microspheres embedded in an epoxy polymer matrix as a model system to investigate water sorption at three water activities. Increase in water activity lead to a decrease in the effective water diffusivity due to trapping, especially at interfaces. Higher water activities favored interfacial water transport, whereas lower water activities favored water transport through the bulk of the polymer.

Ulutan and Balköse (1996), studied the diffusivity, solubility and permeability of water vapor in flexible PVC / silica composite membranes. Using a Cahn 2000 gravimetric adsorption system, equilibrium and rate studies related to water vapor adsorption on membranes have been performed. For the solubility and diffusivity of water vapor in membranes, 4.23 – 7.74$cm^3/(cm^3cmHg)$ and 2.0 - 3.5X$10^{-13}m^2/s$ have been determined respectively. The measured permeability of water vapor through membranes 1.6 – 7.3 X10^{-6} ((cm^2/s)/(cm^2cmHg)) cm were much higher than predicted permabilities 0.85 – 2.73 X10^{-8} ((cm^2/s)/(cm^2cmHg)) cm from solubility diffusion data, indicating that the membranes had a porous structure.

Metayer et al. (1999), studied the diffusion of water through various polymer films as new high performance of characterization method. By testing various polymers, different behaviors with respect to water have been observed, particularly with low density polyethylene which shows significant hydrophobic properties.

Langevin et al. (2001) investigated the water vapor uptake of sulfonated polyimides using an electronic microbalance (IGA, Hiden) from 15 to 55^oC. The sigmoidal shape of the water vapor isotherms obtained is decomposed in three sorption modes: Henry's, Langmuir's, and clustering. These three types of sorption are resumed in Park's phenomenological equation versus activity. Good agreement is obtained between experimental and calculated values.

Although an extensive amount of work has been done in water sorption of pure polymers and polymeric composites, not much information is found in literature about liquid water or water sorption in pure PP and its composites. Therefore in this work, liquid water sorption of PP-zeolite composites prepared by both hot press and extrusion techniques has been studied as a function of zeolite loading. The methodology is presented in experimental (chapter 7), whereas the results are given and discussed in the results and discussion section (chapter 8).

Chapter 5

CHARACTERIZATION OF POLYMER COMPOSITES

Polymer characterization is different from that of 'small' molecule characterization due to a different number of features about polymers. A polymer, unlike a pure small molecule, contains molecules of different molecular weight. Therefore, a polymer molecular weight represents an average distribution of the various molecules with different molecular weights. A bulk of polymeric sample can contain residual monomer as well as other low molecular weight 'oligomeric' species. Some polymers are amorphous and cannot crystallize into more ordered structures. Some are semicrystalline exhibiting crystalline melting points as well as glass transition temperatures and exhibiting x-ray diffraction patterns characteristic of their structures. For polymer characterization, spectroscopic methods, thermal analysis, optical microscopy, can be listed as the most common methods that are in use (Sibilia et al., 1988).

5.1 Thermal Analyses

Thermal analysis (TA) is frequently used to describe analytical experimental techniques, which investigate the behavior of a sample as a function of temperature. A selection of representative TA curves is presented in figure 5.1 (Hatakeyama et al., 1994).

The advantages of TA over other analytical methods can be summarized as follows (Hatakeyama et al., 1994):

(i) The sample can be studied over a wide range temperature using various temperature programmes;

(ii) Almost any physical forms of sample (solid, liquid, or gel) can be accommodated using a variety of sample vessels or attachments;

(iii) A small amount of sample (0.1 μg-10 mg) is required;

(iv) The atmosphere in the vicinity of the sample can be standardized.

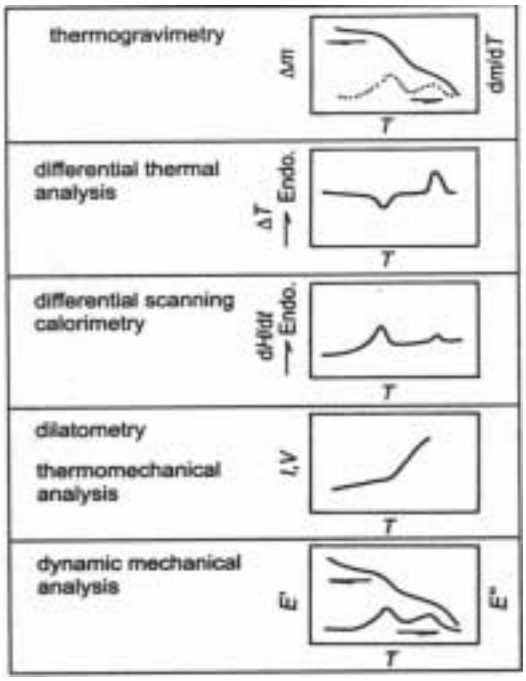


Figure 5.1.Representative TA Curves.

TA data are indirect, and must be collated with results from spectroscopic measurements (for example NMR, FTIR, X-ray) before the molecular processes responsible for the observed behavior can be elucidated. The recorded data are influenced by the experimental parameters, such as the sample dimensions, and mass, the heating / cooling rate, the nature and composition of the atmosphere in the region of the sample. The most common forms of TA are listed in Table 5.1 (Hatakeyama et al., 1994).

5.1.1 Thermogravimetry (TG)

Thermogravimetric Analysis or thermogravimetry (TG) is the branch of thermal analysis that is used to determine changes in sample weight, which may result from chemical or physical transformations, as a function of temperature or time. TG is used to characterize the decomposition and thermal stability of materials under a variety of conditions, and to examine the kinetics of the physico-chemical processes occurring in the sample (Hatakeyama et al., 1994, Sibilia et al., 1988). The TG instrument, in conjunction with differential thermal analysis (DTA) and mass spectrometry, also provides a technique to investigate reactions such as dehydration, polymerization, and

decomposition. Areas of application include purity determination, screening of additives (e.g. plasticizer, filler, flame retardants, etc.), determination of thermal and oxidative stability, and evaluation of moisture, volatiles and residues, determination of catalyst performance, flammability characteristics, and reaction kinetics.

Table 5.1.Conventional Forms of TA.

Property	TA Method	Abbreviation
Mass	Thermogravimetry	TG
Difference temperature	Differential thermal analysis	DTA
Alternating temperature	Alternating current calorimetry	ACC
Enthalpy	Differential scanning calorimetry	DSC
Length, volume	Dilatometry	
Deformation	Thermomechanical analysis	TMA
	Dynamic mechanical Analysis	DMA
Electric current	Thermostimulated current	TSC
Luminescence	Thermoluminescence	TL

5.1.1.1 Polypropylene – Zeolite Composite Characterization by TG

The composite materials as well as their components can be characterized using thermogravimetry. Natural zeolite and pure polypropylene's thermal properties can be examined separately, and then the composite behavior is examined afterwards.

Almost all of the natural zeolites loose water during the heating process. This is easily seen in the thermogravimetric analysis results. Knowlton and White (1981) studied the dehydration of clinoptilolite (natural zeolite) and reported that three types of water are present in natural zeolite; external water, loosely bond water, and tightly bond water. They are removed from the structure upon heating at around 75 ^{o}C, 171^{o}C, and

271^{o}C respectively, and that clinoptilolite contained 4.6 % external water, 6.6 % loosely bond water, and 2.4 % tightly bond water.

For the case of polymers, TG is used to determine the weight loss of polymers upon heating. Depending on the temperature programmed, the filler contents could be checked, and using Kinetic Analysis, the reaction rate parameters (activation energy, and reaction rate), can be calculated. The TGA Kinetic Analysis is based on the known Ozawa method.

Ozawa method assumes that at any given temperature T, the degree of thermal degredative conversion α, of polymer to volatile products changes as a function of time according to equation

$$d\alpha/dt = k\, f(\alpha) \tag{5.1}$$

where k is the rate constant. The function f (α) for the n th order reaction is defined by

$$f(\alpha) = (1-\alpha)^n \tag{5.2}$$

from which

$$d\alpha/dt = A\,(1-\alpha)^n \exp(-E/RT) \tag{5.3}$$

where A is the Arrhenius factor, E is the apparent activation energy of the thermal degradation, and R is the gas constant. If a polymer is heated at a rate of ($\beta = dT/dt$), then this equation becomes

$$d\alpha / (1-\alpha)^n = A / \beta .\exp(-E/RT).\, dT \tag{5.4}$$

Ozawa shows that this equation may be integrated and solved if A, $(1-\alpha)^n$, and E are independent of T and both A and E are independent of α (Horrocks and D'Souza, 1991).

According to Ozawa principle, in a normal reaction,

$$G(x) = A^{*}\theta \tag{5.5}$$

where;

A= frequency factor

$\theta = \exp(-E/RT)Xdt$; reduced time

E= activation energy

R= constant

T= temperature

t= time

If the reaction mechanism is determined, reaction quantity and θ have a linear relationship, with frequency factor A, being the slope of that line. However, in a TGA curve, where the reaction is of the n^{th} order, weight loss C, is equivalent to reaction percent x, but when the sample is a polymer, x is not necessarily equivalent to C. That is, a product resulting from the cutting of a chain need not volatilize at the same temperature, which caused the chain to be broken. Accordingly, the relationship between the weight loss C and the ratio of main chains which are broken may be expressed as follows: (Shimadzu, 1999)

$$1\text{-}C = (1\text{-}x)^{L-1}\left[1+x\frac{(N-L)(L-1)}{N}\right] \quad (5.6)$$

where;

N = degree of polymerization at initial stage

L = degree of polymerization in smallest remaining non-volatilized polymer segment

$$C = 1\text{-}(1\text{-}x)^{L-1}[1+(L-1)x] \quad (5.7)$$

$$G(x) = -\text{Log}(1\text{-}x) \quad (5.8)$$

The Ozawa and similar kinetic treatments cannot be applied in any case, where parallel, competitive reactions occur, and this condition is likely to hold following the introduction of oxidative reaction centers within the polymeric backbone (Horrocks D'Souza, 1991).

Özmıhçı (1999) studied the degradation of PP – zeolite films by TGA and determined E for PP (MH 418) and PP – zeolite composite of 6 % wt zeolite as 59.3, and 42.9 kcal/mol respectively by the Ozawa method.

5.1.2 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

Differential thermal analysis can be used to detect the physical and chemical changes which are accompanied by a gain or loss of heat in a material as its temperature is increased, decreased or held isothermally. Differential scanning calorimetry, on the other hand, can provide quantitative information about these heat changes. In other words, it examines the rate of enthalpy change as a function temperature, which is used for the determination of melting and crystallization points, heat evolved, or temperature of phase transformations (Hatakeyama et al., 1994, Sibilia et al., 1988).

DTA and DSC are techniques for studying the thermal behavior of materials as they undergo physical and chemical changes during heat treatment. Various chemical and physical transformations occur including the absorption of heat (endothermic process) or evolution of heat (exothermic process) during heating. DTA measures the temperature difference arising between a sample and a reference material as both are heated at a constant rate in the same environment, thereby indicating endotherms and exotherms. The DSC technique, however, measures the amount of heat that is evolved as a material undergoes either an exothermic or endothermic transition. These techniques are particularly useful in the characterization of organics, biological materials, inorganics, and amorphous alloys. Some applications are: qualitative and quantitative evaluation of phase transformations such as glass transition, melting, crystallization; study of polymerization, decomposition and curing processes including a kinetic description; determination of thermal and processing histories, simulation of processing conditions and crystal growth (Sibilia et al., 1988).

5.1.2.1 Polypropylene – Zeolite Composite Characterization by DSC

Differential Scanning Calorimetry is used for the determination of the kinetic parameters. Kissinger's method assumes that the reaction rate is described by Equation 5.9.

$$\frac{d\alpha(t)}{dt} = A\exp(-E/RT)(1-\alpha)^n \qquad (5.9)$$

where;

α = reaction rate

A = frequency factor

E = activation energy

T = temperature

n = reaction order

The most important additional assumption of this method is that the maximum in the DSC curve occurs at the same temperature as the maximum reaction rate. The reaction is further assumed to proceed at a rate, which varies with temperature, and therefore the position of the DSC peak is a function of the heating rate. From the variation in the peak temperature with heating rate E can be calculated for any value of n. The maximum reaction rate occurs when d/dt(dα/dt)=0. From Equation 5.9 it follows that

$$\frac{E\phi}{RT_m^{\,2}} = An(1-\alpha)_m^{\,n-1}\exp(-E/RT_m) \qquad (5.10)$$

where T_m is the peak maximum temperature, and ϕ is the heating rate. By substituting an approximate solution to equation (5.8) into equation (5.9) and differentiating, it can be shown that

$$\frac{d(\ln\phi/T_m^{\,2})}{d(1/T)} = -E/R \qquad (5.11)$$

or

$$\frac{d(\ln\phi)}{d(1/T)} = -\frac{E}{R} - 2T \qquad (5.12)$$

for –E/R»2T, the slope of lnϕ versus 1/T equals –E/R.

Under the same assumptions this method has extended to include reactions, which follow Avrami's law (Hatakeyama et al., 1994).

Çaykara and Güven (1998) investigated the effect of preparation methods on the thermal stability of PAA – Al_2O_3 (poly (acrylic acid) – alumina) composites. They studied the thermal degradation reactions of the composites prepared by mixture and polymerization methods, by using thermogravimetry (TGA). The thermal degradation reaction was not found to change very much with the ratio of PAA / Al_2O_3 when the composites were prepared by simple mixing. For the composites prepared by the polymerization method, the thermal degradation reaction was observed to change with percentage conversion. It was concluded that the composites prepared by polymerization method have better thermal stability.

Fernandes et. al (1999) studied the thermal degradation of polyethylene alone and in the presence of an ammonium exchanged zeolite chabazite. It was observed that the presence of chabazite decreased the temperatures corresponding to the initial mass loss, the maximum rate of mass loss, and the final constant mass. The activation energy observed for the degradation of PE was 277.8 kJ/mol, as compared with 197.3 kJ/mol for the chabazite form of natural zeolite. This implies that the zeolite may act as a cracking catalyst for PE, enhancing the generation of light products of potential industrial use.

5.2 IR Spectroscopy

Infrared Spectroscopy (IR) provides information about the chemical composition of the materials. It gives information about the chain structure, degrees of branching, stereoregularity, geometric isomerism, conformation, crystallinity, and functional groups present in the material. In other words, it is used to identify materials, determine the composition of mixtures, monitor the course and extent of reactions, and provide information useful in deducing molecular structure (Sibilia et al., 1988, Cahn et al., 1992).

Analysis by IR spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum: ~ 4000cm^{-1} to ~200cm^{-1}. When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to

molecular vibrational frequencies, but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called the infrared spectrum of the material. Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorptions it is possible to determine whether various chemical groups are present in a chemical structure. In addition to the characteristic nature of the absorptions, the magnitude of the absorption due to a given species is related to the concentration of that species (Sibilia et al., 1988).

5.2.1 Characterization of PP- Zeolite Composites by FTIR

IR spectroscopy can be used to characterize the individual components of the composite, and then the resulting composite material is examined to see the different effects of the materials on each other's properties.

According to Fuentes et al. (1997), two groups of vibration were to be considered in all types of natural zeolites. One is the internal vibrations of T-O and the other is the vibrations of the external linkages between tetrahedra. The internal vibrations T-O is sensitive to the Si / Al ratio of the framework. The internal T-O stretching mode is 650-820 cm^{-1}. Sensitive and internal T-O bonding is 450-500 cm^{-1}. The characteristic peaks of natural zeolite are given in table 5.2.

Table 5.2.Natural Zeolite Characteristic Peaks (Goryainov et al. 1995) .

Vibration	**Wave Number (cm^{-1})**
Isolated OH stretching	3700
Hydrogen bonded H_2O, O-H stretching	3400
H_2O bonding	1620
T-O stretching	1065
External T-O (intense symmetric stretching)	790
External T-O double ring	609
Internal T-O double ring	450

To characterize the polypropylene by FTIR, transparent pp films could be used. Likewise, the polypropylene – zeolite composite films could also be analyzed by placing the sample in the passage of the beam of light.

The characteristic peaks of pure polypropylene are presented in Table 5.3 as follows: (Polymer Handbook, Braundrup et al. (1976), Banwell et al. (1983)).

Table 5.3.Characteristic Peaks of Polypropylene

Vibration	**Wavenumber (cm^{-1})**
i – polypropylene	790, 1158
s – polypropylene	1131, 1199, 1230
t-polypropylene	997, 995
- CH_2 asymmetric stretching	2930
symmetric stretching	2860
Deformation	1470
-CH_3 asymmetric stretching	2970
symmetric stretching	2870
Asymmetric deformation	1460
Symmetric deformation	1375

5.3 Mechanical Properties of Polymer Composites

Most plastic materials are used because they have desirable mechanical properties at an economical cost. For this reason, mechanical properties may be considered the most important of all the physical and chemical properties of high polymers for most applications.

Many physical properties and tests, can be conducted on polymers. Most of these tests are very specialized and have not been officially recognized as standard tests. Some of these tests, however, have been standardized and are described in the publications of American Society for Testing and Materials (ASTM). The tests are usually designed to obtain fundamental property information or about the final end use performance or behavior of the product. Final states of polymers are usually films, fibers, molded parts or coatings (Nielsen et al., 1974, Sibilia et al., 1988).

Mechanical testing methods are used to evaluate materials under a variety of loading conditions. Mechanical properties that can be evaluated include: moduli (characterizing their rigidity); ultimate or other characteristic values of stresses and strains; and specific work or energies characterizing their strength, ductility, resilience, and general toughness, respectively. Such properties can be obtained with a tensile tester, which measures the force to stretch a material until it breaks (Sibilia et al., 1988).

Particulate filled thermoplastic composites have proved to be of significant commercial importance in recent years, as industry and technologists seek to find new and cost effective materials for specific applications. Various additives are often incorporated into polymeric matrices to modify the physical, mechanical, and rheological as well as thermal properties in order to suit a wide range of applications. The major constituents of these additives are inorganic particulate fillers such as talc, limestone, silicates, glassbeads, ceramics, etc. For high filler loadings, it is widely appreciated that the mechanical properties of a moulding are determined primarily by the interfacial interactions between the polymer matrix and the filler. In recent years, great efforts have been made to improve the understanding of the chemistry of the polymer-filler interface, develop methods for enhancing interfacial adhesion and characterizing filler dispersion. In particular, titanate-based coupling agents have been reported to modify the filler surface quantitatively, rendering the polymer composites easily processable due to improved filler dispersion in the polymer through enhanced wettability of the modified filler surface by the former. Besides interfacial adhesion, filler particle size, shape and dispersion (in the polymer matrix) are the other important factors that can have a profound influence on the end-use properties of a composite. The factors are particularly dependent on the efficiency of the mixing process. With dispersive mixing of particulate filler in a polymer melt, the associated shear forces can be so great that fracture of filler particles can occur and lead to a reduction in filler particle size and change the particle size distribution. Even so, where inter-particle surface forces are high, particle agglomeration may still occur. Knowledge of particle size distribution in a composite is critical in relation to the analysis of its mechanical properties (Khunova et al., 1999, Maiti et al., 1992).

5.3.1. Elastic Modulus

The generalization of the Einstein concept by Guth with the introduction of a particle interaction term resulted in the following expression for spherical particles:

$$E_c = E_m (1 + 2.5\ \phi_f + 14.1\phi_f^2) \tag{5.13}$$

where E_c and E_m are the elastic modulus of the composite and matrix respectively and ϕ_f is the filler volume.

Elastic modulus of the pure PP and its composites was calculated according to Equation 5.13 and tabulated in Table 8.26 in Chapter 8.

Using Paul's model, for uniform displacement at the boundary, Ishai and Cohen, obtained a formula as follows

$$E_c = E_m \left[1 + \frac{\phi_f}{m/(m-1) - \phi_f^{\,1/3}} \right] \tag{5.14}$$

where $m = E_f/E_m$, and E_f is the elastic modulus of the fillers,.

Halpin Tsai developed a simple model and generalized equation to approximate the results of more exact equation to approximate the results of more exact microanalysis:

$$E_c = E_m \left(\frac{1 + \zeta\eta\phi_f}{1 - \eta\phi_f} \right) \tag{5.15}$$

and

$$\eta = (m-1) / (m+\xi) \tag{5.16}$$

in which ξ is a measure of reinforcement and depends on the filler geometry, packing geometry, and loading conditions. For spherical particles, $\xi = 2$.

Liang et al. (1997), also proposed a similar equation:

$$E_c = E_m\left[1+\frac{\lambda\phi_f(m-1)}{1+(1-\phi_f)(m-1)s}\right] \tag{5.17}$$

and

$$s=\frac{7-5\nu}{15(1-\nu)} \tag{5.18}$$

where λ is the constant related to particle geometry, distribution in the matrix, and interfacial adhesion between the inclusions and the matrix, and ν is the Poisson's ratio of the matrix.

Levita et al. (1989) considered the two extreme conditions in their study depending on whether uniform strain or stress is assumed. One is the model utilized by Ishai and Cohen in which a cubic particle was surrounded by a cubic matrix shell and the limits were calculated as follows:

$$\frac{E_c}{E_M}=1+\frac{C_F}{m/(m-1)-C_F^{\,1/3}} \tag{5.19}$$

$$\frac{E_C}{E_M}=1+\frac{1+(m-1)C_F^{\,1/3}}{1+(m-1)(C_F^{\,2/3}-C_F)} \tag{5.20}$$

where m is the modulus ratio, and C_F is the volume fraction of the filler.

A much better fit was obtained by the Kerner equation which since $E_F >> E_M$, reduces to:

$$E_C / E_M \sim 1+2.25\ C_F / (1-C_F) \tag{5.21}$$

Maiti et al. (1992) used two of the known predictive models, Kerner Equation (equation 5.22), and Guth-Smallwood Equation (equation 5.13).

$$\frac{E_c}{E_p}=1+\left[\frac{15(1-\nu_p)}{8-10\nu_p}\right]\left[\frac{\phi_f}{1-\phi_f}\right] \tag{5.22}$$

where;

ν_p = Poisson ratio

ϕ_F = volume fraction of filler.

5.3.2 Yield Stress

Interfacial adhesion between the inclusion and the matrix is an important factor affecting the tensile yield behavior of filled polymer composites. In the case of a poor bond between the matrix and the filler, the interaction layer cannot transfer stress. Several equations have been proposed to quantify the influence of fillers on the mechanical strength of polymers. The simplest is based on a random model in which the strength simply relates to the matrix area on the fracture surface (Levita et al., 1989):

$$\sigma_{yc} = \sigma_{ym}(1-\phi_f) \tag{5.23}$$

where σ_{yc} and σ_{ym} are the yield strength of the composite and matrix, respectively, and ϕ is the volume fraction of the filler.

Liang et al. (1998) assumed that the strength of a particulate-filled composite is determined by the effective available area of load borne by the matrix as a result of the absence of the filler. Thus, the yield strength depends on the effective load bearing cross - section area fraction (1-ψ). If it is assumed that ψ is a power law function of the volume of the filler, ϕ_f, then

$$\sigma_{yc} = \sigma_{ym}(1-a\Phi_f{}^{b}) \tag{5.24}$$

where σ_{yc} and σ_{ym} are the yield strength of the composite and matrix, respectively, and a and b are the constants related to stress concentration, adhesion, and the geometry of the particle.

For spherical particles, having no adhesion to the polymer matrix with failure by random fracture, then equation (5.24) becomes

$$\sigma_{yc} = \sigma_{ym}(1-1.21\Phi_f{}^{2/3}) \tag{5.25}$$

where a= 1.21; b=2.3.

Jancar et al. believed that the stress concentration depends upon the content of the particles, with reduction of the effective matrix cross section being the principal factor, and presented a modified form of equation (5.25):

$$\sigma_{yc} = \sigma_{ym}(1-1.21\Phi_f^{2/3})S \tag{5.26}$$

The strength reduction factor S can be determined by finite element analysis and in general varies from 1.0 to 0.2 respectively, for low and high filler volume fractions.

Yield strength of the PP composites was estimated using equation 5.25.

5.4 ICP (Inductively Coupled Plasma Spectrometer)

Trace analyses are important in demonstrating compliance to FDA (Food and Drug Administration), EPA (Environmental Protection Agency), and OSHA (Occupational Safety and Health Administration) regulations; in determining monomer and solvent purity and in assaying small amounts of material that can affect the performance or quality of a product. In general, concentration techniques are a good way of increasing the sensitivity of analytical methodology. Some of the most commonly used trace elemental analysis techniques are AA (Atomic Absorption Spectroscopy), OE (Optical Emission Spectroscopy), ICP (Inductively Coupled Plasma Spectroscopy), and Ion Selective Electrode Analyses (Sibilia et al., 1989).

Inductively Coupled Plasma Emission Spectroscopy, like atomic absorption methods, is a technique for determining the concentration of elements in solution. The advantage of ICP is its ability to analyze many elements, either simultaneously or in a rapid sequential manner depending upon the type of the instrument employed.

The sample may be either liquid or solid, but solid materials must undergo a suitable preparation involving dissolution, decomposition, or extraction.

ICP AES spectroscopy is based upon the principle that the energy of emission is specific for each element. The liquid sample is atomized by a nebulizer into a stream of argon gas, which carries the atomized sample into the plasma where the elements in

solution are thermally excited. The excited elements emit photons, which are detected by one or more photomultiplier tubes, depending upon the type of instrument.

In the present study, ICP AES spectroscopy was used to determine the extent of Ag^+ exchange to the zeolites by analyzing the liquid phase.

5.5 Optical Microscopy

Microscopy techniques such as optical, scanning electron, microprobe and transmission electron microscopy are all useful as trace analysis techniques, especially in the case of inorganic compounds.

Optical Microscopy is used for the examination and characterization of matter using visible light. It is one of the most versatile tools in the study of the microstructure of semicrystalline polymers. In optical microscopy, information is obtained by light transmission through or reflection from matter (Cahn et al., 1993, Sibilia et al., 1989).

Transmission optical microscopy is routinely used for studying different types of materials. Some examples are polymer films or fibers; biological or petrographic thin sections, foam cellular structures, liquids, dispersions, powders and emulsions. The transmission method requires thin (several microns) specimen sections. Polarizing elements along the optical path permit the observation of birefringent differences, thickness differences or orientation variations within the sample (Sibilia et al., 1988).

Reflected light microscopy is often used in the examination of polished / etched metallurgical or ceramic specimens for inclusion size or grain size determination.

In the characterization of PP composites, transmitted optical microscopy was used.

Chapter 6

ANTIBACTERIAL BEHAVIOR

As bacterial resistance to currently used antibiotic increases, studies to identify novel agents and strategies for the prevention and treatment of bacterial infection are being made. In the past, antimicrobial drug discovery efforts have focused on eradicating infection resulting in clearance of the bacterium from the infected host. However, inhibition of the interaction between the bacterium and its host may also be a target (Projan, 2000).

The term antimicrobial or biocide includes algicides, bactericides, bacteriostats, fungicides, germicides, prior to 1930's; the principal biocide was the Bordeaux mixture, i.e., slaked lime (Ca (OH) $_2$) in a copper sulfate ($CuSO_4$) solution. Fortunately, the fungicidal activity of dithiocarbamates and the insecticidal properties of phenothiazine ($C_{12}H_9NS$) were discovered in the early 1930's (Seymour, 1990).

Pathogen is defined as any organism that has the capacity to cause disease in a host at any time (Projan, 2000). Virulence is the quantitative measure of pathogens, that is; it is the degree of pathogenicity. As defined by Projan, all bacteria that invade a host must do the following. First, find a way to enter and then establish a beneficial niche. Secondly the primary defense systems of the host must be prevented and a mounting immune response must be countered. Finally, the bacterium must be able to multiply and then disseminate within its host or to a new host as presented in figure 6.1. Bacteria initiating an infection in vivo leave what corresponds in vitro to lag phase and begin exponential growth, whereupon they begin expression of surface proteins required for adherence and host response avoidance. As the number of cells increases, the post-exponential phase of growth is entered, and protein expression is altered to produce toxins and exoproteins. When an abscess is formed, the growth phase corresponds to stationary phase. Individual cells can break free of the abscess to disseminate and begin the cycle again. The factors involved in virulence are unique to bacteria. An agent that targets an infectious process, by definition may not be likely to be effective in the clearance of an already established infection /

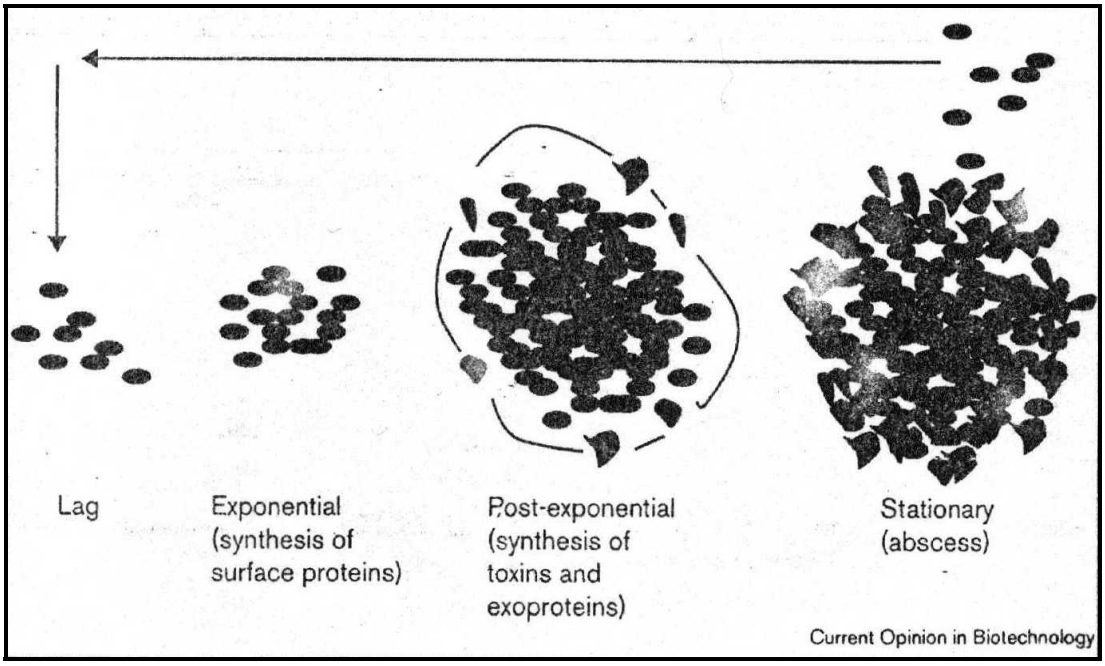


Fig.6.1.Logarithmic growth of pathogens in culture.

colonization (Projan, 2000). If virulence is to be considered a valid target for antimicrobial agents, it must be shown that virulence inhibitors will be able to eliminate or preclude disease-causing organisms.

It has been known for a long time that certain ions; especially Ag, Cu, or Zn possesses antibacterial property. Ag zeolites are increasingly investigated as germicidal, bactericidal, antifungal, and antiseptic components in different compositions (Kawahara 2000, Klasen 2000, Matsuura 1997, Olguin 2000). Metallic silver is one of the common elements used in the dentistry. Ionic silver has the highest antibacterial activity among metal ions, and a variety of silver compounds have been used as topically applied agents for treatment of burns and ocular infections (Kawahara, 2000). Zeolite being a porous crystalline material of hydrated sodium aluminosilicate exhibits a strong affinity for Ag^{+} and can electrostatically bind this ion up to approximately 40% (w/w) in its framework. Such silver ion - containing zeolite (silver – zeolite, SZ) can provide antibacterial activity to resins or synthetic fibers by mixing (Kawahara, 2000). It was thought that this antibacterial activity was caused by adsorption of silver into the microorganisms. But it was reported that there was the case that the microorganisms loose the ability of colony forming

without adsorption of silver. In this case, silver was incorporated in the inorganic compounds not in the solution freely (Inoue et. al, 1997). Recently, the modification of inorganic compound by addition of silver was attractive to protect circumstances from the disease come from the microorganisms. Nowadays, various studies are being carried to attain antibacterial compositions, and many different methods are being proposed.

6.1 Alternative Methods for the Preparation of Antibacterial Compositions

Paik et al., (1998) studied UV- irradiation method on nylon films for packaging applications. Antibacterial packaging could enhance food storage life and safety. The use of 193 nm UV irradiation to convert amide groups, on the surface of nylon to amines having antibacterial activity has been reported. Three food related bacterial strains were exposed to antibacterial film in 0.2 M Sodium Phosphate buffer (pH 7.0). The antibacterial film was effective in reduction of microbial concentration in the bulk fluid for all food- related bacteria tested. The effectiveness was dependent on the bacterial strain. Adsorption of bacterial cells diminished the effectiveness of amine groups. Experimental results indicate that the decrease in concentration of bacterial cells in bulk fluid is more likely to be the bactericidal action than adsorption of live cells.

Worley et al. (1999) studied novel antimicrobial N- halamine polymer coatings generated by emulsion polymerization. A new class of N- halamine polymers can be emulsified in water to produce coatings, which, once chlorinated, act as contact disinfectants. The surfaces inactivate bacterial organisms efficiently, requiring relatively brief contact times of several minutes. These polymers are stable for over a year at room temperature, and they require short contact times to inactivate a broad spectrum of organisms. Their biocidal activities are easily regenerated once exhausted by flowing an aqueous solution of free halogen over them. They show considerable commercial promise for water and air filtration systems, and they are inexpensive to produce.

Olguin et al. (2000) investigated the antimicrobial effect of the Mexican zeolitic mineral exchanged with silver ions. It was found that the Mexican silver clinoptilolite-heulondite mineral eliminated the pathogenic microorganisms *E.coli,* and *S.faecalis* from water with the highest amount of silver supported on the mineral after 2 hours of contact.

Kawahara et al. (2000) evaluated the antibacterial effect of silver-zeolite (SZ) against oral bacteria under anaerobic conditions. SZ inhibited the growth of the bacteria tested under anaerobic conditions showing that SZ may be a useful vehicle to provide antibacterial activity to dental materials used even under anaerobic conditions.

Matsuura et al. (1997) studied the antimicrobial effect of tissue conditioners containing silver-zeolite on *Candida albicans, S. aureus,* and *P.aeruginosa.* The results showed that with the SZ samples, all tested microbes were killed, indicating that tissue conditioners containing SZ have been shown to have antimicrobial effect.

Hagiwara et al. (1990) studied zeolite particles retaining Ag ions having antibacterial properties. A polymeric substance holding the metallic ions was proposed for use of various fields. The important point here is how the polymer will hold the metal ions. Many methods of incorporating the metal ions into a polymeric substance are known such as binding or adding fine powder of the metals themselves to a polymer and a method of incorporating compounds of the metals into a polymer. However, using metals themselves brings a disadvantage that the metals show poor compatibility because the specific weights and Young Moduli of the metals are usually very high compared with those of the conventional polymers (Hagiwara, 1990). Therefore, a method was proposed wherein a polymer contains organic functional groups having an ion – exchange function over a complex forming function and thereby these groups retain the metal ions. A new antibacterial agent, zeolite is now available. It looks like a plain white powder but offers excellent antiseptic and nontoxic effects. Furthermore, it is reported as a tasteless and odorless material. Also these inorganic compounds are very different from other conventional antibacterial agents. These differences include chemical stability such as the melting and volatility points. Furthermore zeolite is more cost effective and no toxicity to humans is reported. In Japan, there are many manufactured goods that have this antibacterial coating, such as toothbrushes, and toothpaste, bath and toilet tiles, kitchen utensils, baby toys and so on. Recently, many medical instruments have begun to be coated (Niira, 1990). The invention provides two processes for producing the polymer article. (Hagiwara, 1990). One process is characterized by admixing zeolite particles retaining at least one metal ion having a bactericidal property with an organic polymer or a mixture of polymers at any stage prior to moulding the organic polymer to form the shaped article.

Another process is characterized in that an organic polymer or a mixture of polymers containing zeolite particles is moulded and then treated with an aqueous solution of at least one metal ion having a bactericidal property to provide at least part of the zeolite particles with so-called metal ion.

According to the studies of Hagiwara et al. (1990), the zeolite particles should retain the bactericidal metal ion in an amount less than an ion – exchange saturation capacity of the zeolite. Otherwise, the bactericidal effect of the polymer article is very poor. The suitable shape of zeolite used in this invention may preferably be fine particulate. A particle size of the zeolite can suitably be selected depending on application fields. When a moulded article has a relatively large thickness, like various types of containers, pipes, granules, or coarse fibers, the particle size may be in the range of a few microns to tens microns or even above several hundred microns. When fibers or films are moulded as an article according to the present invention, preference is given to a smaller size of particle. It's also reported that when the metal ion in amounts such as to saturate the ion – exchange capacity of the zeolite are given to the zeolite, a portion of the metal ion deposits on the surface of zeolite in a form other than an ion, such as silver oxide (in the case of silver ions). These oxides have been found very detrimental to the bactericidal effect of the zeolite – metal ion. When a high degree of bactericidal effect is desired, the moulded article preferably has a large surface area.

Niira et al. (1990) made studies on antibiotic zeolite and an antibiotic resin composition containing the zeolite. The invention relates to an antibiotic zeolite in which all or parts of ion exchangeable ions in a zeolite are replaced with antibiotic metal and ammonium ions. According to the invention, an antibiotic resin composition is provided. The resin composition comprises the aforementioned antibiotic zeolite and a resin such as polyethylene, polypropylene, and polyvinylchloride, etc…

6.2 Preparation of Silver-Zeolite (SZ) Containing Compositions via Ion Exchange

The metal ions should be retained on the zeolite particles through an ion – exchange reaction. Metal ions, which are adsorbed or attached without using an ion – exchange reaction, show a poor bactericidal effect and an insufficient durability. Figure 6.2 shows the three-dimensional structure of the zeolite, which is comprised of aluminosilicates. More

specifically, it is fabricated of a tetrahedron of SiO_4 and AlO_4 and appears as one large cavity in a molecule (Niira, 1990). In this cavity, zeolite has many Na ions as shown in Figure 6.2 (Maeda, 1999).

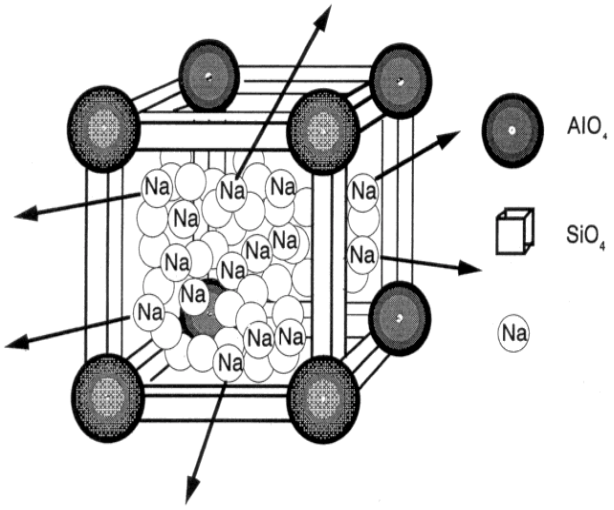


Figure 6.2.Structure of Zeolite.

Hagiwara et al. (1990) reported that substituting a metal ion for the Na ion resulted in a release of the metal ion little by little and semi permanently as presented in Figure 6.3. Because of the antibacterial effects of the metal ion, such zeolite has semi permanent antibacterial effects and is thus antibacterial zeolite (Maeda, 1999).

In usual methods of ion exchanging the sodium ion of the zeolite with other metal ions, a rather high concentration of the metal ions is used aiming a high degree of ion exchange. However in this case, a relatively low degree of ion exchange is not only satisfactory, but also essential for better bactericidal properties of ion-exchanged zeolite. Such ion – exchanged zeolite with a relatively low degree of ion – exchange may be prepared by performing the ion – exchange using a metal ion solution having a concentration rather low compared to the solutions conventionally used.

Hagiwara et al. (1990) proposed two alternative processes, which enable strong retention of the ions on the zeolite particles.

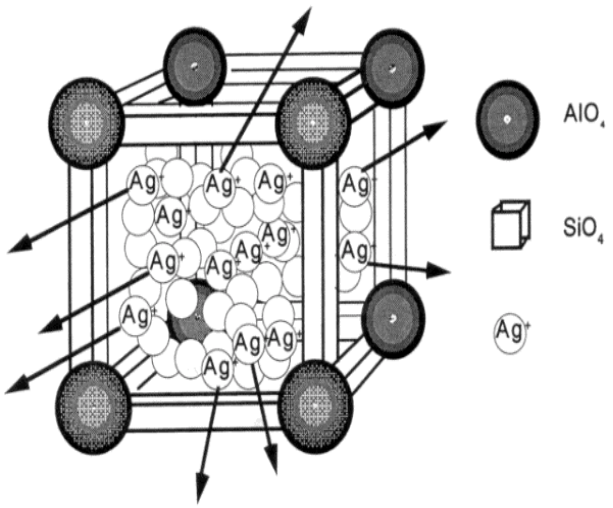


Figure 6.3.Structure of antimicrobial zeolite.

In the *first process*, metal – zeolite having a bactericidal function is added to an organic polymer or a mixture of polymers mixed together. In the case of preparing Ag-zeolite, an aqueous solution of a water-soluble silver salt such as silver nitrate is usually used, and in this case the solution concentration should not be kept too high. That is the precipitation of the silver oxide on the zeolite reduces the porosity of the zeolite, whereby the specific surface area of the zeolite is greatly reduced. Even when the reduction of surface area is not serious, the bactericidal activity is reduced by the presence of silver oxide itself. In order to prevent this deposition, it's reported to keep the Ag concentration at a diluted stage, preferably lower than 0.1 M $AgNO_3$. It has been found that in the case of using aqueous $AgNO_3$ solution of such a concentration, the specific surface area of the Ag zeolite is comparable with that of the original sample and the bactericidal function can be utilized at the optimum condition. The amount of the metal incorporated in the mentioned metal – zeolite may be less than 30 % by weight, preferably 0.001 to 5 %by weight in the case of Ag based anhydrous zeolite + metal.

The metal zeolite thus obtained is added to the organic polymer. In general, it's preferred to add the metal – zeolite to a polymer immediately before moulding. However, in some cases, it may be preferable to add the metal zeolite into a monomer so as to attain a good dispersion of zeolite particles. If desired, the metal – zeolite can be dried before its addition to a polymer preferably at a temperature from 100^oC to 500^oC under a reduced pressure.

In the *second alternative process*, the only difference is the sequence of the ion exchange treatment. The possible range of a content of the zeolite is the same as that in the first process. Zeolite may be added at any time from a stage of preparation of raw material for polymerization to a stage of moulding, as in the first process. The resulting polymer containing zeolite is moulded into an article and then subjected to an ion – exchange treatment. The manner of ion – exchange treatment is basically similar to the first alternative. That is, a polymer article containing zeolite is treated with a solution of a water-soluble salt of metal having a bactericidal property. The Ag^+ concentration should again be preferably kept below 0.1 M. The treatment may be carried either batchwise or continuously. In order to increase the amount of metal ions retained in the article, the batch treatment may be repeated or the period of time of continuous treatment may be prolonged. It depends on the nature of the polymer that how much zeolite in a polymer article be ion exchanged. Even in the case of a hydrophobic polymer, it has been found that the zeolite present around the surface area is ion -–exchanged to a considerable extent.

According to the study of Hagiwara et. al (1990), the polymer article containing zeolite particles may contain components other than the metal zeolite, such as polymerization catalysts, stabilizers, organic or inorganic pigments, inorganic fillers and so on.

Niira et. al (1990) prepared the antibiotic zeolite and an antibiotic resin composition and more particularly, an antibiotic zeolite which does not cause discoloration with time as in the second process of Hagiwara et al. (1990).

6.3 Test Methods on Antibiotic Action

In order to investigate the antimicrobial effects of the newly developed antimicrobial materials certain test methods are currently available some of which can be listed as Agar Diffusion Method (Disc Method), and the Broth Dilution Method.

6.3.1 Agar Diffusion Method (Disc Method)

Disc Method evaluates the bactericidal activity by observing the presence of an inhibition zone formation after cultivating the samples for a period of time under a set

temperature. Hagiwara et. al (1990) used the disc method to determine the bactericidal activity. That is, a polymer article containing zeolite particles was cut into a disc of 20 mm in diameter to provide a test disc. In the tests, Escherichin coli, Pseudomonas aeruginosa, Staphylococeus aureus as bacteria, and Candida albicans were used. A Mueller Hinton culture medium was used for bacteria and a Sabouraud medium was used for Eumycetes. Test bacteria or fungi were floated on a physiological saline solution at 10^8 /ml and then was dispersed in the culture medium by means of a Conradi rod of 0.1 ml. The bactericidal activity was evaluated by observing the presence of an inhibition zone formation after cultivating for 18 hours at 37^oC in the case of bacteria and by observing the presence of an inhibition zone formation after culturing for one week at 30^oC in the case of Eumycetes.

6.3.2 Broth Dilution Method

In the Broth Dilution Method, the mixture containing the antibacterial material and the bacterial cells are incubated for a period of time under the specified temperature with the necessary conditions, and then the bacterial colonies were counted and compared with the negative control sample.

Olguin et al. (2000) studied the antimicrobial effect of natural Mexican clinoptilolite supporting Ag ions. *E coli* and *S. faecalis* were chosen as indicators for fecal contamination. For the microbial experimentation, Broth Dilution method was used. Each growth essay was performed with three replicated samples.

Matsuura et al. (1997) evaluated the antimicrobial effect of tissue conditioners containing silver zeolite on *Candida albicans, S. aureus,* and *P. auroginosa* using Broth Dilution Method. The microbial suspension was added to the wells containing the silver zeolite and the specimens. After the incubation for 24 hours at 37^oC in humid conditions, viable cells in the suspension were counted and expressed as a percentage of the initial number of viable cells.

Kawahara et al. (2000) investigated the antibacterial effect of silver zeolite against oral bacteria under anaerobic conditions by determining the minimum inhibitory concentration (MIC) by the broth dilution method. The MIC was defined as the lowest concentration of silver zeolite at which no visible bacterial growth could be detected.

In the studies of Niira et. al (1990), the antibiotic action was determined on the following 3 strains: Mold, Yeast and General Bacteria. As culture medium for proliferation of microorganisms, different mediums for each of them were used. Bacteria solutions, for inoculation were prepared as follows:

For bacteria: In this case, the bacteria solution was prepared by inoculating a test strain, which had been subcultured on a medium for proliferation of bacteria, culturing it and diluting the medium with the same medium for proliferation of bacteria so that the number of bacterial cells was equal to 10^6/ ml.

For mold: The bacteria solution for proliferation of mold was prepared by inoculating a test strain which had been subcultured to a medium for proliferation of mold, culturing it and floating the resulting conidium on a sterilized solution of 0.05% polysorbate 80 so that the number of microorganisms was equal to 10^6ml.

For yeast: The solution for inoculation was prepared by inoculating a test strain which had been subcultured on a medium for proliferation of yeast, culturing it and floating the resulting cells of yeast on a sterilized physiologic saline so that the number of yeast cells was equal to 10^6/ml.

Culture of each microorganism was carried out in the following manner:

The bacteria solution for inoculation was sneared on the plate for measuring sensitivity in the form of a line of 2cm long with a loop of nichrome wire (inner diameter = about 1 mm) followed by culturing it at 37^{o}C, for 18 to 20 hours for bacteria, at 25^{o}C for 7 days for mold. After culturing these for a desired time, MIC was determined as the concentration at which the growth of microorganisms was completely inhibited.

6.4 Tests on the Amount of Ag^+ Leach Out

The amount of Ag^+ leach out from the silver containing compositions is critical for the antibacterial activity to be long lasting. Munstedt et al. (1999) reported that the release of about 0.1 ppm (mg/L) of Ag^+ possesses antibacterial effect. In all of the studies conducted for the investigation of antimicrobial properties of certain materials, the release of silver ions was also considered.

Niira et al. (1990) studied the silver release process in a continuous system. Different samples were charged in a column and then tap water was passed there through and water samples were collected at time intervals when 10, 50, 100, or 200 liters of water was passed through the column to determine the concentration of silver ions.

Kawahara et al. (2000) examined the silver release profile after 0.5, 1, 2, 4, 8, and 24 hours of incubation. At all concentrations, of silver zeolite, Ag^+ was not detected in distilled water, but its level in PBS (Phosphate –Buffered Saline) was 0.53±0.06μg/ml.

Olguin et al. (2000) showed that there is a direct proportion between the silver amount in water and the contact time. Mexican normativeness established that the silver level in ware should be kept below 50μg/l. Olguin et al.'s study showed that 2 hours of contact time with a 24 A Ag content in contact with water is sufficient to remove both pathogenic microorganisms: *E. coli*, and *S. faecalis*. Under these conditions, (26.2 μg Ag l^{-1}) remains within the limit established by the Mexican normativeness.

6.5 Test on Discoloration

As reported in a variety of different studies, antibiotic zeolite exhibits excellent antibiotic property. However, such an antibiotic zeolite suffers from the disadvantage that it gradually discolors in the course of time. While this discoloration has no effect on the antibiotic effect, depending on the nature of the product containing this antibiotic zeolite, this feature may greatly reduce their commercial value. The discoloration parameters and their corresponding values are given in Figure 6.4.

In order to prevent this undesired feature a discoloration inhibitor must be used. As such discoloration inhibitors it is possible to use at least one member of selected from the groups consisting of, for instance, benzotriazole type compounds, oxalic acid anilide type compounds, salicyclic acid type compounds, hindered type amine compounds, and the like (Niira, 1990).

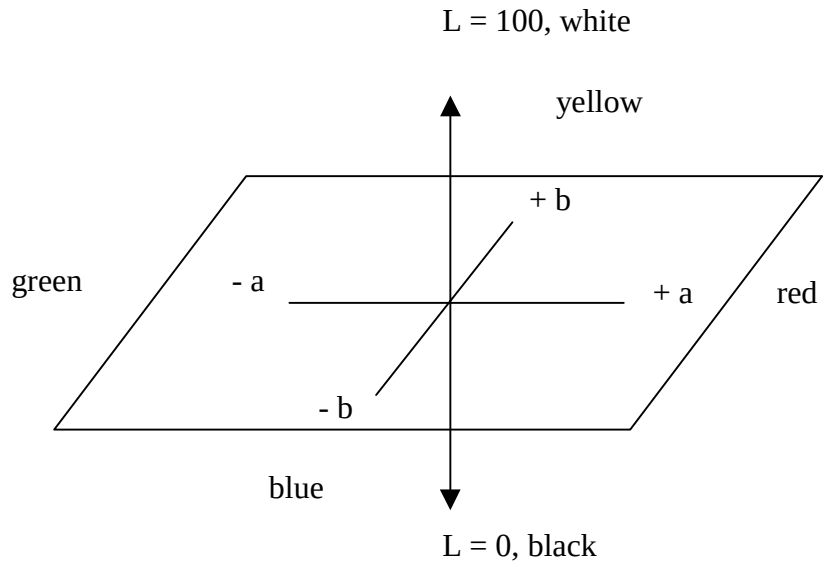


Figure 6.4.Discoloration parameters.

Niira et al. (1990) gave the the L, a,b values of the different samples measured on the day of start, after 10,30, and 60 days from the treatment. Samples of antibiotic zeolite, which had been dried under heating, were kneaded with different resins. The resultant samples were exposed to sunlight in the air. The color of the samples was determined by placing them on a white Kent paper (L^* a^* b^* 93.1; -0.7; -0.5) with Minolta color- color difference meter CR-100 (using D-65 rays). The results for the case of PP – zeolite composites tested after 10 days are tabulated in Table 6.2 (Niira, 1990), and Figure 6.5 shows the color change with the course of time of PP - zeolite composites. Samples of the antibiotic zeolite are as follows:

Sample 1: A-type; NH_4 0.5 %; Ag 3.0 %; Cu 5.0 %;
Sample 2: A-type; Ag 3.0 %, Cu 5.0 %;
Sample 3: A-type; NH_4 1.0 %; Ag 5.0 %; Zn 5.0 %;
Sample 4: A-type; Ag 2.0 %; Zn 10.0 %;

Table 6.1.Discoloration Test Results of PP-Zeolite Composites (Niira et al.1990)

Sample #	Heating Temperature (^oC)	Heating time (hr)	Moulding Temp (^oC)	L^*	a^*	b^*
1	260	3	260	64.0	-9.8	1.5
2	260	3	260	44.0	3.0	29.5
3	260	3	260	67.6	-0.7	8.9
4	260	3	260	56.0	1.5	19.4
Blank	-	-	260	74.7	0.1	4.5

The results of the different studies suggested that silver-zeolite could be beneficial for use in various application fields as an antibacterial agent. Thus, silver-zeolite can exhibit long-term antimicrobial activity since in water it released no detectable amounts of Ag^+.

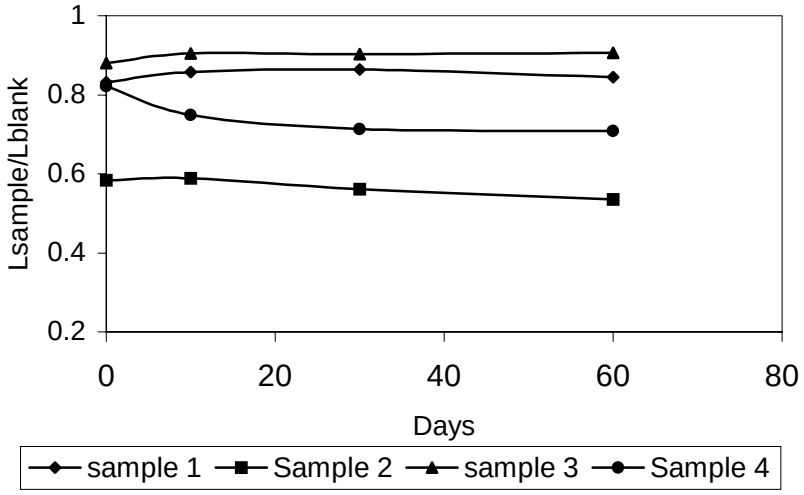


Figure 6.5.Change in the L parameter with respect to blank sample.

Chapter 7

EXPERIMENTAL

This chapter mainly focuses on the materials, equipments, techniques and the analyses performed throughout this study. For the preliminary studies, water sorption behavior of PP- zeolite composite films prepared by hot press and extrusion methods was examined. To investigate the effect of silver as an antibacterial agent, silver loaded PP - zeolite composites were prepared with two different methods. Method I is the treatment of extruded PP- pure zeolite composite films with Ag^+ containing solutions. Method II is the molding of Ag^+ exchanged zeolites with polypropylene via extrusion technique. Silver zeolite containing PP films prepared by different methods were then characterized using different characterization techniques such as optical microscopy, FTIR (Fourier Transform Infrared Spectroscopy), and thermal analysis.

7.1 Water Sorption Behavior of PP-Zeolite Composite Films

7.1.1 Materials

PP – zeolite composite films prepared by Özmıhçı (1999) were used to investigate the water sorption behavior of PP – zeolite composite films. PP in powder form supplied by Aldrich was used for the preparation of PP – zeolite composites by hot press method. PP in pellet form, with a trademark of MH 418 supplied from Petkim Petrochemicals Company was used for the preparation of PP – pure zeolite composites by extrusion method. The composition of the additives present in the MH 418 PP is given in Table 7.1 (Quality Control Laboratory of Petkim, 2001). The additives used amd their functions are as follows : Calcium Stearate is used for neutralization of the catalyst residuals, color stability, and for processing ease. Primary oxidant is used during the processing of the polypropylene to increase its resistance to heat, and prevent oxidation. Antioxidant (aryl phpsphite) is used to prevent degradation during processing. Finally, the secondary antioxidant is used for processing ease during fiber production.

Table 7.1. Properties of MH-418 PP

Additive material	Chemical Formula	Amount (wppm)
Calcium Stearate	$Ca\ (H_{35}C_{17}\text{-}C(=O)\text{-}O\text{-})_2$	750
Primary Antioxidant	$C_{73}H_{108}O_{12}$	470
Antioxidant (Aryl Pohosphite)	Tris (2,4-di-ter-butyl-phenyl) phosphite	312
Secondary Antioxidant	Tris(3,5-di-tert-butyl-4-hydroxy-benzyl)isocyanurate	312

Natural zeolite, clinoptilolite, from Gördes, Turkey, was used as a filler, with average particle sizes of 2 μm and 45 μm. For the surface modification of the zeolite, PEG 4000 (Aldrich) was used to prevent agglomerations and provide uniform distribution along the PP phase. During the modification process, the zeolite to solution ratio was taken as 1:0.3 on w/v basis.

7.1.2 Composite Preparation

Two different methods were used during the composite preparation. One of which was the hot press method and the other was the extrusion method. The preparation of PP – pure zeolites by two methods was given by Özmıhçı (1999) in detail.

7.1.2.1 Hot Press Method

PP and zeolite (2 μm) compounds were compression molded at 200 ^{o}C and 100 bar pressure at Ege University. The composites were prepared at five different zeolite loadings; 6, 10, 20, 30, and 40 % respectively.

7.1.2.2 Extrusion Method

Composites containing 2, 4, and 6 % zeolite (2μm and 45 μm) were prepared via extrusion technique using Tonable Plastic Machinery Extruder in Petkim Petrochemicals Company (Aliağa). The temperature of extruder was 260 ^{o}C, and the screw speed was 550 rpm. The L/D ratio of the extruder was 24. The cast film taken from the flat die was quenched using a polished drum cooled by water and then film was drawn by rollers.

7.1.3 Liquid Water Sorption Studies

Water swelling experiments were conducted at 25 ^{o}C using pure PP film and PP – zeolite composite films having different zeolite loadings (6 – 40 % wt for hot press; and 2 – 6 % for extrusion) for 12 days. The increase in their weights was recorded daily after removing them from the swelling media and blotting with absorbent tissue. The experiments were conducted until the samples reached equilibrium uptake. The water uptakes were plotted as a function of time.

7.2 Preparation of Silver Containing Zeolite – PP composites

To attain antimicrobial compositions in polymer composite films, ionic silver was used as an antibacterial agent due to the highest antimicrobial activity among other metal ions and its safety from toxicity (Hagiwara et. al 1990, Matsuura et al.1997, Klasen et al. 2000). Polymer composites having antimicrobial properties can be prepared by two alternative methods. Either the antimicrobial agent, silver is introduced to the system by treating the polymer zeolite composite film with the silver containing solution (Method I) or the silver treated zeolites are incorporated with the polymer (Method II).

7.2.1 Material

PP – zeolite composite films prepared by Tonable Plastics machinery were used to conduct the experiments according to Method I. Films containing 2, 4, and 6 %

zeolites with two different sets of particle sizes, 2 and 45 μm were prepared by Özmıhçı (1999).

PP in pellet form (MH-418, Petkim Petrochemicals Co.) was used as a matrix material in the composite preparation by Method II. Clinoptilolite, a natural zeolitic tuff from Gördes 1 region of Turkey was treated with silver and used as filler by Method II. $AgNO_3$ (Merck) was used for the treatment of the both the zeolite itself and the PP- zeolite composite films.

7.2.2 Method I - Ag^+ Exchange to Zeolite- PP Composite Films

Method I is the treatment of extruded films with $AgNO_3$ solutions making use of the ion exchange property of natural zeolite. It was applied to the extruded films with different zeolite loadings (2, 4, 6 %), and particle sizes (2 μm and 45 μm). The densities of the 2 μm, and 45 μm zeolite filled polypropylene composites from different regions of the films are given in Tables 7.2, and 7.3 respectively.

Table 7.2.Densities of the PP – Pure Zeolite Composite Films, 2 μm (Özmıhçı, 1999)

Zeolite %	Film thickness (mm)	Density (g/cm^3)
2 (beginning)	0.01	0.87
2 (middle)	0.02	0.82
2 (end)	0.04	0.77
4 (beginning)	0.05	0.73
4 (middle)	0.02	0.87
4 (end)	0.03	0.73
6 (beginning)	0.05	0.83
6 (middle)	0.03	0.78

Table 7.3.Densities of the PP – Pure Zeolite Composite Films, 45μm (Özmıhçı, 1999)

Zeolite %	Film thickness (mm)	Density (g/cm^3)
0 (Polypropylene)	0.01	0.88
2 (beginning)	0.07	0.86
2 (end)	0.06	0.9
4 (beginning)	0.07	0.89
4 (end)	0.03	0.88

7.2.2.1 Silver Sorption Experiments

The extruded PP – pure zeolite films were treated with an initial $AgNO_3$ solution concentration of 50 ppm. Silver sorption experiments were conducted using two different sample sizes and geometry (discs and strip shape). First, the samples were prepared in the form of small discs, however, all of them floated on the surface of the water and sticked to each other. In order to see whether this happening affected the extent of the ion exchange process, the samples were cut in the form of long strips and wrapped around their axis so that floating was prevented.

7.2.2.1.1 Polypropylene – Zeolite Composite Discs

The extruded films with a zeolite loading of 2, 4, and 6 % were cut into discs of diameter 28 mm. 10 pieces of discs each of which their weights were recorded, were treated with 100 ml of $AgNO_3$ solution with an initial $AgNO_3$ concentration of 5 to 50 ppm at 25^oC using a water bath equipped with a shaker for 24 hours. Due to the fact that the densities of the composite films were about 0.86 g/cm^3, the samples floated at the top of the solution all stacked to each other. After the ion exchange treatment of the films, the samples were washed with water twice for the removal of excessive Ag^+. The films were then dried in a vacuum oven at 400 mbar and 100^oC for an hour.

7.2.2.1.2 Polypropylene – Zeolite Composite Strips

In order to prevent the floating of the films at the top all stacked to each other films of strips with an area of about 30 cm^2 (15x2) cm were used instead of small discs. Films wrapped around their axis were fully in contact with the solution of concentration 40 ppm. The silver loaded samples were again dried at 400 mbar and 100^oC in a vacuum oven for an hour. The block diagram of this process is given in Figure 7.1.

7.2.2.2 Desorption Experiments

Desorption experiments from the film strips were carried out with deionized water at 25^oC for 24 hours using a water bath equipped with a shaker just as the sorption experiments. However, as reported in literature, silver release to water is considerably low that it was not possible to detect the extent using ICP - AES. As a second alternative desorption of Ag^+ to 0.9 (w/v) % NaCl solutions was conducted again at 25^oC for 24 hours in a shaking mode. In this case silver release was possible to be detected.

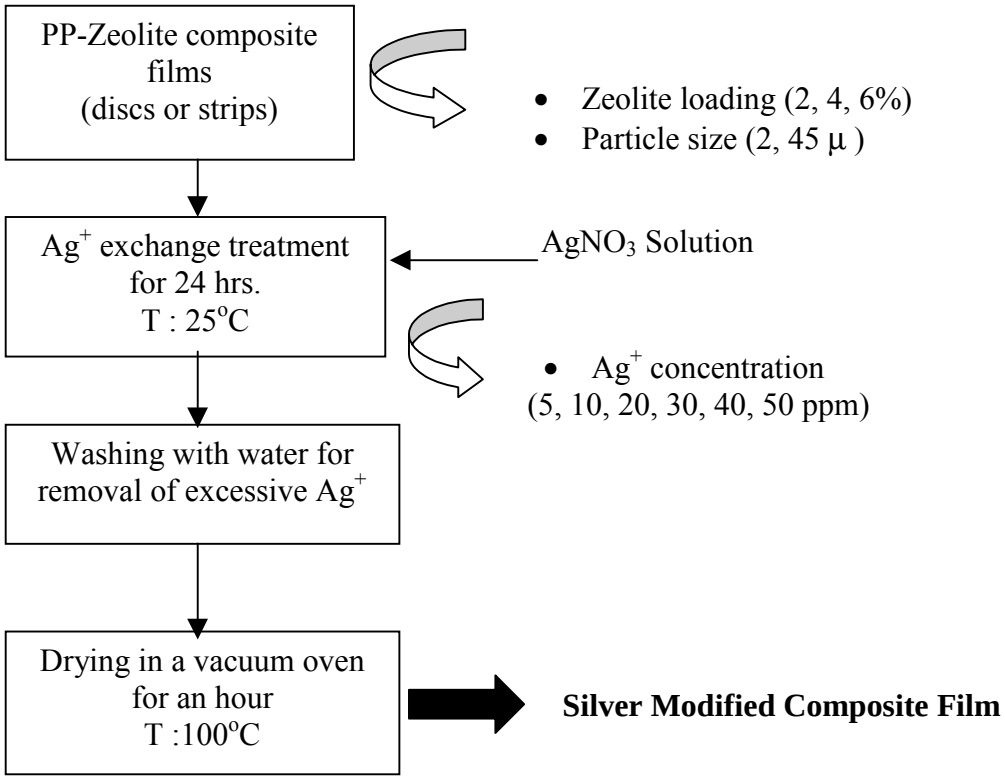


Figure 7.1. Experimental Steps for the Silver Treatment of Composite Films According to Method I.

7.2.3 Method II - Preparation of Ag – Zeolite –PP Composite Films

Method II is the compounding of PP with the silver form of natural zeolite; that is the silver treatment is performed before the composite film drawing process.

7.2.3.1 Size Reduction of Zeolites

The zeolites were first hammered to break down into smaller particles. These smaller particles were then grinded using Multifix Ball- Mill with ethanol for 4 hours. After the grinding step, the slurry was dried at 110 ^{o}C for sufficient time to remove the ethyl alcohol from the mixture. The dried zeolites were then sieved from the 45 μm sieve.

7.2.3.2 Ag^{+} Ion Exchange to the Zeolite

In order to see the extent of silver sorption onto Gördes1 clinoptilolite mineral, zeolites were treated with a series of $AgNO_3$ solutions of initial concentrations 50, 100, 200, 400, 750, 1000 ppm. At each set of experiment the solid to liquid ratio was kept constant as 1 g: 100 ml. The samples were kept at 25^{o}C for 24 hours using a water bath equipped with a shaker and a top cover preventing light to pass through. Frequently the silver exchange treatment, by fully precipitating, the liquid parts of the slurries were removed from the solutions. For convenience the solutions were centrifuged before used in ICP – AES for the determination of silver ion concentration.

After analyzing the silver exchange to zeolites, it was decided to work with initial $AgNO_3$ concentrations of 50, 500, and 5000 ppm at 25^{o}C for 24 hours using a water bath equipped with a shaker and a top cover preventing the passage of light. Following the ion exchange process, by precipitating, the solid and the liquid part of the slurry was separated. The liquid phase was centrifuged for convenience to be analyzed for the remaining silver ions present in the solution. The solid phase was washed twice for the removal of excessive silver ions. The samples then were dried in a vacuum oven at 400 mbar and 110^{o}C for 3 hours.

7.2.3.3 Surface Modification of Silver Form of Zeolites

Surfaces of silver – zeolites were modified with PEG 4000 to obtain homogeneous distribution in the PP phase. Silver forms of zeolites were mixed with 50 % aqueous ethanol solution containing 10 % modifier. Zeolite to solution ratio was taken as 1: 0.3 on weight / volume basis (Özmıhçı, 1999). The block diagram of the zeolite preparation is given in Figure 7.2.

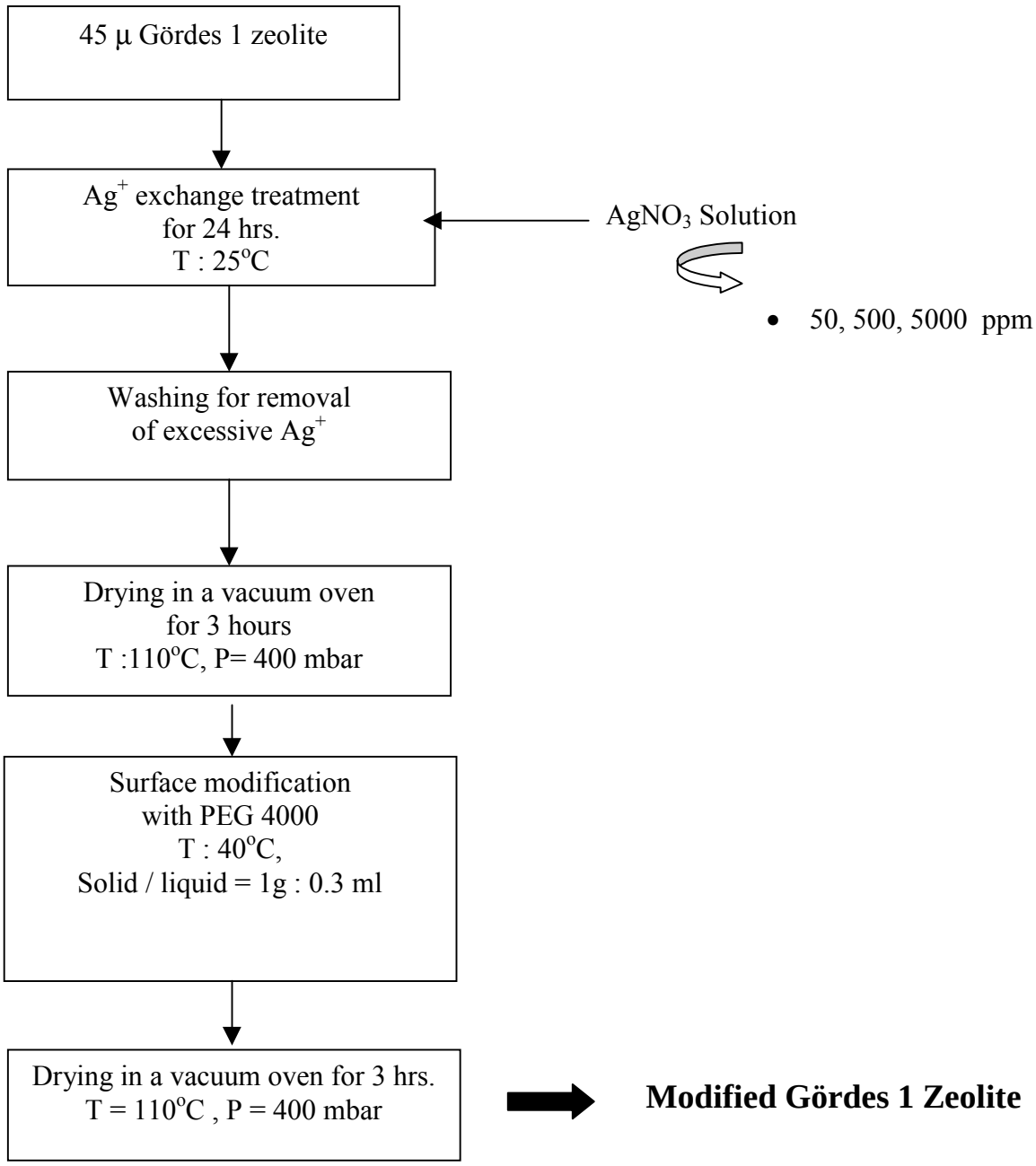


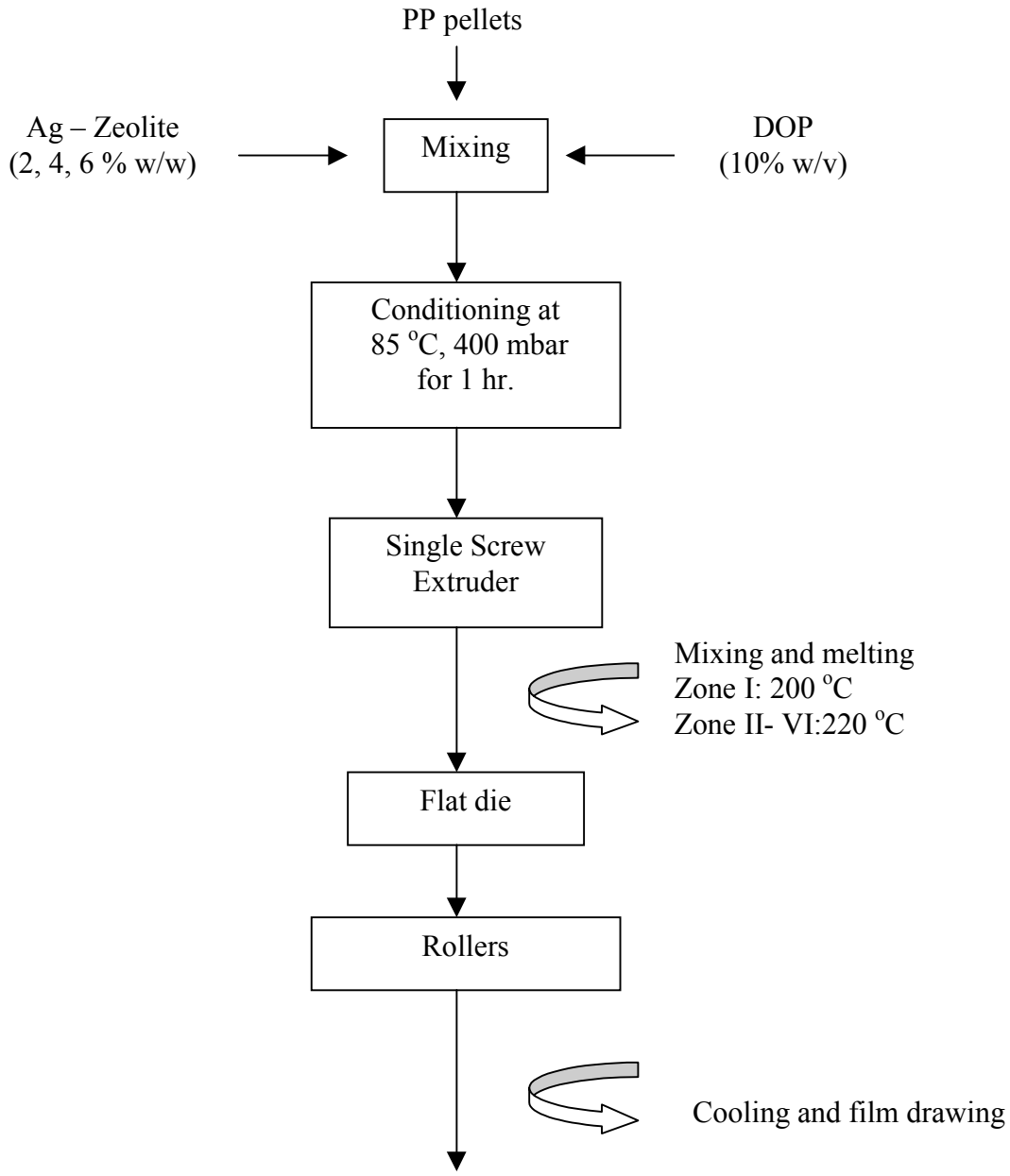
Figure 7.2 Experimental Steps for Silver Treatment of Gördes 1 Zeolite.

7.2.3.4 Silver - Zeolite - PP Film Drawing

Zeolites treated with different amounts of Ag^+ (50, 500, 5000 ppm) were mixed with PP pellets. Due to the density difference between the PP and zeolite particles, the zeolites agglomerated at the bottom of the container. In order to prevent agglomeration and provide the macromolecules slide by each other dioctyl phthalate (DOP) was used as a plasticizer. PP pellets, 45 μm zeolite particles (2, 4, and 6 wt %), and DOP (10 % total w /v) were mixed and conditioned at 85 ^oC at 400 mbar pressure for an hour before the film drawing process. The conditioned mixture of materials was then fed to the hopper of the mini extruder (BX – 18, Axon, Sweden) provided by TÜBİTAK for the extrusion process. The experimental conditions, all of which were kept constant during the experimentation for the film drawing process, are given in Table 7.4. The block diagram of the film drawing scheme using Method II is shown in Figure 7.3. Experimental set up for the film extrusion process; the single screw extruder, flat die, and the two-roll mill is shown in Figure 7.4. The extruder has an L/D ratio of 18, and a flat die of dimensions (50x1mm). Axon two roll mill (AXON, 2R-180) was used to cast the film from the extruder. Tap water was circulated in polished rolls in order to solidify the polymer melt from the extruder.

Table 7.4.Experimental Conditions of the Extrusion Process

Screw Frequency (Hz)	Motor Voltage (V)	Motor Current (A)	Roller Frequency (Hz)	Zone Temperatures (^oC)					
				1	2	3	4	5	6
20	38	4.5	15	200	220	220	220	220	220



PP – Ag – Zeolite Composite Film

Figure 7.3.Block Diagram of Film Drawing Process by Method II.

Figure 7.4.Experimental Set up for Film Drawing Unit (BX-18, AXON)

7.2.3.5 Desorption Experiments

Desorption experiments were carried out with water at 25^{o}C for 24 hours using a water bath equipped with a shaker just as the desorption experiments conducted for the composites prepared by Method I. Both of the alternatives; deionized water and 0. 9 % NaCl solutions were used. The results of these two cases were then compared.

7.3 Characterization of Composite Films

PP – silver zeolite composite films that were prepared using two different methods were characterized using various characterization techniques.

7.3.1 ICP – AES Analyses

The extent of silver exchange onto the zeolites was determined by analyzing the remaining Ag^{+} concentration in the liquid phase using Varian ICP – AES (Inductively Coupled Plasma Atomic Emission Spectrometer). First, a set of standard solutions with known silver concentrations was prepared. Using these standards, a calibration curve is constructed by the instrument at a wavelength of 328.068. The concentrations of the different samples were then detected according to that calibration curve.

7.3.2 Thermal Analyses

Thermal analyses of the Ag^+ treated films prepared by the two methods were conducted using Shimadzu Differential Scanning Calorimeter (DSC, 50), and Shimadzu Thermal Gravimetric Analyzer (TGA, 51). The experiments were carried out from room temperature up to 500 ^oC for the DSC analyses and up to 1000 ^oC for the TGA analyses, at heating rates of 5, 10, and 20 ^oC/min. The analyses were performed in a dry nitrogen atmosphere. N_2 flow rate was 40 ml/min and kept constant through out the experiments.

7.3.3 Optical Microscopy

Optical micrographs of the samples with different zeolite loadings, and Ag^+ concentrations, and the tensile tested samples were taken using transmission optical microscope fitted with Olympus BX-60 using different magnifications.

7.3.4 Density Measurements

Sample densities of 12 mm diameter films were measured with the density kit of Sortorius YDK 01 balance making use of the Archimedes' Principle. For the tensile tested samples, due to the elongation, a decrease in the samples' width was observed. Therefore, samples of 1x10 cm samples were used for density measurements. Both the sample weight and the weight of the water displaced by the sample were recorded. The weights of the samples lighter than water were measured when the sample was under a basket immersed in water, and the ones, which are heavier than water, were put on the basket.

7.3.5 Infrared Analyses

In order to obtain information on the quality and the relative quantity of the inorganic phases, the Fourier Transform Infrared Spectroscopy (FTIR) was used. The IR Spectra of the composite films were taken by placing the samples on the way of the beam using the transmission technique. The liquid plasticizer material (DOP) was analyzed by preparing KBr pellets. All spectra were taken between 400 cm^{-1} to 4400 cm^{-1} with a Shimadzu FTIR 8201 model instrument.

7.3.6 Mechanical Characterization of the Composites

Mechanical tests of the extruded composite films were performed with a Universal testing machine Instron Corporation, Series IX Automated Materials Testing System (Petkim). The samples were tested according to ASTM 822 standard. The tensile tests of the films were carried at a crosshead speed of 500 mm / min, with a load cell of 50 kgf. Each test was repeated three times and the mean values were used.

7.3.7 Test on Discoloration

Samples of composite films containing silver zeolite were exposed to sunlight in the air. The color of the samples was determined by placing each sample on a white paper with Minolta color – color difference meter 2600D (using D 65 rays). The results are compared with respect to the reference sample, pure polypropylene film.

7.3.8 Test on Antibacterial Activity

Polypropylene-zeolite composites, treated with 50 ppm Ag^+ containing solutions, were tested for their bactericidal activity with Broth Dilution and Agar Diffusion methods. The equipment and media used for this purpose are given below.

- Mueller-Hinton Broth (Oxoid) CM 405
- Mueller-Hinton Agar (Oxoid) CM 337
- Potassium dihydrogen phosphate, KH_2PO_4 (Merck) 1.04871
- Potassium hydrogen phosphate, K_2HPO_4 (Merck) 1.05101
- Sodium chloride, NaCl (Merck) 1.06400
- Antibiotic discs (Oxoid) (Cefotaxim for *E.Coli*)

7.3.8.1 Preparation of Media and Solutions

Mueller- Hinton broth and Mueller-Hinton agar were prepared as described by the manufacturer. The broth and agar were dissolved in deionized water and distilled water in separate flasks by mixing with a magnet on magnetic stirrer. Before completed

desired volume, pH of the medium was adjusted to 7.3-7.4 with 1M NaOH or 1 M HCl. After that the volume of medium was completed to desired volume with dH_2O. media were autoclaved at 121°C for 15 minutes. Mueller-Hinton agar was cooled to 45-50°C and 25 ml of medium were poured into sterile petri plates with a sterile 25 ml volumetric flask. After cooling, plates were stored at + 4°C with inverted position, and Mueller-Hinton Broth was stored at + 4°C.

Phosphate-Buffered Saline (PBS), pH 7.4 was prepared by dissolving 0.34 g KH_2PO_4, 1.58 g K_2HPO_4 and 8.0 g NaCl in distilled or deionized water. PH was adjusted to 7.4 and volume was completed to 1 liter. PBS was autoclaved at 121°C for 15 minutes and stored at + 4°C.

7.3.8.2 Broth Dilution Method

E.coli from frozen glycerol stock at –20°C was grown by streaking on a Mueller-Hinton agar plate and incubated at 37°C for overnight. The next day, one young colony was picked up with a cotton swap and the colony was dissolved in 4 ml of sterile dH_2O. The turbidity was adjusted to McFarland 0.5 (= 10^8 CFU/ml) by checking visually. 100 µl bacterium suspension was added to 4.9 ml Mueller-Hinton broth in sterile glass tubes with a final concentration of $5x10^4$ CFU /tube. Test samples were placed into the tubes and all tubes were labeled. Medium and test samples were mixed by vortexing slowly. The tubes were incubated at 37°C with shaking at 90 rpm in thermo shaker for overnight. Next day, the tubes were mixed again by vortexing slowly. 10 µl was transferred into 990 µl sterile dH_2O or Phosphate Buffered Saline (PBS) (pH 7.4) in sterile eppendorf tubes to make 10^{-2} dilution. Similarly, 10µl from 10^{-2} dilution was transferred into 990 µl sterile dH_2O to make 10^{-4} dilution. 10^{-6} and 10^{-8} dilutions were prepared. 100 µl from dilution were taken and spread on Mueller-Hinton agar plates with a glass spreader. Duplicate plates were prepared to compare number of colonies for exact results. The plates were incubated at 37°C for overnight. The following day, the number of colonies in the plates was counted. The number was then compared with negative control (broth + bacteria, no test sample), sterility control of medium (only broth) and sterility control of sample (broth + test sample, no bacteria).

7.3.8.3 Agar Diffusion Method

One colony from overnight grown culture on blood agar or Mueller-Hinton agar was taken with a cotton swap an dissolved in 1ml sterile dH_2O. The turbidity of bacterial suspension was adjusted to McFarland 0.5 ($=10^8$ CFU/ml). Bacterial suspension was spread onto Mueller-Hinton Agar plates with a swap of two directions. Sterilized test samples were put onto agar surface. The plates were left for absorption of bacteria on agar surface. The plates were incubated at 37^oC with inverted position for overnight. Next day; inhibition zones around test samples and positive controls were measured. In this method; test samples have to dissolve in agar medium to inhibit bacterial growth.

Chapter 8

RESULTS AND DISCUSSION

Polypropylene films embedded with untreated natural zeolite and silver form of natural zeolite were prepared for the purpose of combining the individual advantages of both materials to be used in different applications. The effects of number of parameters such as zeolite loading, silver concentration, and preparation techniques were investigated. The results and assessments of the analyses of the composites prepared by different techniques are given below.

8.1 Liquid Water Sorption Behavior of PP - Zeolite Composites

For preliminary studies**,** the equilibrium uptake of water for both the hot press and extruded samples was investigated with respect to the amount of filler (zeolite). As expected in both cases, the uptake values showed an increasing trend with the increasing zeolite content.

8.1.1 Water sorption of PP-Zeolite Composites Prepared by Hot Press Method

Figure 8.1 shows the water uptake of the composites containing 0 – 40 wt % zeolites. Oscillatory behavior was observed in water uptake of the composites with different zeolite loadings. It might be due to the migration of the PP or zeolite into the aqueous phase causing weight loss. PP, being a hydrophobic polymer, does not absorb any water at its pure state. However, the composites containing 6, 10, 20, 30, and 40 % wt zeolite have sorbed 0.062, 0.47, 0.54, 1.37, and 3.03 % wt water, respectively. The zeolite mineral used in the present study itself at the same conditions sorbed 24.5 % wt water. As the filler loading in composites increased, equilibrium uptake values increased too. The results for the composite samples were lower then expected, corresponding to the adsorption capacity of zeolites. It was due to the fact that zeolite is distributed along the PP phase, and the passage of water was limited that the zeolites within the composites could not adsorb water with full capacity.

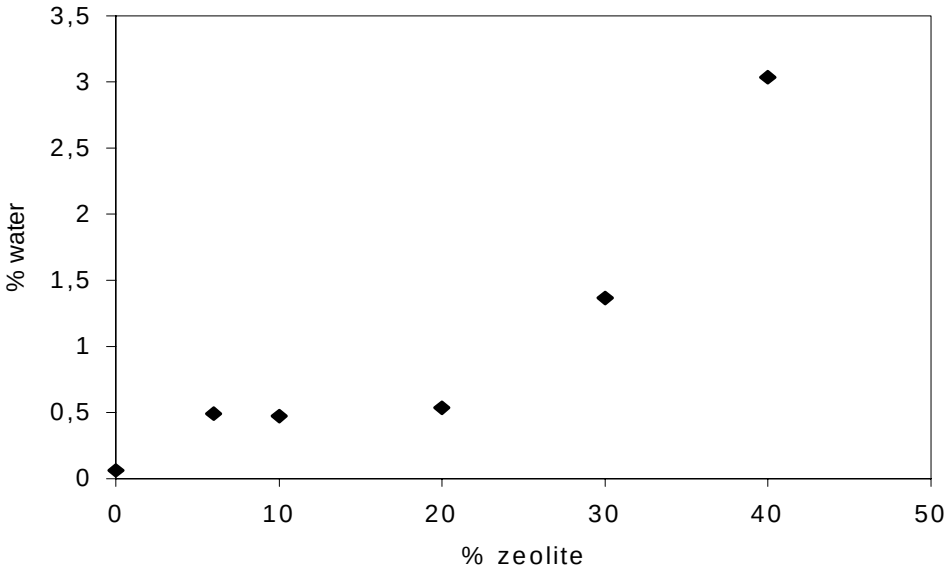


Figure 8.1. Equilibrium Uptake of Water for Hot Press Samples with Respect to Zeolite Content.

The theoretical water sorption capacities of the composites were calculated using Equation 8.1, taking into account the additivity of the matrix and filler phases on the sorption capacity (Marshall, 1990; Ulutan, 1996).

$$q=q_1W_1+q_2W_2 \tag{8.1}$$

where;

q: adsorption capacity of composite (% water, g/g)
W: weight fraction
1,2: matrix, and filler respectively.

The comparison of the theoretical and experimental results is given in Table 8.1. As shown in Table 8.1, if 10, 20, 30, and 40 % wt zeolite containing composites were fully saturated with water, they would sorb 2.45, 4.9, 7.35, and 9.8 % wt liquid water, respectively.

Sorption process could be modeled with one-dimensional diffusion equation to determine the concentration within the sample with respect to time and position (Crank,

Table 8.1.Water Sorption Results of Hot Press Samples.

Zeolite Loading (%)	Water sorption (Experimental), %	Water sorption (Theoretical), %
6	0.062	1.47
10	0.47	2.45
20	0.54	4.9
30	1.37	7.35
40	3.03	9.8

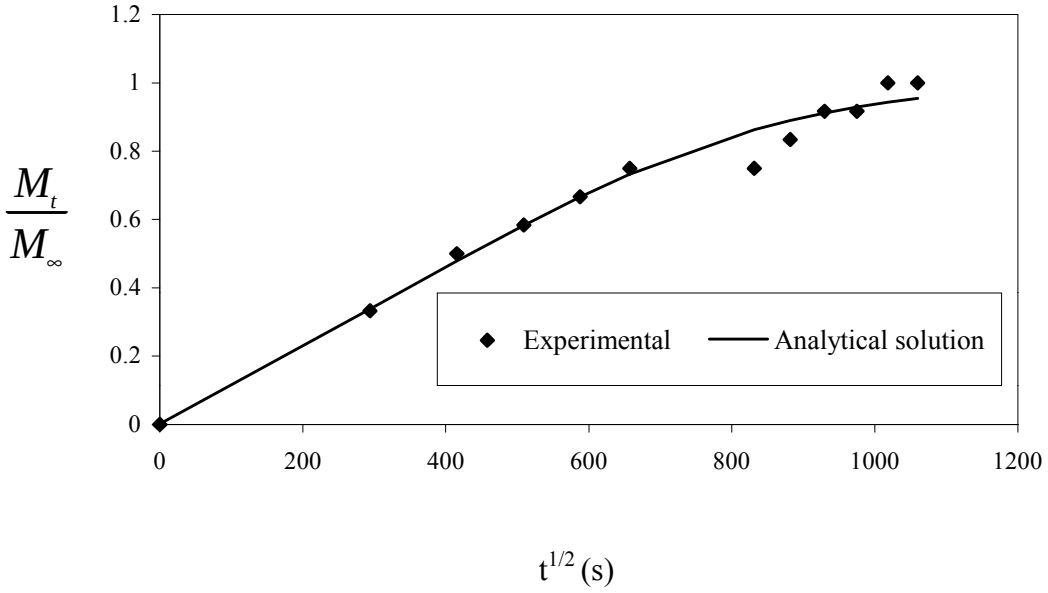


Figure 8.2. Fractional Water Uptake versus $t^{1/2}$ for 20 % wt Zeolite - PP Sample.

1968). In the water sorption study, with the hot press samples, the maximum weight gain was observed in the 40 % wt zeolite-containing sample. The equilibrium uptake of the sample with 20 % wt zeolite is given in Figure 8.2. The diffusivity of this sample calculated using Equation 4.4, was found to be 2.35 $x10^{-10}$ cm^2/s. Figure 8.2 also shows the comparison of the experimental data with the analytical solution of Equation 4.2 (Crank, 1968). The effective diffusivity values of liquid water in the composites are given in Table 8.2.

Sequential increases of the initial slope of the M_t/M_∞ with respect to the amount of filler were observed in Figure 8.3.

Table 8.2.Effective Diffusivity of Liquid Water in the PP - Zeolite Composites.

Zeolite loading %	$D_e x 10^{10}$ (cm^2/s)
6	0.33
10	3.01
20	2.35
30	8.60
40	9.90

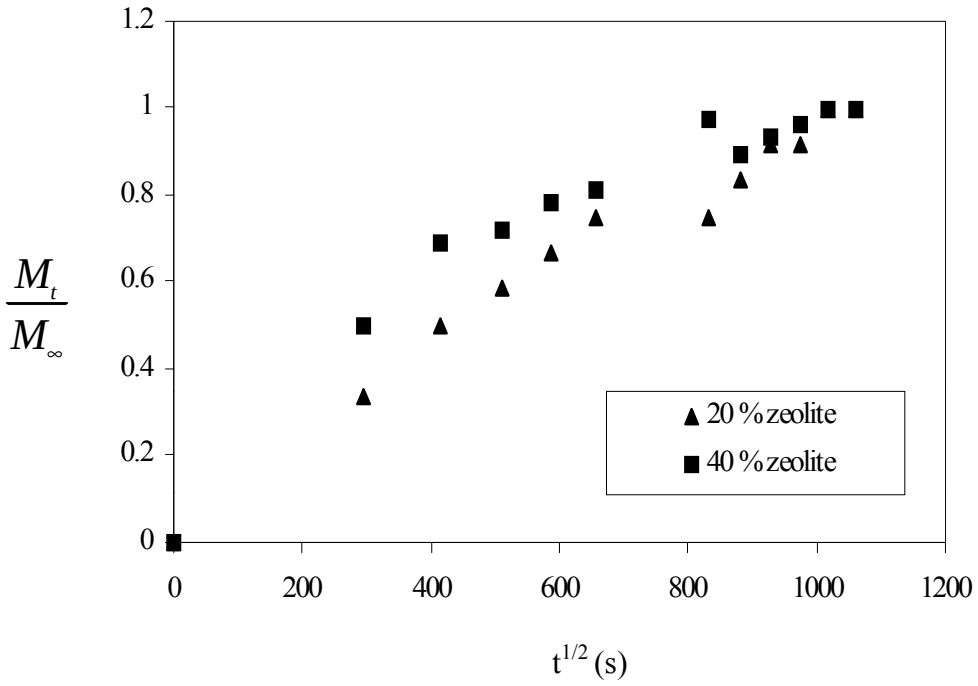


Figure 8.3.Comparison of Water Uptake Curves of 20 and 40 % wt Zeolite Containing Composites.

The higher the amount of zeolite in the composites, the higher the slope of the water uptake and the higher the diffusion coefficient of water in the composites.

8.1.2 Water Sorption to Extruded Films

The water sorption behavior was also examined with the extruded samples prepared in Petkim. The extruded samples contained 2, 4, and 6 % wt zeolite. Figure

8.4 shows the equilibrium uptake of water for the composites containing 2, 4, and 6 % wt zeolite containing films.

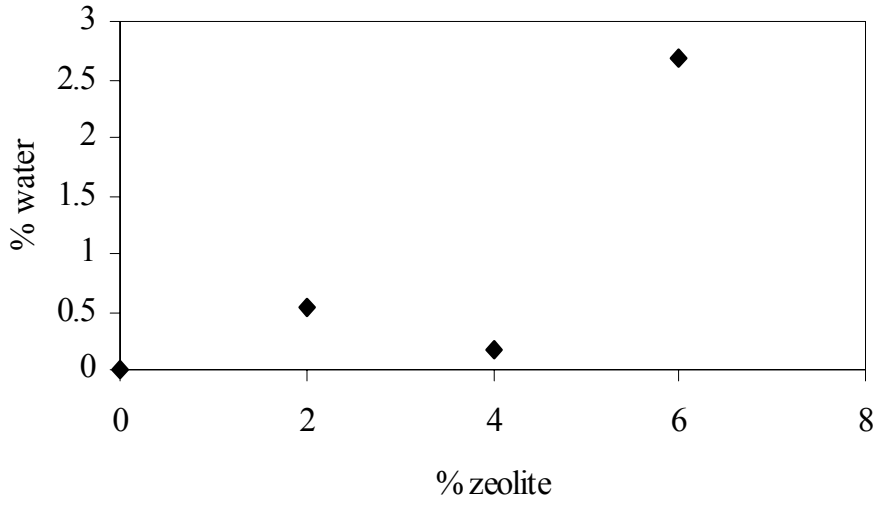


Figure 8.4.Equilibrium Uptake of Water for Extruded Samples with Respect to Zeolite Content.

The experimental water sorption capacities of the extruded composites are shown in Table 8.3 in comparison with the theoretical results, calculated by Equation 8.1.

The results for the 2 % wt zeolite containing samples coincides with each other while the experimental and theoretical results for the 4 and 6 % wt samples differ from each other. This is due to the nonuniform zeolite distribution in the test samples.

The differences between the theoretical and the experimental sorption capacities of the hot press samples were more significant compared to that of the extruded samples. This might be due to the fact that the hot press samples were considerably thicker than the extruded samples and that water could not penetrate into the zeolite phase.

The effective diffusivity values of water in the extruded samples with respect to zeolite content are given in Table 8.4. It was observed that the diffusion coefficient of liquid water through the extruded samples is smaller than that of the hot press samples. The equilibrium uptake of the 4 % sample with the experimental data compared with the analytical solution is illustrated in Figure 8.5. The experimental data were in good agreement with the analytical solution.

Table 8.3.Water Sorption Results of Extruded Samples.

Zeolite Loading (% wt)	Water Sorption (Experimental), %	Water Sorption (Theoretical), %
2	0.54	0.49
4	0.17	0.98
6	2.68	1.47

Table 8.4.Effective Diffusivity of Liquid Water in the Extruded Composites.

Zeolite content, %	$D_e x10^{12}$ (cm^2/s)
2 (2 μm)	0.13
2 (45μm)	1.33
4 (2μm)	2.4
4 (45μm)	3.34
6 (2μm)	0.22

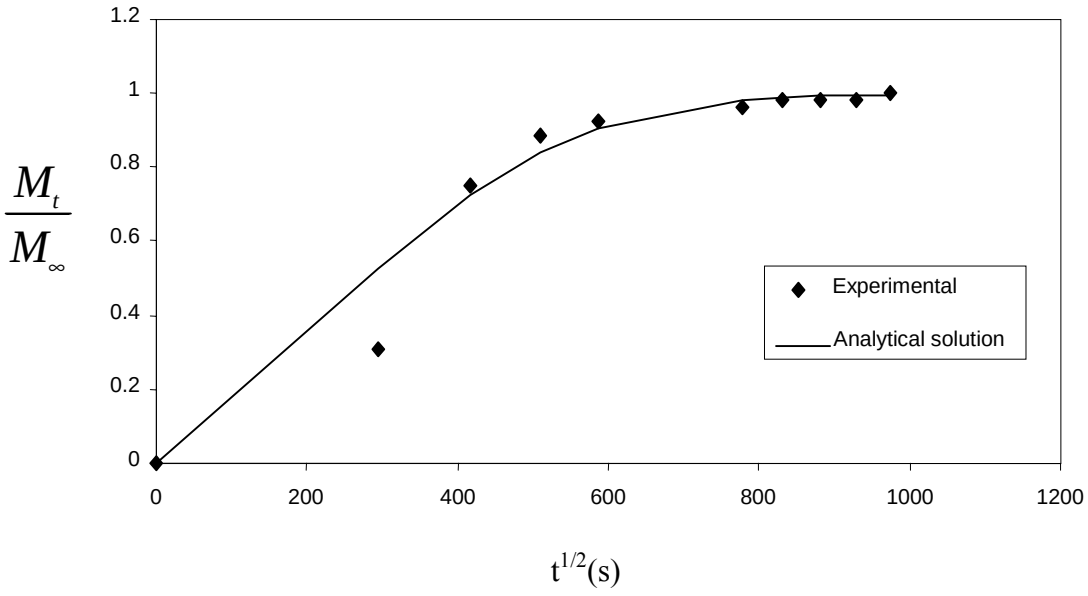


Figure 8.5.Fractional Uptake versus $t^{1/2}$ for Extruded Film With 4 % Zeolite.

Figure 8.6 shows the comparison of the water sorption behavior of the composites containing 6 % wt zeolite prepared by hot press and extrusion methods. Since the thickness of the samples prepared by hot press and extrusion methods differs from each other, M_t / M_∞ was plotted against $(t/l^2)^{0.5}$ instead of $(t)^{0.5}$ to normalize sample thickness.

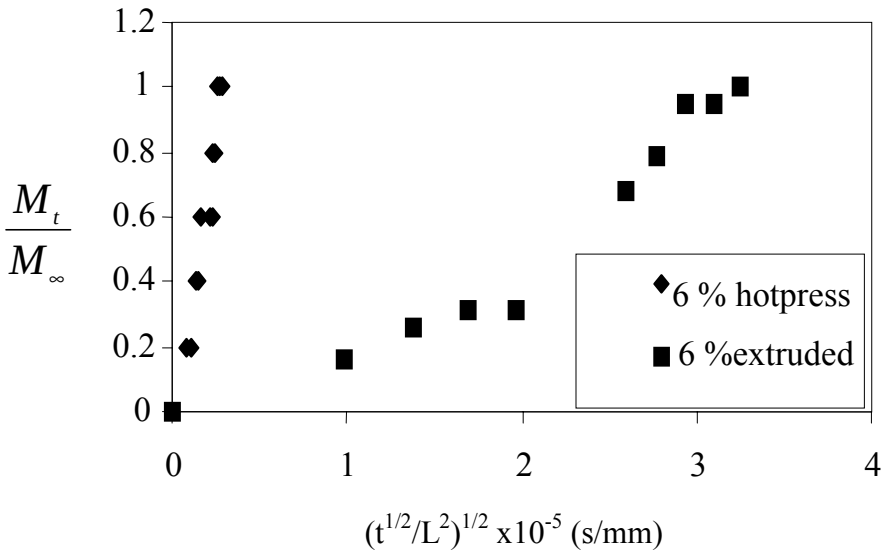


Figure 8.6.Fractional Uptake versus $(t^{1/2}/L)$ for Extruded and Hot Press Films Containing 6 % wt Zeolite.

Higher diffusivity coefficient values were obtained for hot press films on the order of –10 vs –12. Although the extruded samples were expected to sorb water faster than the hot press films, the results were came out to be the opposite. This might be due to the fact that zeolite distribution along the PP phase was significantly better for the hot press samples compared to the extruded samples.

8.2 Silver Sorption Results on PP- Zeolite Composite Films

Silver sorption capacities of PP - zeolite composites treated with $AgNO_3$ solution according to Method I were determined at 25°C using ICP technique. Effect of zeolite loading and initial Ag^+ concentration on the sorption capacities of the composites was investigated.

8.2.1 Silver Sorption on PP-Zeolite Composite Discs

Silver sorption capacities of the PP – zeolite composite films in the form of small discs were determined at various initial $AgNO_3$ solution concentrations of 5 to 50 ppm at 25^oC. Although the initial solution concentrations were considerably low, still considerable amount of silver sorption was observed with the films containing 2, 4, and 6 % wt zeolite. Figures 8.7 through 8.12 show the silver sorption results of the composites at various silver concentrations with respect to zeolite loading and particle size. However the effect of either the zeolite loading or the particle size of zeolite was not significant as can be seen from Tables 8.5 to 8.10, and Figures 8.7 to 8.12 due to the nonhomogeneous distribution of the zeolite particles in the PP phase. The theoretical sorption capacities of the composites were determined according to Equation 8.1. The experimental results were found to be lower than the calculated values using equation 8.1, that are given in Figures 8.13 to 8.15 for the composites having 2 – 6 % wt zeolites (2μm), respectively. This result was due to the fact that, the zeolite loading is not constant throughout the films and that the extent of the sorption process strongly depends upon the zeolite content. If the particles were uniformly distributed in the PP matrix phase, an increase in the sorption capacities would be expected with the increasing zeolite loading and decreasing particle size. This is easily seen especially from the Figures 8.7 to 8.9 that the sorption capacity was higher in the composites containing 2μm zeolite particles compared to that of the 45μm zeolite containing samples.

Table 8.5.Silver Sorption Results onto Composite Films (Initial conc: 4.65 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.139	4.60	0.04
2	2	0.183	4.17	0.37
2	45	0.141	4.45	0.28
4	2	0.156	4.60	0.03
4	45	0.324	4.79	0.02
6	2	0.164	4.39	0.28

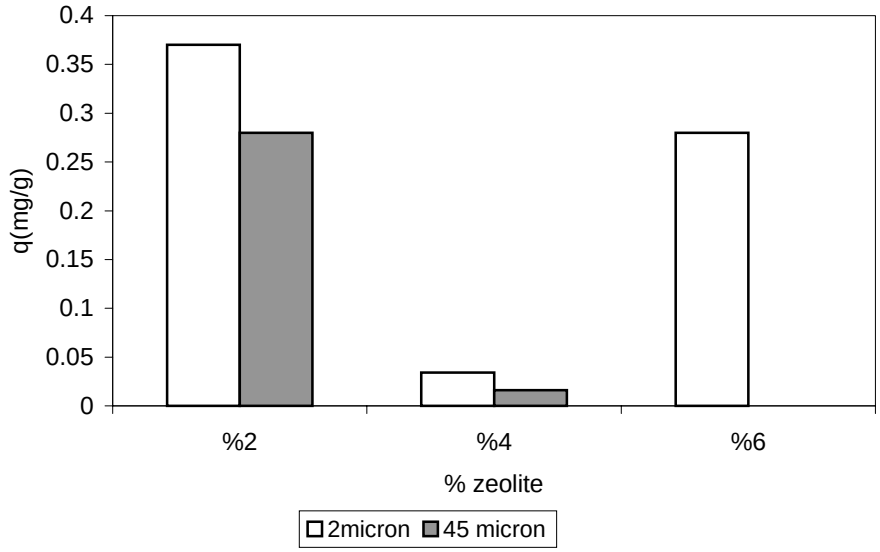


Figure 8.7.Silver Sorption Results of Composite Films Equilibrated with 4.65 ppm Ag^{+} Solution with Respect to Zeolite Loading and Particle Size.

Table 8.6.Silver Sorption Results onto Composite Films (Initial conc: 8.67 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.13	8.03	0.43
2	2	0.11	7.91	0.66
2	45	0.16	7.86	0.51
4	2	0.16	7.84	0.51
4	45	0.27	8.43	0.07
6	2	0.17	8.56	0.07

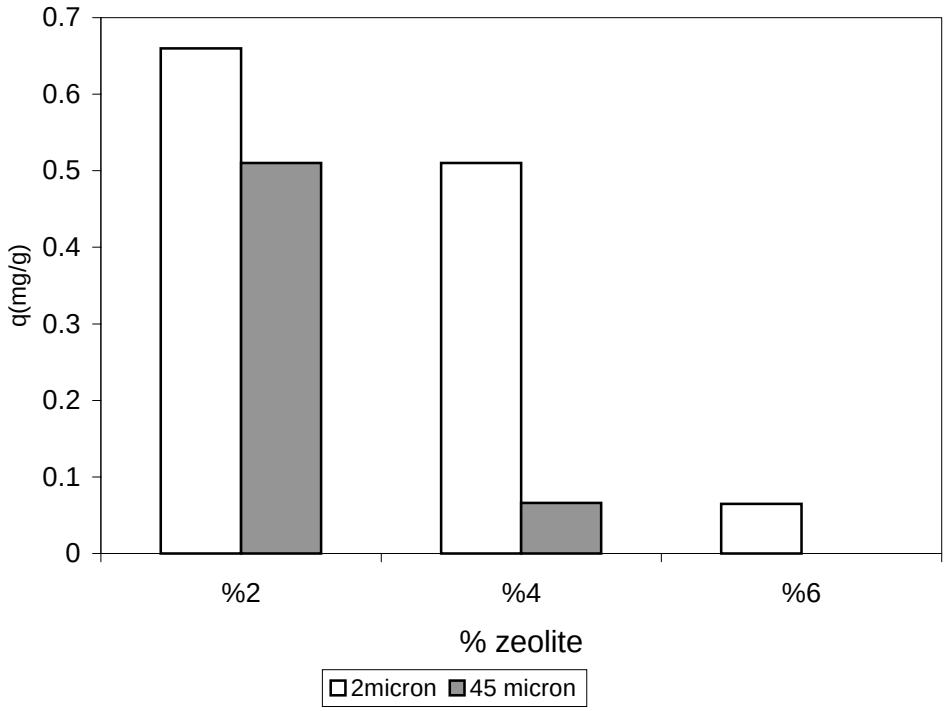


Figure 8.8.Silver Sorption Results of Composite Films Equilibrated with 8.66 ppm Ag^{+} Solution with Respect to Zeolite Loading and Particle Size.

Table 8.7.Silver Sorption Results onto Composite Films (Initial conc: 18.08 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.13	17.55	0.41
2	2	0.14	17.46	0.46
2	45	0.15	17.43	0.44
4	2	0.17	17.37	0.42
4	45	0.31	17.52	0.18
6	2	0.18	17.30	0.44

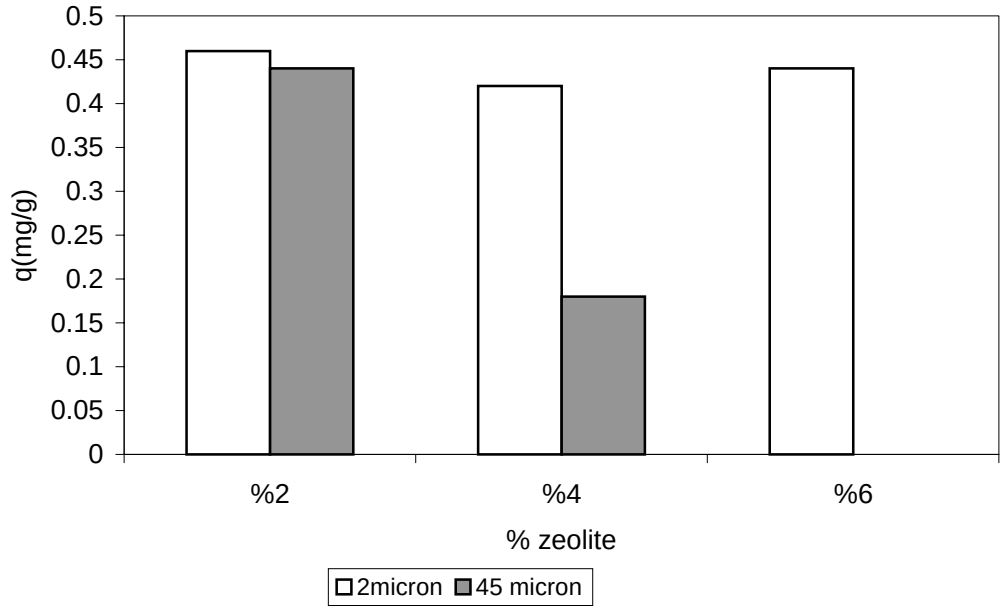


Figure 8.9.Silver Sorption Results of Composite Films Equilibrated with 18.08 ppm Ag^+ Solution with Respect to Zeolite Loading and Particle Size.

Table 8.8.Silver Sorption Results onto Composite Films (Initial conc: 24.61 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.13	24.67	0
2	2	0.14	24.61	0.002
2	45	0.15	24.49	0.08
4	2	0.17	24.53	0.05
4	45	0.31	24.39	0.07
6	2	0.17	24.15	0.28

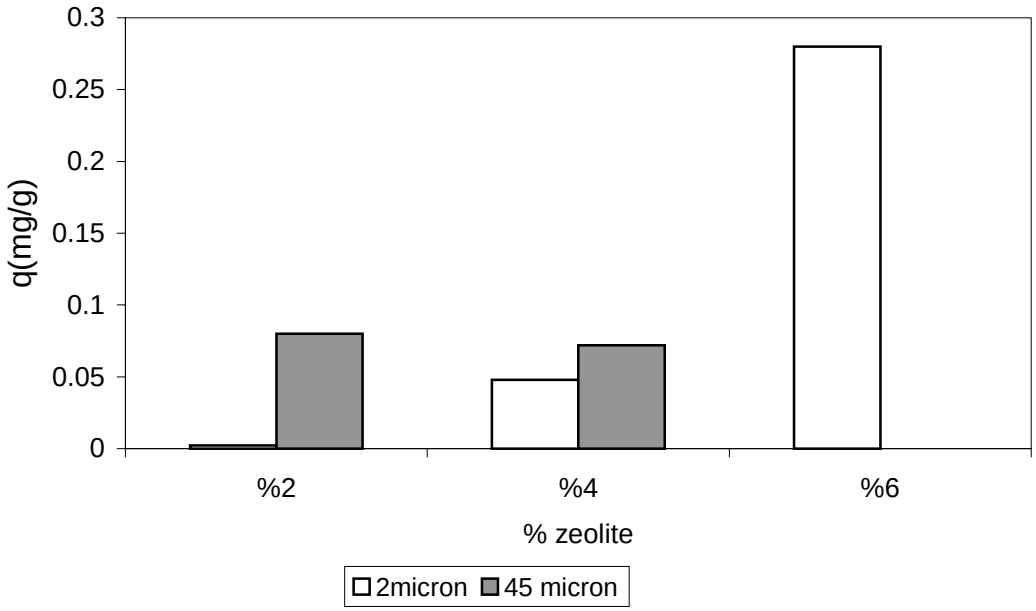


Figure 8.10.Silver Sorption Results of Composite Films Equilibrated with 24.61 ppm Ag^{+} Solution with Respect to Zeolite Loading and Particle Size.

Table 8.9.Silver Sorption Results onto Composite Films (Initial conc: 38.93 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.14	38.24	0.50
2	2	0.16	38.06	0.55
2	45	0.19	38.15	0.48
4	2	0.18	38.31	0.35
4	45	0.35	37.98	0.28
6	2	0.17	38.02	0.52

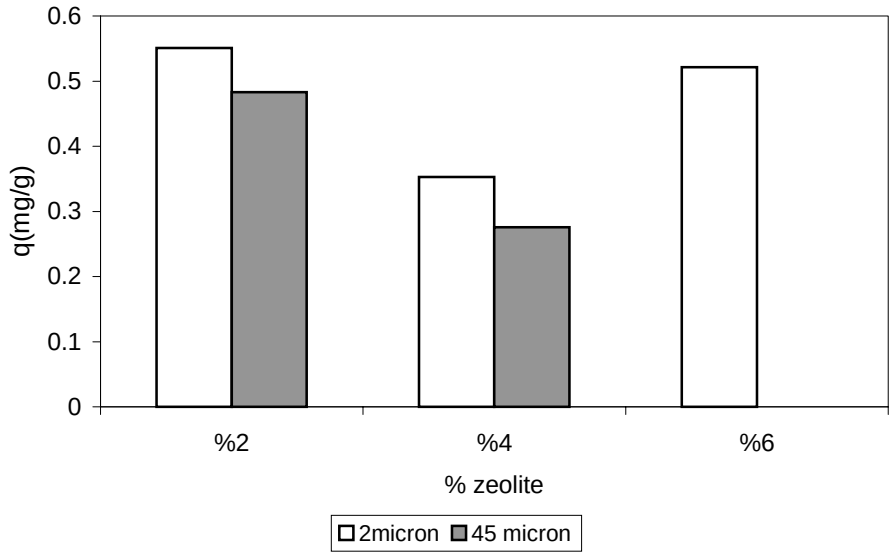


Figure 8.11.Silver Sorption Results of Composite Films Equilibrated with 38.93 ppm Ag^{+} Solution with Respect to Zeolite Loading and Particle Size.

Table 8.10.Silver Sorption Values onto Composite Films (Initial conc: 47.22 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.14	46.84	0.27
2	2	0.16	47.41	0
2	45	0.17	46.93	0.17
4	2	0.19	47.34	0
4	45	0.34	46.52	0.21
6	2	0.18	46.87	0.20

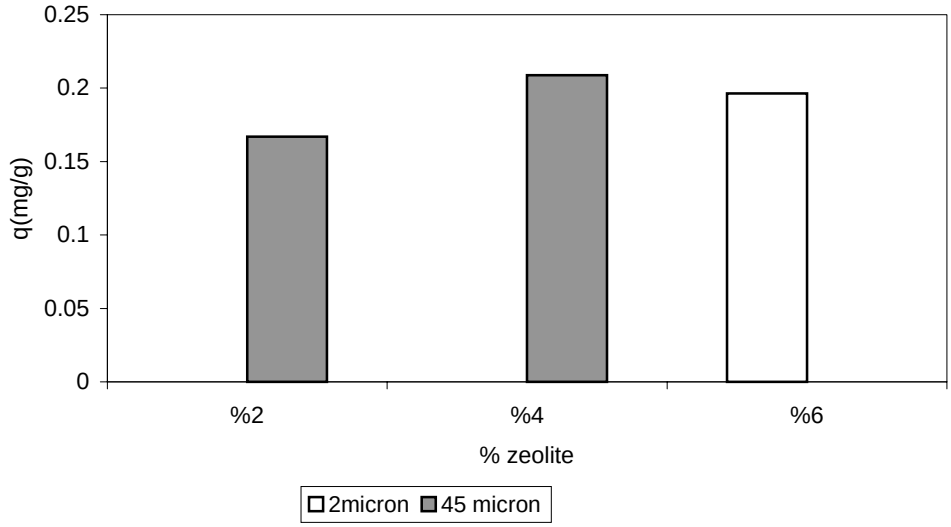


Figure 8.12.Silver Sorption Results of Composite Films Equilibrated with 47.22 ppm Ag^{+} Solution with Respect to Zeolite Loading and Particle Size.

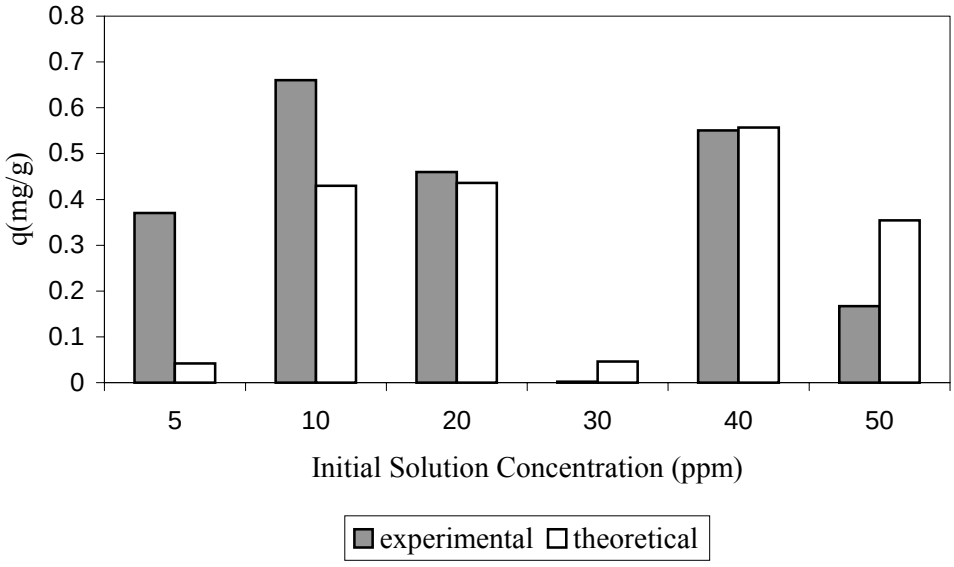


Figure 8.13. Comparison of Experimental and Theoretical Sorption Capacities for 2 % Zeolite Containing Films (2μm).

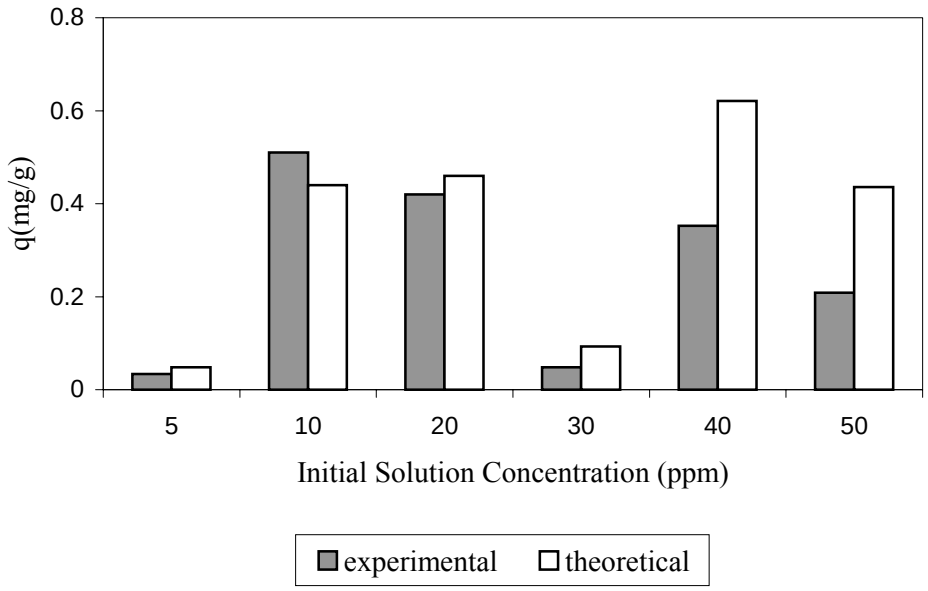


Figure 8.14. Comparison of Experimental and Theoretical Sorption Capacities for 4 % Zeolite Containing Composite Films (2μm).

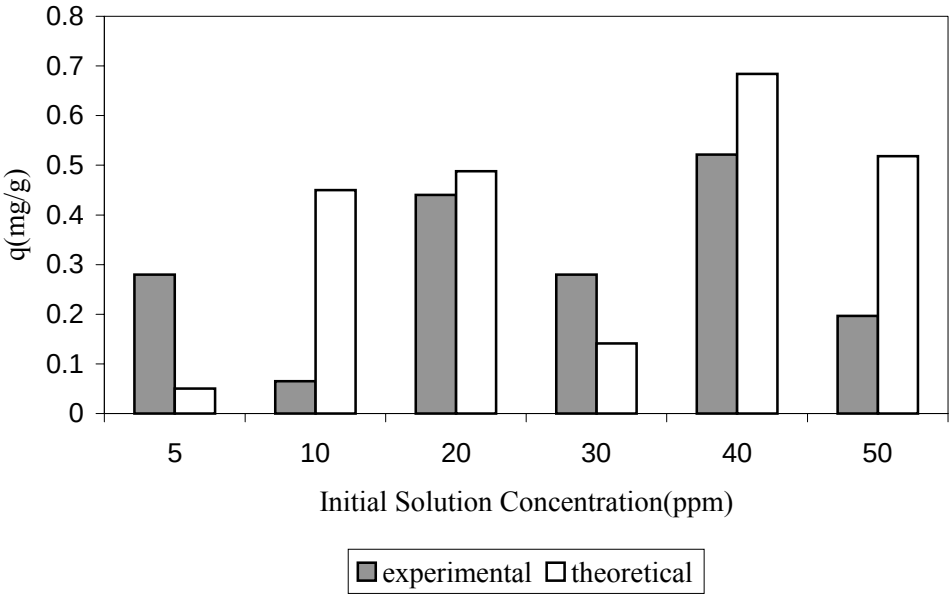


Figure 8.15. Comparison of Experimental and Theoretical Sorption Capacities for 6 % Zeolite Containing Films (2μm).

8.2.2 Silver Sorption to Polypropylene – Zeolite Composite Strips

In the case of small discs, it was observed those circular films all stacked to each other and floated just at the surface of the solution. In order to make sure that all the films were fully in contact with the solution strips of (15x2) cm films were used instead of the discs for 40 ppm Ag^+ trials. The results however, showed no enhancement in terms of Ag^+ sorption compared with the disc samples. Therefore, this fact was neglected. Silver sorption results of the strip samples are given in Table 8.11.

Table 8.11.Silver Sorption Results onto Composite Strip Films (Initial conc: 38.6 ppm).

Zeolite Loading (%)	Particle Size (μm)	Mass of film (g)	Eq. Solution Concentration (ppm)	q (mg/g)
0	0	0.42	38.09	0.12
2	2	0.28	38.13	0.16
2	45	0.45	37.94	0.14
4	2	0.53	37.67	0.17
4	45	0.73	37.62	0.13
6	2	0.47	37.99	0.13

When the results of the disc and strip samples treated with 40 ppm $AgNO_3$ solution for were compared, the sorption capacities of the disc samples were even higher than that of the strip samples.

8.2.3 Results of Ag^+ Release from Composites

As reported in literature SZ (silver zeolite) releases very small amount of Ag^+, which is the critical point for the antimicrobial activity. Silver release to water from composites was investigated and found to be negligible. However, when NaCl solution was used as a desorption media instead of deionized water, composites equilibrated with 50 ppm of Ag^+ released about detectable amounts of Ag^+ to NaCl solution as given in Table 8.12 due to the formation of an ion exchange media between Ag^+ and Na^+ ions.

The release of Ag^+ from SZ containing films is given in Figure 8.16. Release of Ag^+ from silver zeolite containing films changed between 0.15 – 0.17 ppm.

Table 8.12.Ag^+ Release From Composite Films to NaCl Solution.

Zeolite Loading (%)	Particle Size (μm)	Ag^+ in solution (ppm)
0	0	0.167
2	2	0.174
2	45	0.156
4	2	0.175
4	45	0.173
6	2	0.150

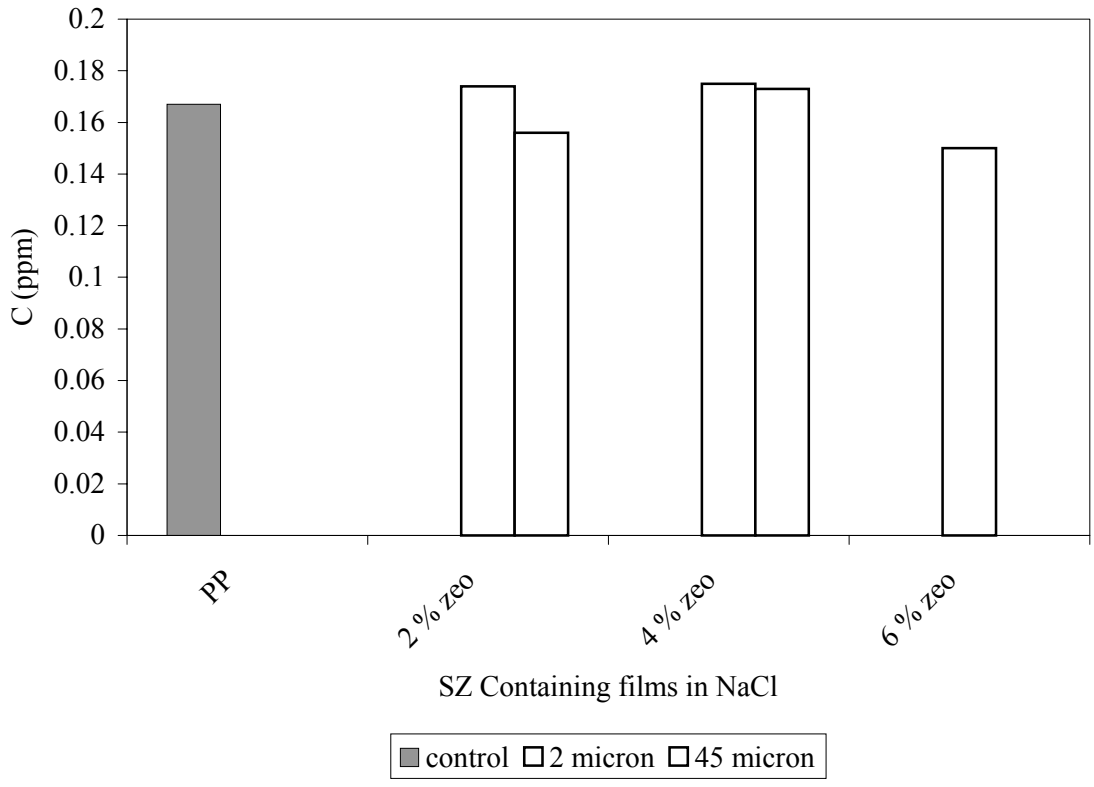


Figure 8.16.Release of Ag^+ from SZ Containing Composite Films to NaCl Solution

8.3 Preparation of Ag-Zeolite-PP Composite Films

As a second alternative the zeolite was treated with silver before molding with polypropylene. Although, it is difficult to cope with the powder form of zeolite during the ion exchange process, in terms of washing, filtering, and drying; treating the filler with the antibacterial agent before molding is more practical and sensible for industrial applications.

8.3.1 Ag^+ Exchange to Zeolite

Gördes Clinoptilolite minerals (45μm) were treated with $AgNO_3$ solutions of initial concentrations changing between 0 to 5000 ppm. The sorption isotherm of Ag^+ on zeolite is given in Figure 8.17. The figure compares the experimental data with the solution of Langmuir and Freundlich Isotherm Equations (Equation 8.2 and 8.3 respectively). The constant parameters determined for both of the isotherm equations are given below in Table 8.13. As reported in literature zeolite has a strong affinity towards cations especially Ag^+, likewise the extent of Ag^+ exchange to zeolite was considerably high as shown in Table 8.14.

Table 8.13 Constant Parameters of Langmuir and Freundlich Isotherms

Freundlich Equation		Langmuir Equation	
K	1.73	q_s	35.65
N	2.08	B	0.01

$$q = [(bC)/(1+bC]q_s \tag{8.2}$$

where;

q= amount sorbed (mg Ag^+ / g zeolite)

q_s= maximum sorption capacity

C= equilibrium solution concentration (ppm)

b= constant

$$q = KC^{1/n} \tag{8.3}$$

where;

q= amount sorbed (mg Ag^{+} / g zeolite)

C= equilibrium concentration (ppm)

K= constant

n= constant

Table 8.14.Silver Sorption Values onto Zeolite.

Initial Solution Concentration (ppm)	Eq. Solution Concentration (ppm)	q (mg / g zeolite)
5	1.14	0.35
10	1.52	0.71
20	0.89	1.72
30	1.22	2.34
40	2.23	3.67
50	3.58	4.36
100	33.91	6.6
200	77.59	12.24
400	186.24	21.3
500	238.57	27.85
750	411.40	33.8
1000	643.51	35.64
5000	3234.60	183.78

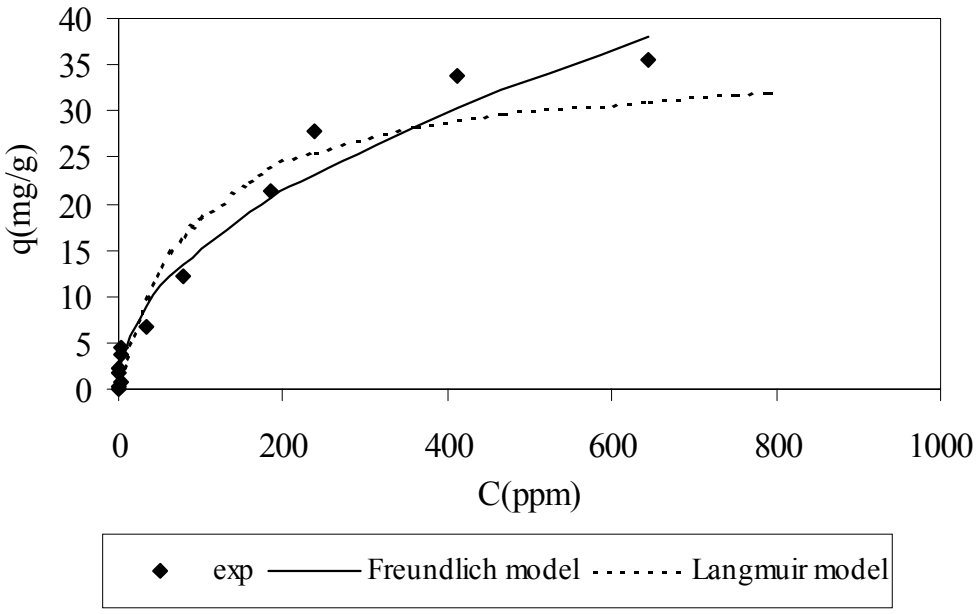


Figure 8.17.Sorption Isotherm of Ag^+ onto Zeolite.

The experimental data and the Freundlich isotherm solution showed a better agreement with each other compared to the Langmuir isotherm.

The maximum amount of silver taken by Gördes 1 zeolite (183.78 mg Ag^+/ g zeolite), in the present study, is comparable with the silver uptake in different monocationic forms of clinoptilolite. The original clinoptilolite, NH_4 – form, K – form, and Na- form of clinoptilolite were determined to take 74.0, 84.3, 86.6, and 120.7 mg Ag^+/g clinoptilolite respectively. The good exchangeability of silver ions into zeolite can be explained by the high polarizability of silver ions. The electrostatic charge of zeolite lattice is capable of polarizing silver ions so that they become dipoles directing their positively charged end to the lattice (Czaran, 1988).

8.3.2 SZ - PP Film Drawing

BX – 18 Axon Extruder shown in Figure 7.4 was used for polymer film drawing process in the present study. The extruder being a laboratory scale machine has a low L/D ratio of 18, and it is single screw type, therefore the mixing process was not sufficient. The films were thicker compared to the PP – zeolite composite films prepared with the Tonable Plastics machinery (Petkim, Aliağa). The film thickness values for the samples prepared in Petkim changes between 10 – 50 μm, while the film

thickness values of the samples prepared in the present study changes between 230 – 320μm. Zeolite particles, although they were grinded down to 45 μm, agglomerated in quite large diameters, and they were not homogeneously distributed along the composite film. In order to avoid these agglomerations, and provide compatibility between the zeolite particles and PP phase, DOP (dioctylphthalate) was used to establish a plasticizer effect. Although the agglomerations were not totally prevented, DOP gave considerably better results.

8.3.3 Release of Ag^+ from Composite Films

The composites prepared by Method II, were also tested for their silver releases. It was expected that more amounts of silver would be released to both water and NaCl solutions compared with the previous set, because the silver concentrations were comparably higher this time. In the case of deionized water, detectable amounts of silver ions were present, however for NaCl solution the results were of the same magnitude with the previous method. Figures 8.18 and 8.19 show the desorption of the silver ions to water and NaCl solution, respectively. However the effect of either the zeolite loading or the silver concentration was not seen in the Ag release to water experiments as shown in Figure 8.18. Silver release to water is in the range of 0.077 – 0.06 ppm level. In the case of NaCl solution, the silver release showed an increasing trend with the increasing zeolite loading at constant silver concentration as shown in Figure 8.19. Silver release to NaCl solution is between the range of 0.05 and 0.14 ppm level. The results of the silver release experiments are tabulated in Tables 8.15 and 8.16.

Although silver releases of the composites to water prepared by Method II was detectable, they are considerably lower compared to the releases to NaCl.

Table 8.15.Ag^+ Release from Composite Films to Water.

Zeolite Loading (% wt)	Initial $AgNO_3$ Concentration (ppm)	Amount of Ag^+ exchanged on composites (mg/g zeolite)	Ag^+ in solution (ppm)
2	50	4.36	0.06
4	50	4.36	0.02
6	50	4.36	0.02
2	500	27.85	0.04
4	500	27.85	0.007
6	500	27.85	0.01
2	5000	183.78	0.06
4	5000	183.78	0.03
6	5000	183.78	0.03

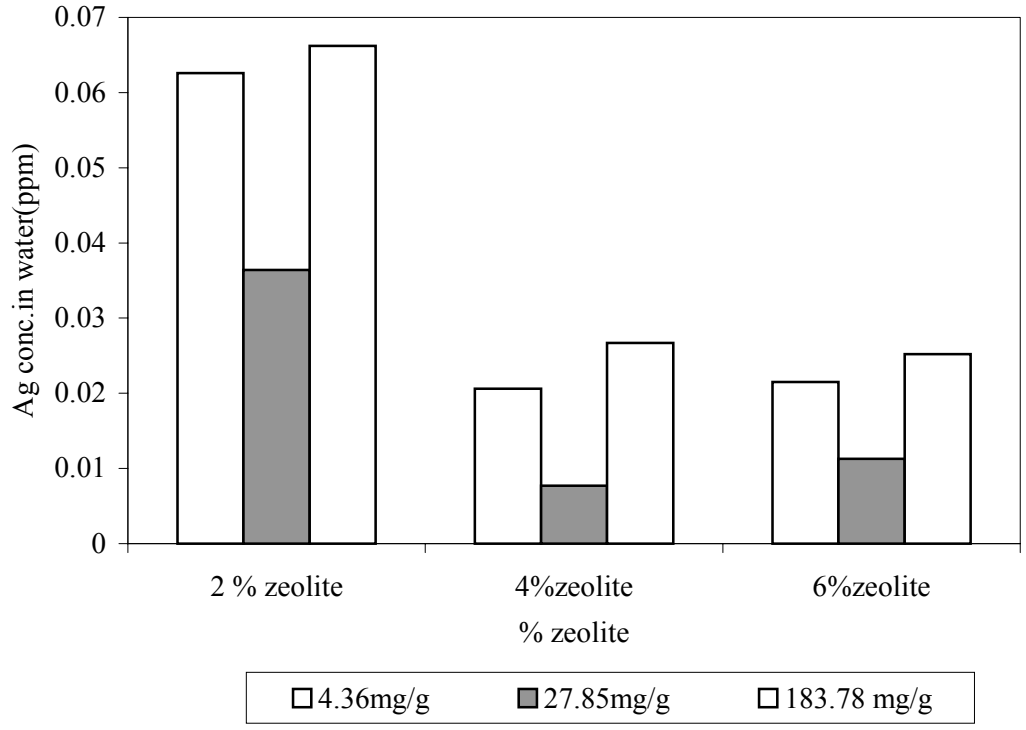


Figure 8.18.Ag^+ Release to Water from Composite Films Prepared by Method II.

Table 8.16.Ag^+ Release from Composite Films to NaCl Solution.

Zeolite Loading (% wt)	Initial $AgNO_3$ Concentration (ppm)	Amount of Ag^+ Exchanged on composites (mg/g zeolite)	Amount of Ag^+ (ppm)
2	50	4.36	0.05
4	50	4.36	0.13
6	50	4.36	0.14
2	500	27.85	0.07
4	500	27.85	0.09
6	500	27.85	0.09
2	5000	183.78	0.04
4	5000	183.78	0.06
6	5000	183.78	0.08

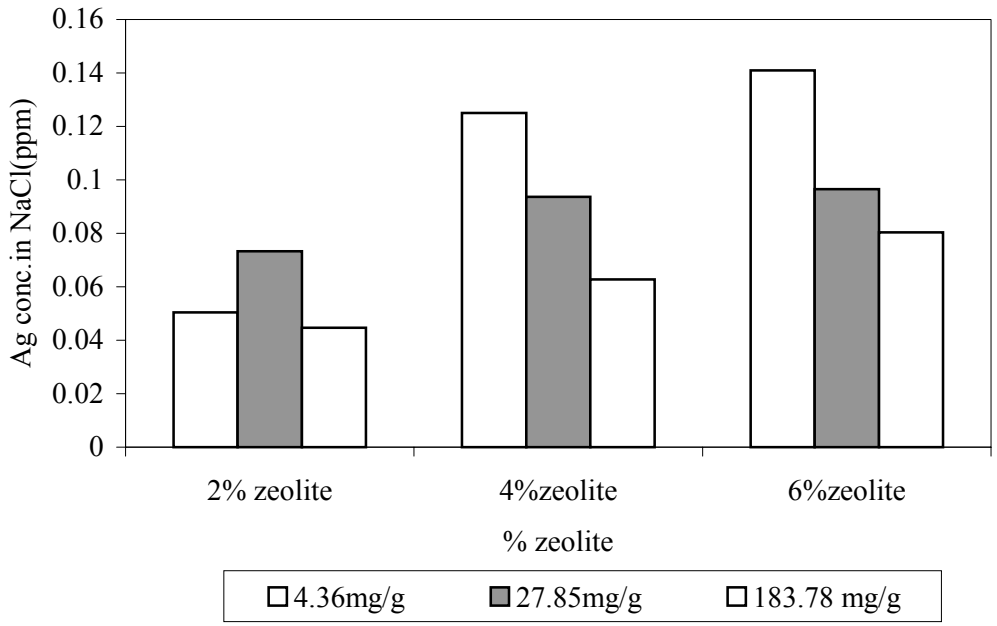


Figure 8.19.Ag^+ Release to NaCl Solution from Composite Films Prepared by Method II.

8.4 Characterization of Ag - Zeolite – PP Composite Films

The polypropylene – zeolite composites prepared by Method II were characterized using different methods to examine the effects of silver and zeolite into PP matrix by different means.

8.4.1 FTIR Spectroscopy Results

To investigate the structure of the PP – zeolite composite films, FTIR spectroscopy was used. As in the case of polymer films, polymer composites were analyzed using transparent films. DOP and natural zeolite were analyzed by preparing KBr pellets.

The FTIR spectra of PP, Gördes1 zeolite and DOP used throughout this study are given in Figures 8.20 to 8.22. As seen from the figures all characteristic peaks of polypropylene and zeolite given in Table 5.2 and 5.3 are present in their spectra. In Figure 8.20, broad peaks at 3100 cm^{-1} and 1640 cm^{-1} come from the antioxidants used in polypropylene. The 450 cm^{-1} and 609 cm^{-1} peaks in Figure 8.21 show the internal and external T- O - double ring respectively, and are known as the characteristic peaks of natural zeolite. The 609 cm^{-1} peak was used to determine the clinoptilolite content in zeolite (Krivascyet al, 1992; Özmıhçı,1999). The 1750 cm^{-1} peak stands for the carbonyl group, here corresponding to the DOP peak in Figure 8.22.

The FTIR spectra of the samples loaded with 4.36 (mg/g) silver and a zeolite loading of 2, 4, 6 % are given in Figures 8.23 to 8.25. Although the 450 cm^{-1} peak is reported as the characteristic peak for natural zeolite it is also seen in the spectrum of pure polypropylene as shown in Figure 8.20. This might be due to the additive materials present in the polypropylene. As seen in Figures 8.23 to 8.25, 450 cm^{-1} peak is greater in PP – silver loaded zeolite composites than that of in pure PP. The peak intensity at 450 cm^{-1} was increased with the increasing zeolite content in the composites.

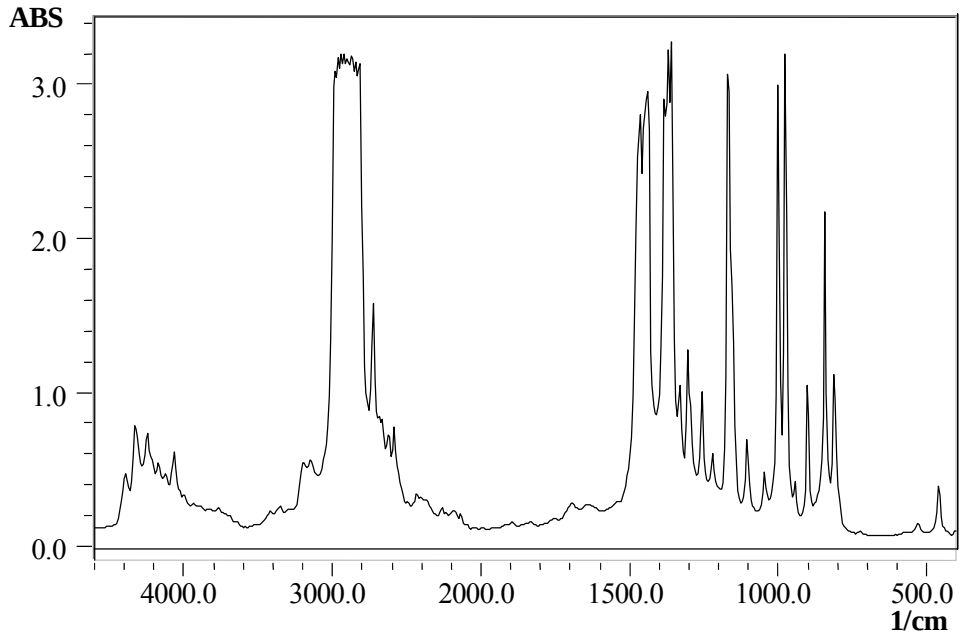


Figure 8.20.FTIR Spectrum of Polypropylene

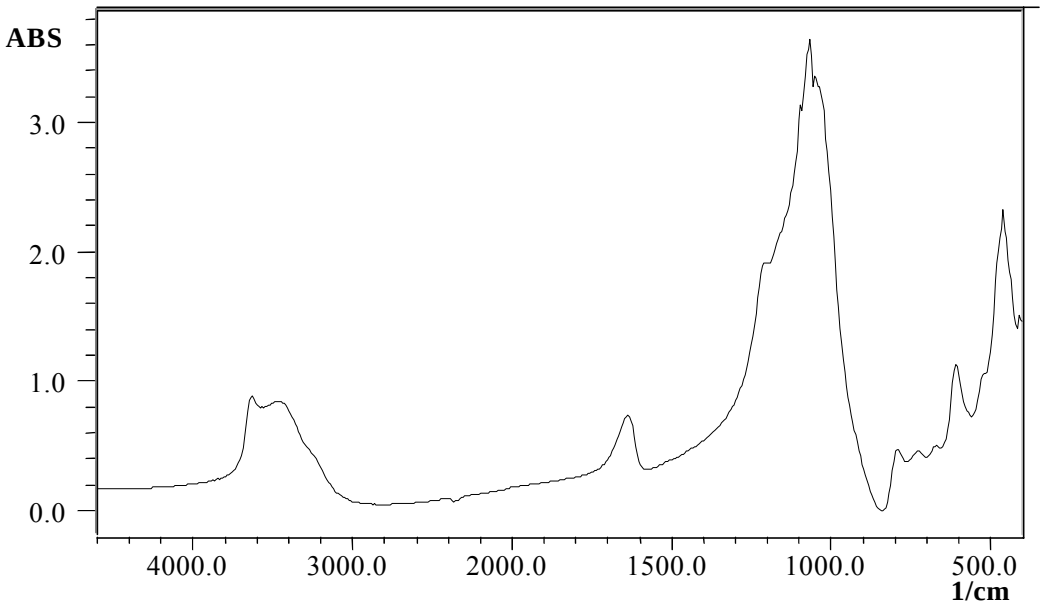


Figure 8.21.FTIR Spectrum of Gördes 1 Zeolite.

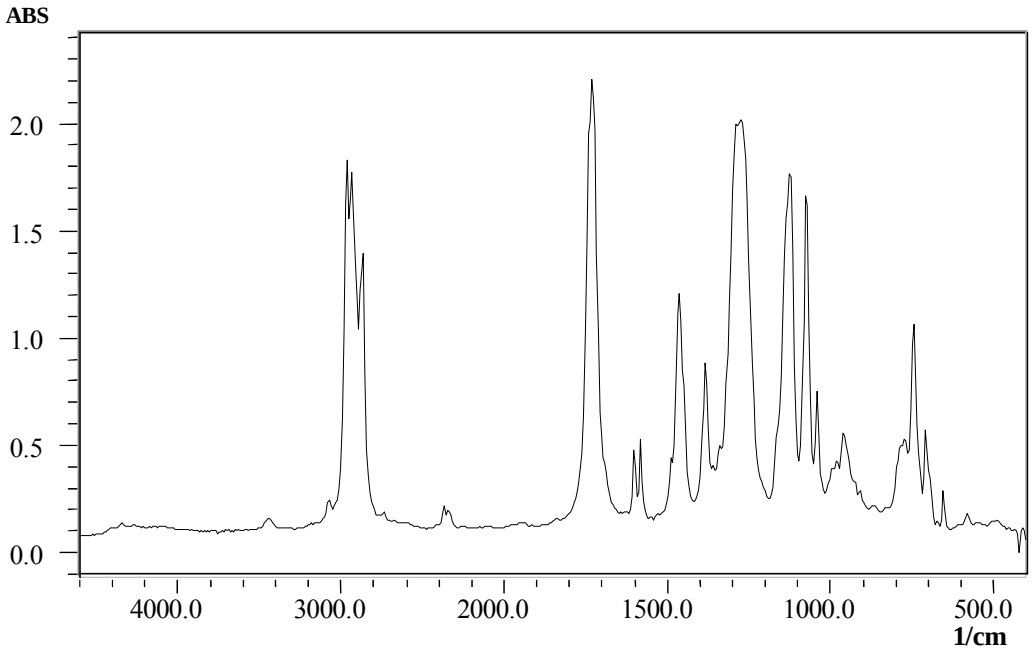


Figure 8.22.FTIR Spectrum of DOP.

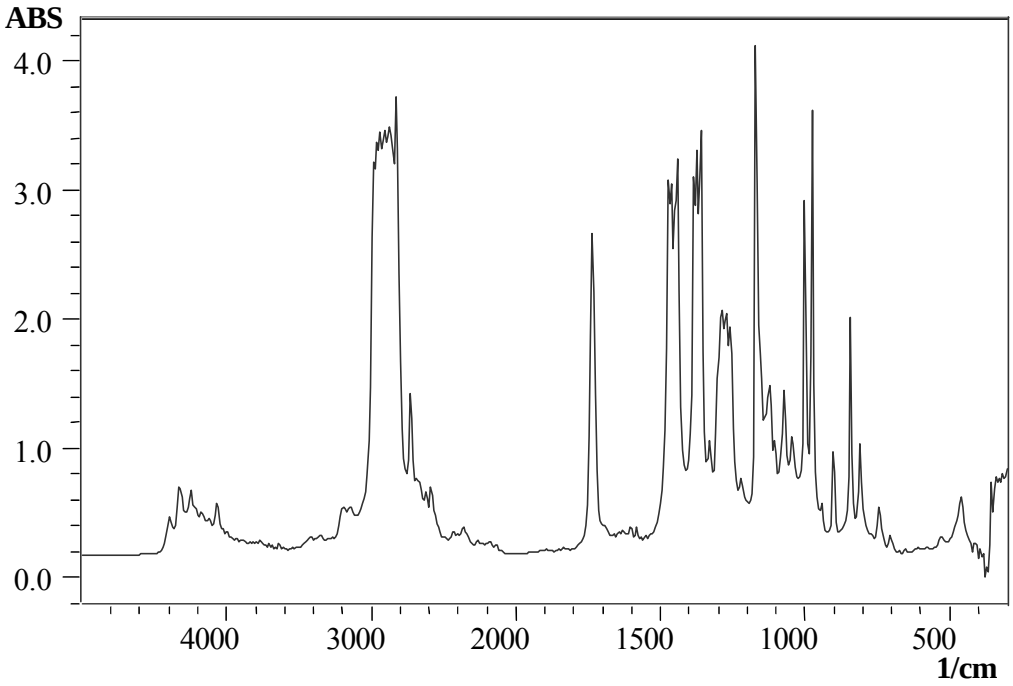


Figure 8.23.FTIR Spectrum of 2 % Zeolite, 4.36 (mg/g) Silver Containing Sample.

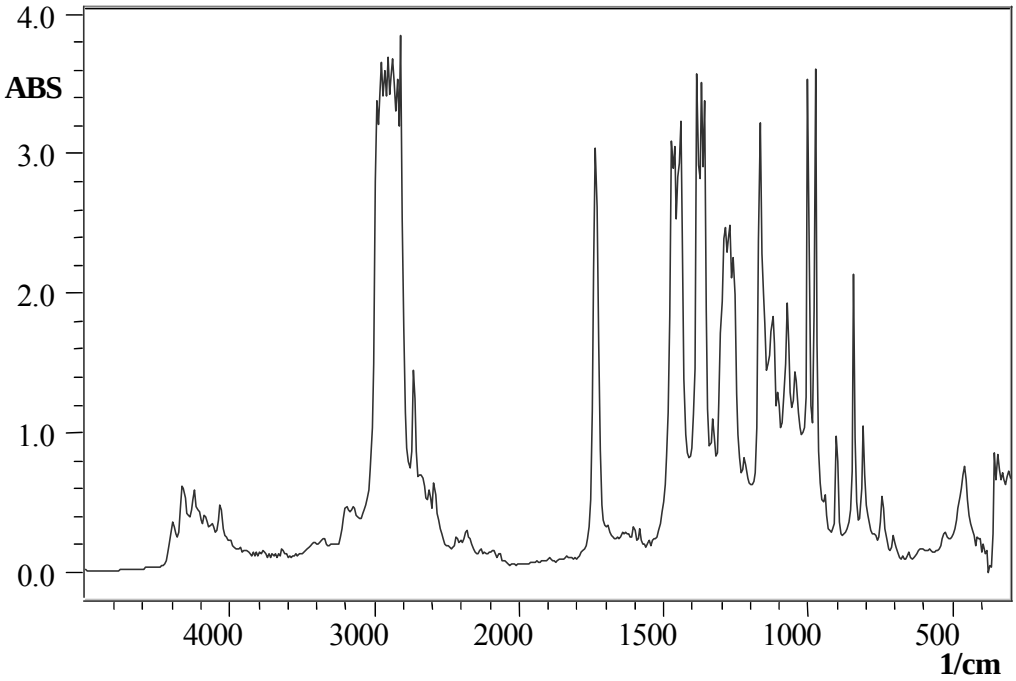


Figure 8.24.FTIR Spectrum of 4 % Zeolite, 4.36 (mg/g) Silver Containing Sample.

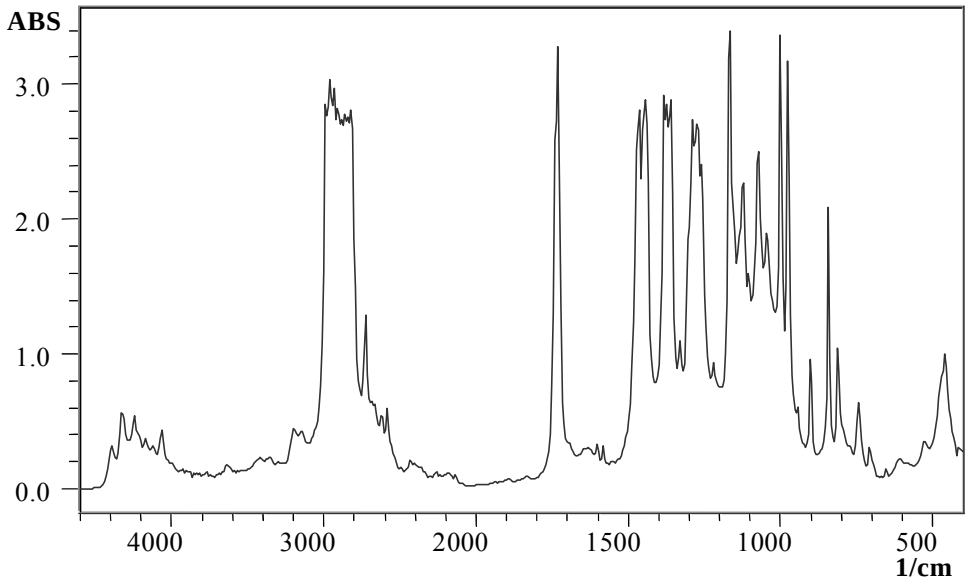


Figure 8.25.FTIR Spectrum of 6 % Zeolite, 4.36 (mg/g) Silver Containing Sample.

For all the samples prepared by Method II, the change of zeolite peak with respect to the DOP peak was investigated. In order to see this effect, b/a calibration curve with respect to zeolite content was constructed. Here b and a represent the absorbance values for the DOP (1750 cm^{-1} peak) and the combination of pp - zeolite peaks (450 cm^{-1} peak), respectively. Of all the peaks, the maximum b/a value occurred for sample with a zeolite loading of 2 % wt. The variation of b/a with changing zeolite loading and amount of Ag^{+} / g zeolite concentration is presented in Figure 8.26. With the increasing silver concentration, it was observed that the effect of DOP was suppressed.

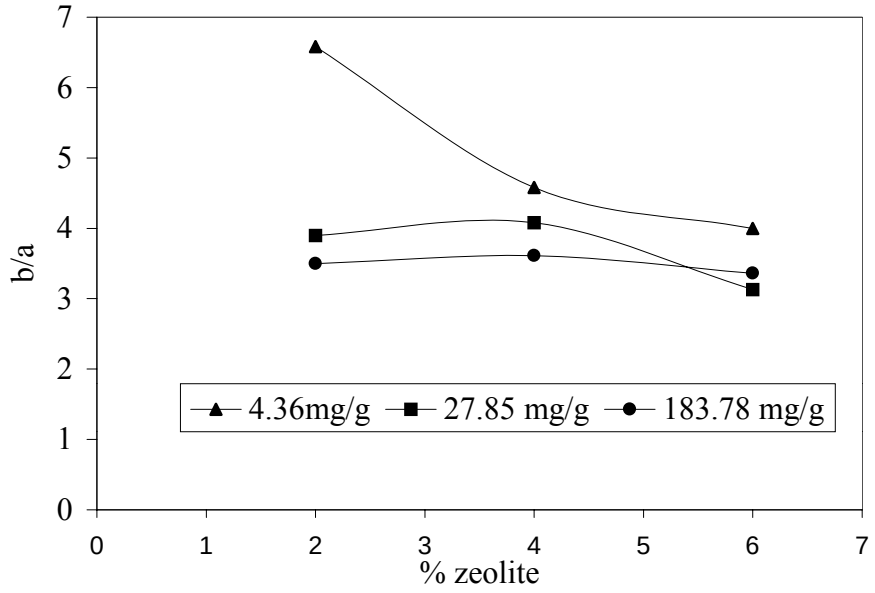


Figure 8.26. Variation of b/a with Respect to Zeolite Content at Various Ag^{+} Concentration.

Figure 8.27 shows the effect of Ag^{+} loading on b/a values of the composites at a constant zeolite loading of 4% wt. At a specified zeolite loading the effect of silver concentration is not so significant. There is a slight decrease in the b/a value for the 4 % sample as seen in Figure 8.27.

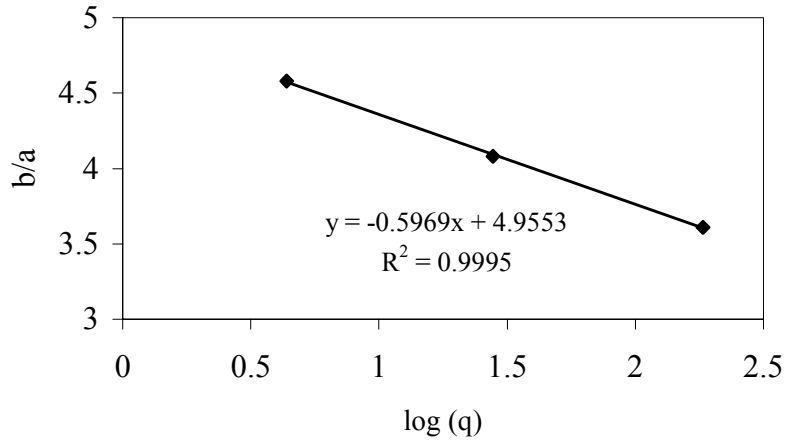


Figure 8.27.Variation of b/a for 4% Sample with Respect to Ag^+ Concentration.

The presence of zeolite and silver ions may have caused catalytic degradation of DOP since the higher the zeolite and silver content the lower the b/a value. For the films containing 2 % wt zeolite and 4.36 mg Ag^+ /g zeolite (Table 8.14), the absorbance value of the DOP was maximum. Thus, this film contained optimum amounts of silver and zeolite that did not cause any degradation of DOP.

8.4.2 Results of Thermal Analyses

In this study, DSC and TGA were used for the thermal characterizations of the PP, natural zeolite, and PP – silver zeolite composite films. The melting, crystallization, and degradation behaviors, and the kinetic analysis of the composites were investigated.

8.4.2.1 DSC Studies

8.4.2.1.1 Characterization of PP

DSC analysis of PP (MH 418) was performed up to 250 ^oC by Özmıhçı (1999). In the present study, the experiments were carried out up to 500 ^oC to observe the degradation behavior of PP. Figure 8.28 shows the DSC curve of PP at a heating rate of 10 ^oC /min in a stream of dry nitrogen gas.

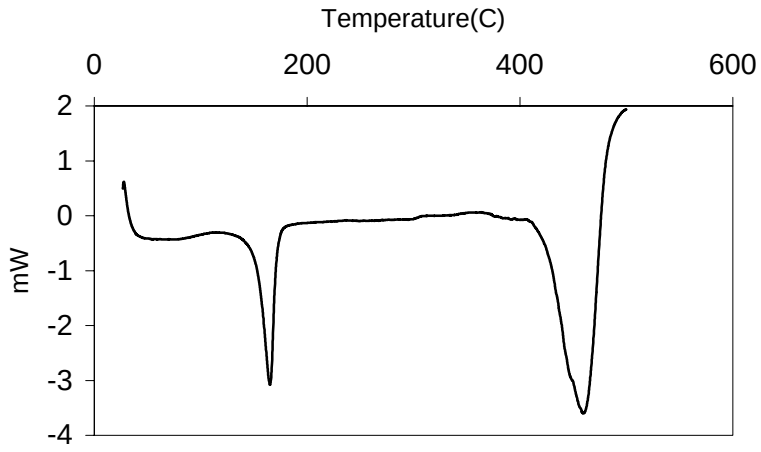


Figure 8.28.DSC Curve of MH 418 Polypropylene.

As seen from the figure, the melting and the degradation temperatures were found to be 165.0^{o}C, and 459.9^{o}C respectively. The heat of fusion (ΔH_f) of the sample came out to be 59.6 kJ/kg. The heat of fusion and the melting temperature of PP was found to be 61.5 kJ/kg, and 163.8 ^{o}C respectively by Özmıhçı (1999) which are in close agreement with the results of the present study.

The energy of the second endotherm, (ΔH_d) that was attributed to degradation of PP, was found as 258.1 kJ/kg.

8.4.2.1.2 Characterization of Natural Zeolite

The DSC curve of natural zeolite mineral is given in Figure 8.29. From the DSC curve, it is concluded that the external and the loosely bond water was removed around 70^{o}C, whereas the tightly bond water was removed around 350^{o}C. The energy required from that for these processes are determined to be 69.12 kJ/kg, and 9.66 kJ/kg, respectively.

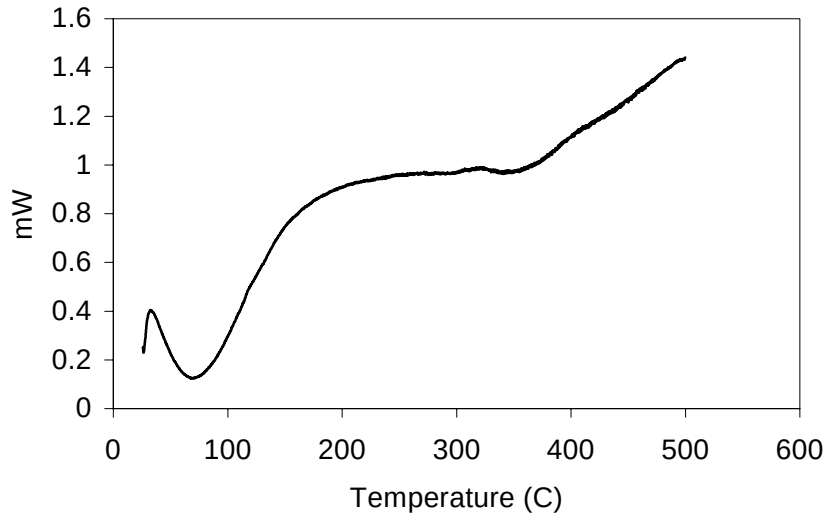


Figure 8.29.DSC curve of Gördes 1 zeolite.

8.4.2.1.3 Characterization of Composite Films Prepared by Method I

Polypropylene – zeolite composites prepared by Method I were used in the DSC analyses. The DSC curves of the PP – zeolite composites impregnated with 50 ppm $AgNO_3$ solution at three different zeolite loading (2, 4, and 6 %) at a heating rate of 10^oC/ min are shown in Figure 8.30.

In the DSC curve, the first and the second peak temperatures show the melting and the degradation temperatures of the composites, respectively. All the composites melt between 161 – 162 ^oC, and degraded between 459 – 465 ^oC as seen from Figure 8.30. Although the melting temperatures of the composites did not change with respect to zeolite loading, the degradation temperatures seemed to increase slightly with the addition of zeolite into PP matrix from 459 to 465 ^oC. At a heating rate of 10^oC/min, the quantitative information about peak temperatures for melting and degradation, heat of fusion (ΔH_f) and degradation values (ΔH_d), and the % crystallinity values are tabulated in Table 8.17 for the composite films impregnated at 50 ppm $AgNO_3$ solution. The % crystallinity of the films was determined using Equation 8.4.

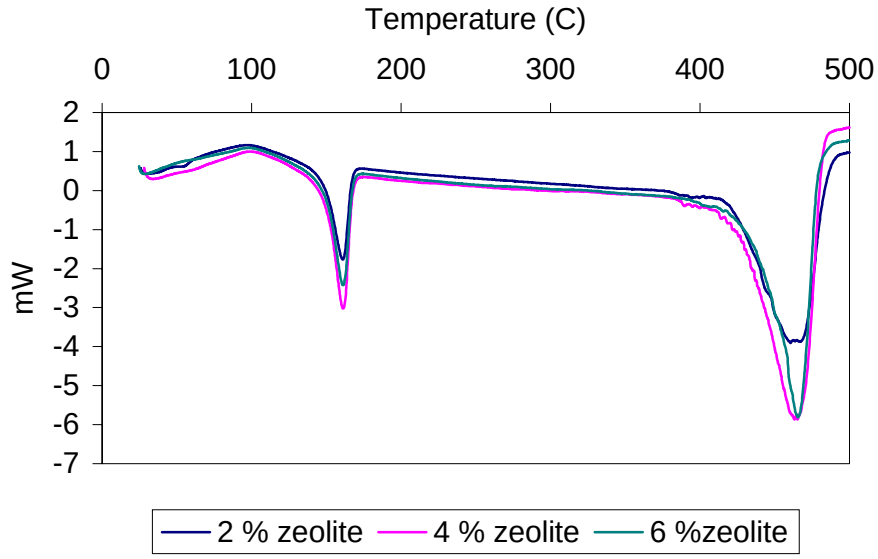


Figure 8.30.DSC Curves of Composite Films Prepared by Method I.

$$\% \text{ Crystallinity} = \frac{\text{(Heat of fusion of sample)}}{\text{(Heat of fusion of 100 \% crystalline sample)}} \text{ x100} \qquad (8.4)$$

The ΔH_f value for 100 % crystalline PP is cited in literature as 209 kJ/kg (Horrocks and D'Souza, 1991). This value is used to determine the % crystallinity of the composites.

As shown in Table 8.17, % crystallinity of PP was increased with the increasing zeolite content with the exception of the 6 % zeolite sample. This might be due to the fact that the non homogeneity problem of the filler exists especially for the 6 % wt loading. It is concluded that zeolite acts as a nucleating agent in the PP matrix. The higher the zeolite content the higher the crystallinity values were obtained for the composites.

Figure 8.31 shows the relation between the heat of fusion of the composites and the zeolite content. The heat of melting values for the composite films with respect to zeolite content showed an increasing trend except for 6 % wt zeolite loaded composite

films. This might be due to the non-homogeneous distribution of the zeolite particles within the composite films especially for the 6 % wt zeolite containing samples. As will be discussed later, the TGA results also showed that the filler distribution along the composite films is not uniform.

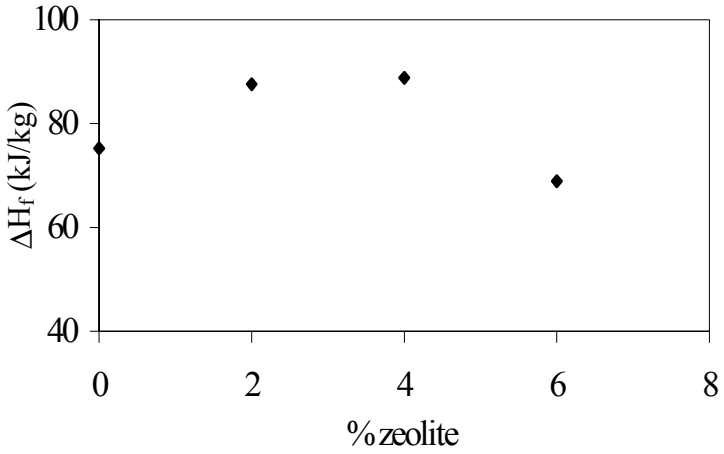


Figure 8.31.Effect of Zeolite Content on the Heat of Fusion Values.

Table 8.17.DSC Analysis of Composite Films Impregnated with 50 ppm Ag^{+}.

Zeolite Loading (%)	1st Peak Temperature (C)	2nd Peak Temperature (C)	ΔH_f (kJ/kg)	ΔH_d (kJ/kg)	% Crystallinity
0	161.7	459.2	75.2	365.6	35.9
2	160.3	465.6	87.6	387.8	41.9
4	161.2	463.2	88.8	386.9	42.5
6	162.2	460.7	68.9	356.8	33.0

8.4.2.1.4 Characterization of Composites Prepared by Method II

Composite films prepared by Method II were all analyzed using DSC with a heating rate of 10°C/min. The DSC curves of the composites having 4 % wt zeolite loaded with 4.36, 27.85, and 183.78 mg Ag^+ /g zeolite are given in Figure 8.32.

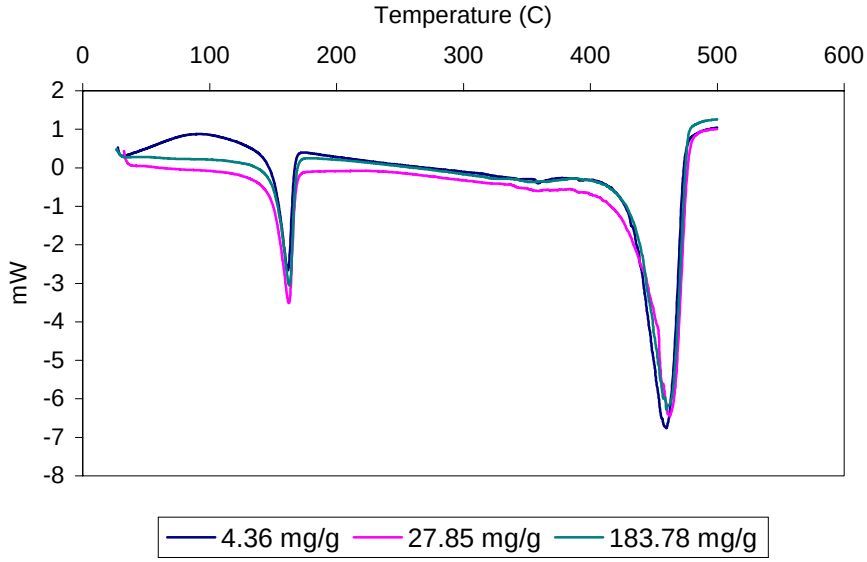


Figure 8.32.DSC Curves of the Composites Containing 4 % wt Zeolite Loaded with Different Amounts of Silver.

The DSC curves of the composites loaded with 27.85 mg Ag^+ /g zeolite containing different amounts of zeolite is shown in Figure 8.33. In both of the Figures, 8.32 and 8.33, the DSC curves of the samples showed very similar results. Thus, all the samples' first and second peak temperatures were between 161 – 165 °C, and 459 – 466 °C, respectively. This shows that silver concentration and zeolite loading do not affect the peak temperatures of melting and degradation significantly. However, ΔH_f and ΔH_d values showed an increasing trend with increasing zeolite loading and silver concentration except for the case of samples with 183.78 mg Ag^+/ g zeolite. At low silver concentrations, zeolite behaved as a decelerating agent in PP, while at high silver concentrations zeolite accelerated the decomposition reaction of PP.

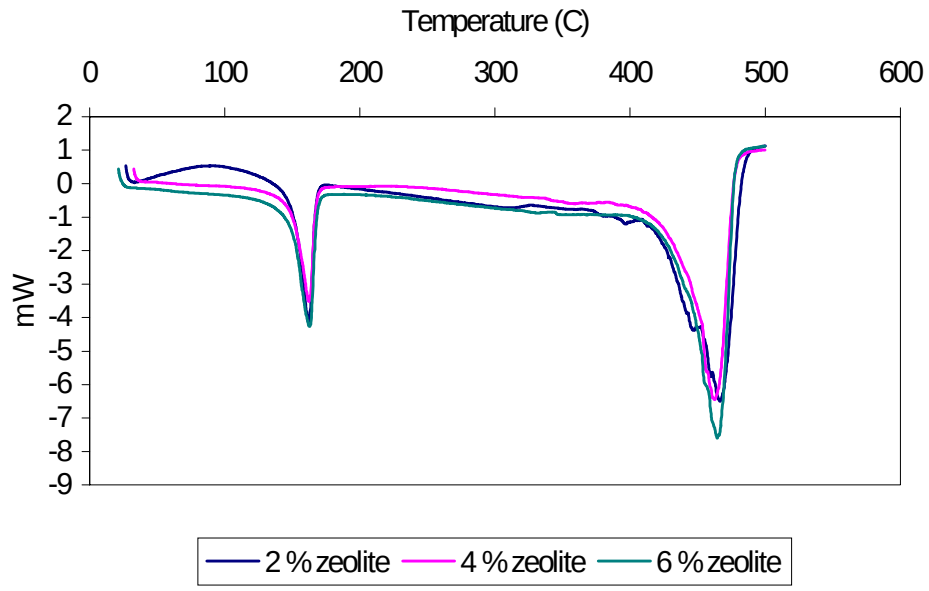


Figure 8.33.DSC Curves of the Composites Loaded with 27.85 mg Ag^{+}/g Zeolite, for Different Zeolite Loadings.

Table 8.18 gives the quantitative results for the composites of different zeolite loadings in detail.

Table 8.18.DSC Analysis of Composites by Method II.

Zeolite Loading (%)	Ag^{+} conc. (mg/g)	1st Peak temperature (C)	2nd Peak Temperature (C)	ΔH_f (kJ/kg)	ΔH_d (kJ/kg)	% Crystallinity
0	0	165.0	459.89	59.57	258.21	28.5
2	4.36	161.03	464.19	58.41	321.80	27.9
4	4.36	161.53	459.89	70.00	352.05	33.49
6	4.36	165.60	459.32	79.17	363.55	37.88
2	27.85	158.35	464.08	72.74	315.89	34.8
4	27.85	162.72	462.81	79.31	360.47	37.94
6	27.85	165.70	465.7	83.80	319.43	40.09
2	183.78	162.71	466.54	78.18	390.23	37.4
4	183.78	162.74	459.91	69.66	335.30	33.33
6	183.78	162.60	462.6	81.46	314.60	38.97

8.4.2.1.5. Kinetic Analyses of the Thermal Decomposition of the Composites

Kinetic analysis of the thermal decomposition was carried out according to both Ozawa and Kissinger Methods. The methods were explained in detail in Chapter 5. Thermal decomposition was studied at heating rates of 5, 10, and 20^{o}C/min in a nitrogen atmosphere. Kinetic analysis was applied to samples prepared by both of the methods, I and II only for a single zeolite loading of 4 % wt. Figure 8.34 and 8.35 shows the DSC curves of the composite films treated with 50 ppm $AgNO_3$ solutions prepared by Methods I and II respectively.

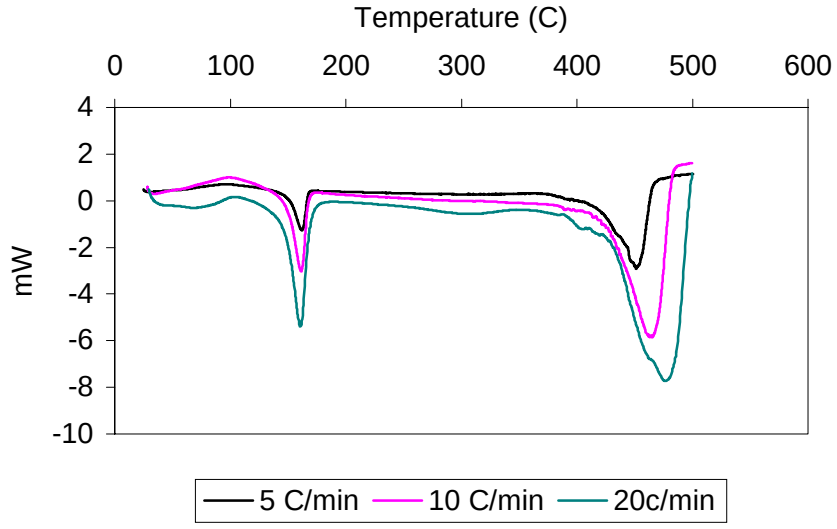


Figure 8.34.DSC Curves of 4 % wt Zeolite Composite films Prepared by Method I (Impregnated with 50 ppm Ag^{+}).

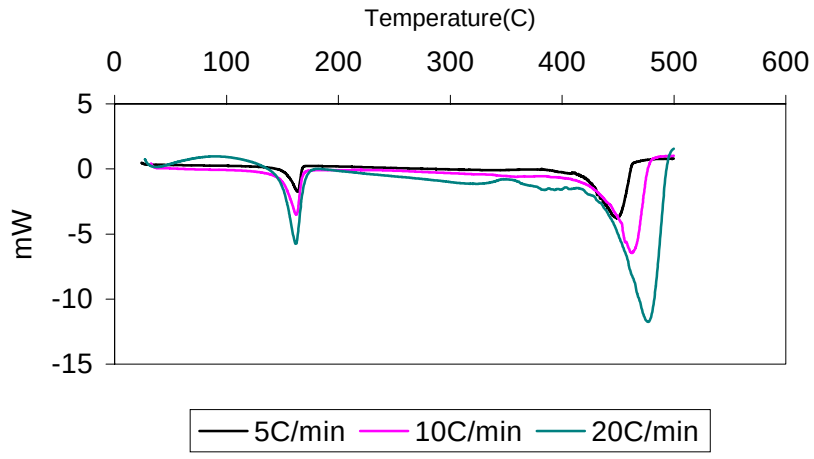


Figure 8.35.DSC Curves of 4 % wt Zeolite Composites Prepared by Method II (4.36 mg/g Silver).

According to the Kissinger method, described in detail in Chapter 5 (Equation 5.12), activation energy of the composites for the decomposition reaction was determined from the plot of the logarithmic heating rate (lnQ) against $1/T_d$. The thermal degradation temperature, T_d was measured from the DSC curves of the composites for various heating rates. The plot of ln Q vs $1/T_d$ for the 4 % wt zeolite loaded composites treated with 50 ppm Ag^+ with Methods I and II are illustrated in Figures 8.36 and 8.37.

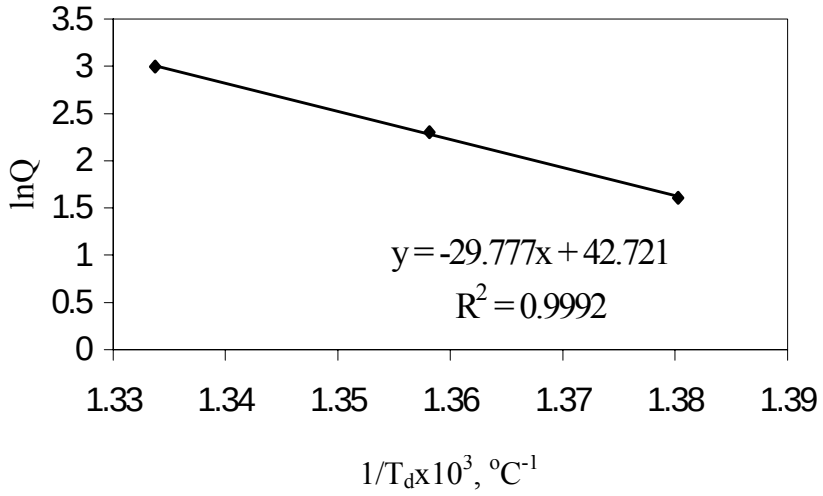


Figure 8.36.Kissinger Plot of 4 % wt Zeolite Sample Treated with 50 ppm Ag^+ by Method I

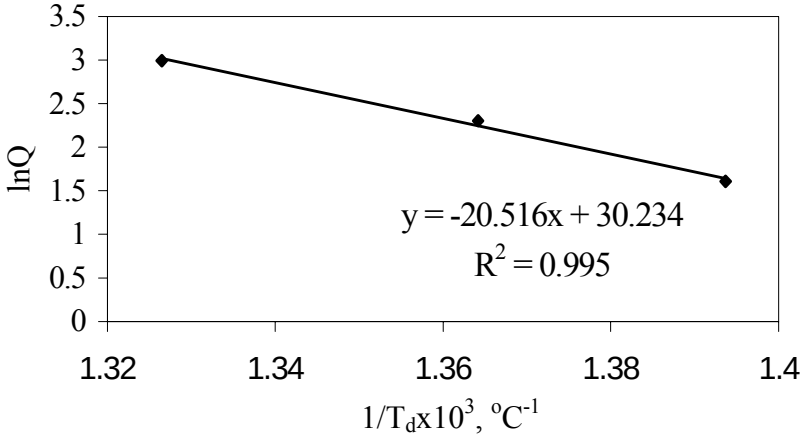


Figure 8.37.Kissinger Plot of 4 % wt Zeolite Sample Treated with 50 ppm Ag^+ by Method II.

The thermal degradation activation energy of the composites was determined from the slopes of the Kissinger plots, corresponding to $-E_a/R$. DSC curves were also analyzed according to the Ozawa Method using kinetic analysis software of Shimadzu 50. The kinetic analysis software is based on the Ozawa principle.

The activation energies for the decomposition reactions were calculated from the slopes of the lines. The quantitative information obtained from the kinetic analysis of the samples performed with both the Ozawa and the Kissinger Methods were tabulated in Table 8.19. As seen from the table the activation energies obtained by the two methods are in agreement with each other.

Table 8.19.Degradation kinetic constants for the 4 % wt zeolite composite films.

Method	Initial $AgNO_3$ Concentration (ppm)	Kissinger Method Activation Energy (kJ/mol)	Ozawa Method		
			Activation Energy (kJ/mol)	Frequency factor (min^{-1})	k $X10^2$ @ 450 ^oC
I	50	247	242	$8.62X10^{16}$	0.282
II	50	170	168	$4.09X10^{11}$	0.297
II	500	221	226	$6.2X10^{15}$	0.291
II	5000	215	214	$8.68X10^{14}$	0.299

Since the thermal decomposition occurs around 450 ^oC, the reaction constant k was calculated at 450^oC using the Arrhenius Equation (Equation 8.5).

$$k = A\exp(-E/RT) \tag{8.5}$$

where;

E = activation energy (kJ/mol)

A = frequency factor (min^{-1})

R = gas constant

T = temperature (K)

It was observed that the reaction constant was not significantly affected by the increasing silver concentration, and that slight increases occurred.

8.4.2.2 Results of the TGA Studies

The weight losses of pure PP, natural zeolite, and PP – zeolite composites prepared by methods I and II were investigated with respect to the increase in temperature.

8.4.2.2.1 Characterization of Polypropylene by TGA

Figure 8.38 shows the TGA curve of the polypropylene analyzed with a heating rate of 10^{o}C/min in a nitrogen atmosphere.

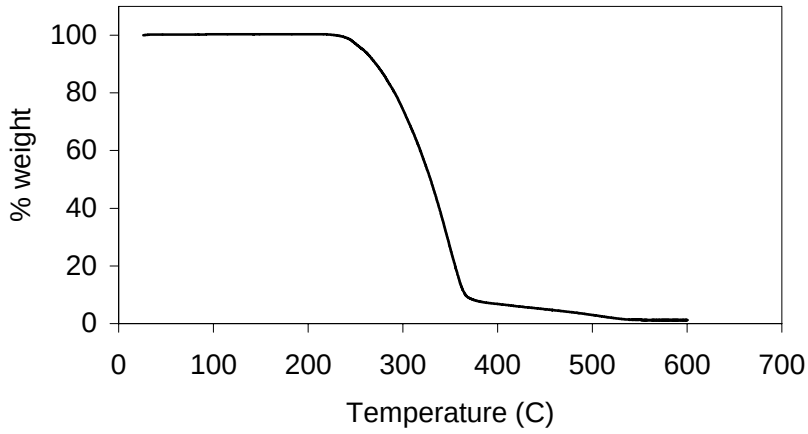


Figure 8.38.TGA Curve of MH- 418 PP.

The weight loss started at around 230^{o}C, and at about 390^{o}C, the 93 % of the polypropylene was lost. The mass loss occurs at two steps. The first and the sharp decrease in the mass occurred at between 230 and 390^{o}C. The second and the slow mass loss step was observed around 390 - 600^{o}C. Figure 8.39 shows the effect of heating rate on the degradation of polypropylene. With the increase in the heating rate, while the thermograms shifted towards the right, the onset of degradation temperature increased, and the termination of degradation temperatures decreased. That is, the onset of

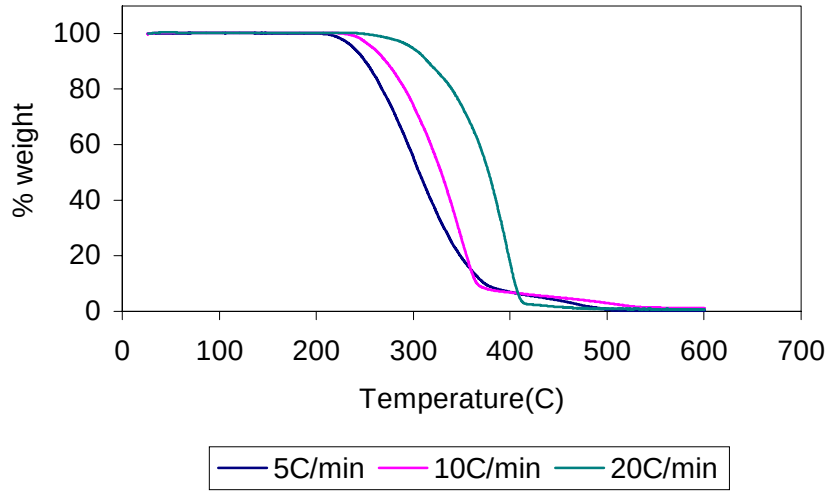


Figure 8.39.Effect of Heating Rate on PP egradation.

degradation temperatures, and the termination of degradation values for the heating rates of 5, 10, 20 ^{o}C/min, were about 220 ^{o}C, 240 ^{o}C, 275 ^{o}C, and 550 ^{o}C, 525 ^{o}C, 420 ^{o}C respectively.

8.4.2.2.2 Characterization of Composites Prepared by Method I Using TGA

The samples with zeolite loading of 2, 4, and 6 % wt zeolite, prepared by the two different methods; Method I, and II were analyzed by TGA with a heating rate of 10 ^{o}C/min. Figure 8.40 shows the TGA curves of the composite films prepared by Method I while Table 8.20 presents the information about the degradation behavior of the composite films. Here, the degradation trend of the 2, 4, and 6 % wt zeolite containing samples impregnated with 50 ppm of $AgNO_3$ solution is seen.

As shown on the TGA curve, all the samples were stable below 250 ^{o}C, but above 300 ^{o}C, the weight losses increased abruptly. Samples containing 2 and 6 % wt zeolite behaved very similar to each other. Their onset and termination of degradation temperatures were very close as seen in Figure 8.40 and Table 8.20. However, the 4 % wt sample started to degrade earlier, the onset of degradation decreased and termination of degradation temperature increased. Pure PP started to degrade around 200 ^{o}C, and the degradation was terminated around 550 ^{o}C, however PP treated with 50 ppm $AgNO_3$

solution, started to degrade later around 260 ^{o} C indicating that the addition of silver shifted the degradation temperatures up to higher values. The same behavior was also observed from the DSC analysis. However, with the addition of zeolite into the PP matrix, the onset of degradation temperature for PP decreased from 260 ^{o}C to 218 ^{o}C while the termination of degradation temperature values increased with the increasing zeolite content. Consequently, it can be concluded that zeolite decelerates the thermal decomposition reactions at 50 ppm conditions.

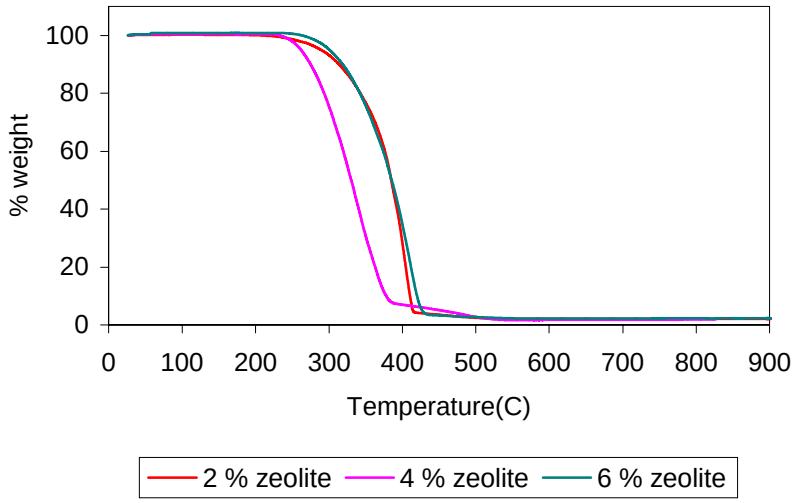


Figure 8.40.TGA Curves of Composites Prepared by Method I.

Table 8.20.TGA Analysis Results of the Composites Prepared by Method I

Zeolite content (% wt)	Onset of Degradation Temperature (^{o}C)	Termination of Degradation Temperature (^{o}C)	Weight Loss (%)
0 (PP)	257	537	100
2	218	526	97.87
4	251	535	98.11
6	237	563	97.74

8.4.2.2.3 Characterization of Composites Prepared by Method II Using TGA

Composite films prepared by Method II were all analyzed using TGA with a heating rate of 10 ^{o}C/min. The TGA thermograms of the 4 % wt zeolite sample with respect to silver concentration are shown in Figure 8.41.

The TGA analyses of the three different samples showed very similar results. With the increasing silver concentration, the onset of degradation shifts slightly to higher values as shown in Table 8.21. On the average, the degradation started at around 220^{o}C, and terminated at about 550^{o}C. The TGA curves of the samples containing 27.85 and 183.78 (mg/g) silver almost overlapped each other, while the sample containing 4.36 (mg/g) silver showed a slower decrease compared to the other two samples. The weight losses of the 4.36, 27.85, and 183.78 (mg/g) silver containing samples came out to be 98.6, 98.2, and 96.9 % respectively. Although all the samples were supposed to contain 4 % zeolite, the TGA results did not agree with this indicating that the zeolite distribution along the composite films was not uniform. Table 8.22 presents the quantitative information of the TGA results as a function of zeolite content and silver concentration.

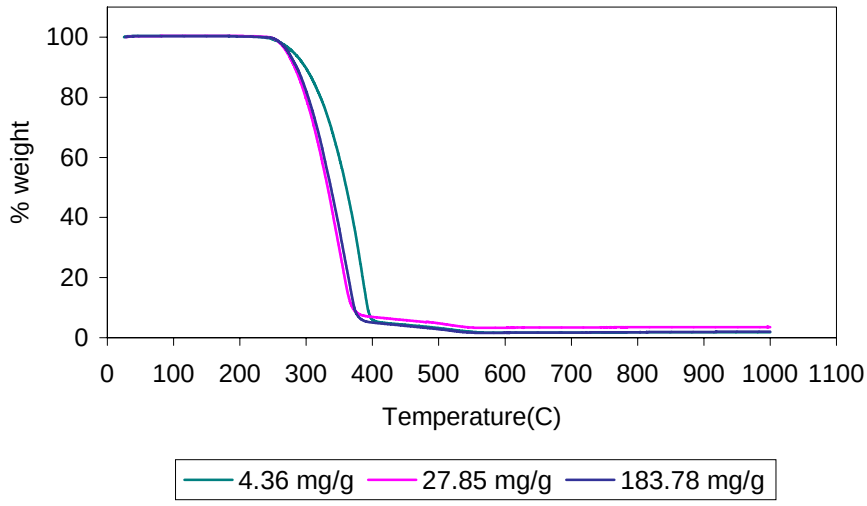


Figure 8.41.TGA Curves of 4 % wt Zeolite Sample Prepared by Method II.

Table 8.21.TGA Analysis Results of the 4 % wt Composites Prepared by Method II.

Amount of Ag^+ Exchanged on composites (mg Ag^+/g zeolite)	Onset of Degradation (^oC)	Termination of Degradation (^oC)	Weight Loss (% wt)
4.36	212.2	556.9	98.6
27.85	224.6	553.8	96.9
183.78	225.5	552.3	98.3

8.4.2.2.4 Kinetic Analysis of the Composites by TGA

The kinetic analysis was performed with heating rates of 5, 10, and 20 ^oC/min for the 4 % wt zeolite samples, which were prepared by Method I, and II. Figure 8.42 shows the TGA curves of the 4 % wt zeolite samples containing 27.85 (mg/g) silver prepared by Method II.

Table 8.22.TGA Results for the Samples Prepared by Method II.

Zeolite Loading (%)	Initial $AgNO_3$ Solution (ppm)	Amount of Ag^+ Exchanged on zeolites (mg Ag^+/g zeolite)	Weight Loss (%)
2	50	4.36	98.9
2	500	27.85	100.8
2	5000	183.78	100.2
4	50	4.36	98.6
4	500	27.85	96.9
4	5000	183.78	98.3
6	50	4.36	98.19
6	500	27.85	99.5
6	5000	183.78	99.5

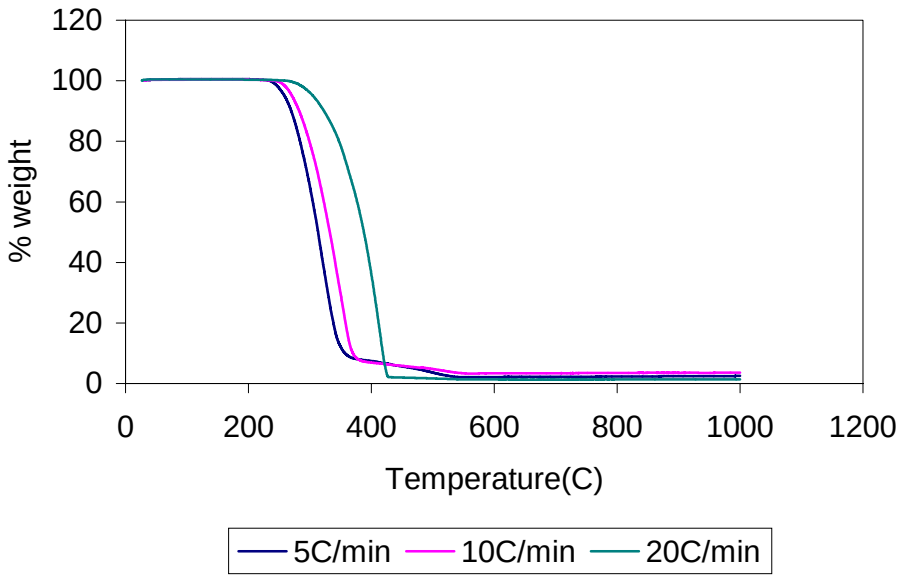


Figure 8.42.TGA Curves of the 4 % wt Zeolite, 27.85 mg Ag^{+}/g Zeolite Containing Samples Prepared by Method II.

As the heating rates increased, the thermograms shifted toward the right and the degradation temperature increased. Kinetic analyses of these composites were performed using Shimadzu 51 TGA kinetic analysis software within a temperature range of 250 - 550^{o}C. The Ozawa plot shows the logarithm of heating rate versus 1/T at constant x values (reaction percent) for different conversions (weight loses). From the slope of the lines, the activation energy, E, is calculated for different weight losses and averaged by the software. The kinetic energies and the related parameters obtained for the 4 % zeolite containing samples are shown in Table 8.23.

Reaction rate constant for the degradation reaction was determined using Arrhenius equation at 250^{o}C. It was observed that silver treatment of the samples prepared by Method I accelerated the degradation of pure PP (MH418), while zeolite decelerates the degradation reaction. The TGA kinetic analysis results of the samples prepared by method II also showed that zeolite addition into the PP matrix speeds down the decomposition reaction, however activation energies of the samples with a specified zeolite loading decreased with the increasing silver concentration. This showed that PP is much more susceptible to thermal decomposition in the presence of silver exchanged zeolite compared to the pure PP.

Table 8.23.Kinetic Analysis Results for 4% samples of Method I and II.

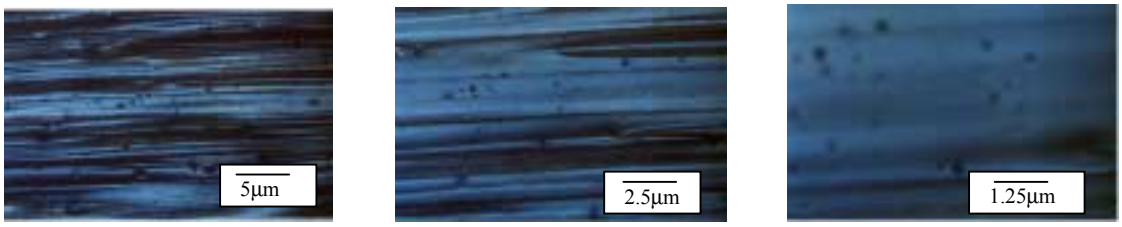
Method	Zeolite %	Initial $AgNO_3$ Conc. (ppm)	E (kJ/mol)	L	A (min^{-1})	$kX10^3$ @ 250°C (min^{-1})
Control	0	0	56.1	5	$4.79x10^3$	11.9
I	0	50	53.9	3	$5.84x10^3$	24.3
I	4	50	61.3	3	$1.68x10^4$	12.6
II	4	50	96.5	5	$9.98x10^6$	2.28
II	4	500	56.5	4	$7.75x10^3$	17.4
II	4	5000	64.6	5	$2.78x10^4$	9.7

8.4.3 Optical Microscopy

The microstructure of the composite materials without any treatment was examined by their optical micrographs. Figure 8.43 shows the optical micrographs of the samples containing 6 % zeolite loaded with 183.78 (mg/g) silver. The agglomerates of the zeolites, which are the spherical dark particles, could easily be seen within the horizontally aligned PP molecules. Although the zeolite particles were grinded down to 45 microns, due to the interface incompatibility between the matrix and the filler, very large agglomerates formed, leading a non-uniform zeolite distribution throughout the composite films.

The micrographs of the tensile tested films were also examined in order to see the effect of stretching. In Figure 8.44 the tensile tested polypropylene is given with different magnifications. In the tensile tested examples, it is easier to see the horizontal alignment of the PP molecules.

For the silver treated case, the 6 % zeolite samples, failed in the tension tests. All the samples broke without elongating just as the tension process started. Therefore it was not possible to examine the optical micrographs of the tensile tested 6 % wt zeolite samples. However, the samples, which are free of silver, behaved different then the silver loaded samples. Figure 8.45 shows the tensile tested micrographs of the 6 % zeolite samples that are free of silver.

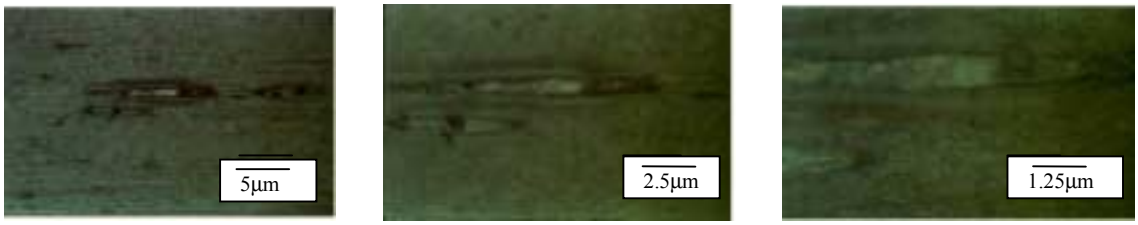


(a) (b) (c)

Figure 8.43.Transmitted Optical Micrographs of the 6 % wt Zeolite, Loaded with 183.78 (mg/g) Silver Samples Prepared by Method II: (a) 50 times Magnified, (b) 100 times Magnified, (c) 200 times Magnified.

(a) (b) (c)

Figure 8.44.Transmitted Optical Micrographs of Tensile Tested Polypropylene: (a) 50 times Magnified, (b) 100 times Magnified, and (c) 200 times Magnified.



(a) (b) (c)

Figure 8.45.Transmitted Optical Micrographs of Tensile Tested 6 % wt Zeolite Composite Films: (a) 50 times Magnified, (b) 100 times Magnified, and (c) 200 times Magnified.

It is observed that the stretching along the machine direction can be detected as another layer and that the air is entrapped around the zeolite particles. More uniform

structures are observed after the tensile tests. This suggests that if the composites could have been prepared using a biaxial orientation, the non-uniformity problem would have been solved in large scales.

8.4.4 Density Measurements

Density of a composite material is one of the most important factors to be considered in terms of a manufacture point of view. Improvement of the microporous structure and the lowering of the density are the primary features of the pearlescent PP films. The fillers used in the pearlescent films could be particulates or the fibers. While stretching the films, in machine or the transverse directions, pores form around the filler particles, causing a decrease in the density and consecutively decreases the manufacturing cost.

The densities of the samples prepared by Method II were measured by the density kit of the Sartorious YDK 01 balance as mentioned in the characterization section. Also the theoretical densities were determined using Equation 8.6 for comparison with the experimental results.

$$d_c = \sum M_i / \sum (M_i / d_i) = [\ (M_1 + M_2 + M_3) / (M_1 / d_1 + M_2 / d_2 + M_3 / d_3)\ ] \qquad (8.6)$$

where;

d_c = theoretical composite density
M = mass
d = density
1, 2, 3 = zeolite, PP, and DOP respectively
$d_{zeolite}$ = 1.8 g/cm^3 (Özmıhçı, 1999)
d_{pp} = 0.89 g/cm^3 (Petkim)
d_{DOP} =0.981 g/cm^3 (Aldrich)

The void fractions in the composites were determined using Equation 8.7. The experimental and the theoretical densities and the void fraction values for the samples are tabulated in Table 8.24.

$$d_{c,e} = (1-\varepsilon)xd_{c,t} \quad (8.7)$$

where $d_{c,e}$, and $d_{c,t}$ are the experimental and the theoretical densities of the composites respectively, and ε is the void fraction in the composite.

Experimental densities of the composites were found to be slightly lower than the theoretical density of pure PP as seen in Table 8.24 except for the 6 % wt samples. The results indicate that the experimental and the theoretical densities did not show a systematic agreement with the increasing zeolite content, which is again due to the non-uniformity of the zeolite distribution along the PP phase. The desired level for the density in terms of commercial means is 0.6 g/cm^3. When the tensile tested film densities are considered, it is observed that smaller values are obtained compared to the original samples. Although the results are not as low as desired commercially, there is a considerable enhancement with respect to the original samples. If perhaps the films could have been biaxially oriented, the results would be even more close to the desired level.

8.4.5 Mechanical Tests Results of the Composites

Mechanical tests of the samples prepared by method II as well as the control samples that are free of silver were conducted. All the samples were tested for three times and the mean values were used. Yield stress, stress at break, elongation at break, and Young modulus values measured are shown in Table 8.25.

The results of the mechanical tests show that the addition of DOP decreases the yield stress, however, increases the stress at break and elongation at break values. It is observed that the addition of pure zeolite into the PP matrix increases the Young Modulus values, while the Young moduli slightly decreases with the increasing silver concentration. Figure 8.46 shows the change of Young modulus values as a function of zeolite content at different silver loadings. Considering the variation of Young modulus values between 1100 – 1300 MPa, it is concluded that silver concentration does not quite affect the Young modulus values of the composites. The effect of silver concentration on the yield stress values of the composites for a specified zeolite loading

Table 8.24 Density Results of the Extruded Samples by Method II.

% wt Zeolite	Amount of Ag^+ exchanged on composite. (mg/g)	DOP (w/w %)	Thickness (mm)	Theoretical density. $d_{c.t}$ (g/cm^3)	Experimental density. $d_{c.e}$ (g/cm^3)	Experimental density of tensile tested films (g/cm^3)	ε
0	0	0	0.270	0.890	0.857	0.760	0.036
0	0	10	0.233	0.890	0.875	0.781	0.016
2	0	10	0.266	0.899	0.871	0.662	0.031
4	0	10	0.263	0.908	0.830	0.877	0.085
6	0	10	0.276	0.917	0.966	0.584	-
2	4.36	10	0.263	0.899	0.763	0.782	0.150
4	4.36	10	0.283	0.908	0.856	0.691	0.057
6	4.36	10	0.306	0.917	0.947	-	-
2	27.85	10	0.260	0.899	0.829	0.712	0.077
4	27.85	10	0.253	0.908	0.874	0.625	0.037
6	27.85	10	0.333	0.917	0.748	-	0.184
2	183.78	10	0.263	0.899	0.823	0.687	0.084
4	183.78	10	0.276	0.908	0.849	0.638	0.064
6	183.78	10	0.320	0.917	0.919	-	-

is presented in Figure 8.47. A linear decrease is observed in the yield stress values with the increasing silver concentration for the 6 % wt samples prepared by Method II.

Table 8.25.Tensile test results of the pp-zeolite composite films.

Zeolite %	DOP % (v/w)	Ag^+ Conc. (mg/g))	Yield Stress (MPa)	Stress at Break (MPa)	Elongation at break (%)	Modulus (Mpa)
0(PP)	0	0	24.59	29.18	389.20	1608.32
0(PP)	10	0	23.63	31.29	410.60	1315.95
2	10	0	20.83	31.26	424.33	867.90
4	10	0	27.93	18.75	188.41	1273.60
6	10	0	27.64	24.08	319.72	1483.04
2	10	4.36	22.32	29.47	404.27	1057.67
4	10	4.36	21.92	21.70	382.33	1258.09
6	10	4.36	15.15	15.36	6.39	1189.33
2	10	27.85	27.20	24.40	343.2	1322.96
4	10	27.85	23.22	17.66	344.93	1233.10
6	10	27.85	14.31	15.78	5.99	1190.0
2	10	183.78	29.46	26.49	395.86	1288.43
4	10	183.78	22.78	15.67	205.78	1269.22
6	10	183.78	12.78	13.33	5.03	1129.24

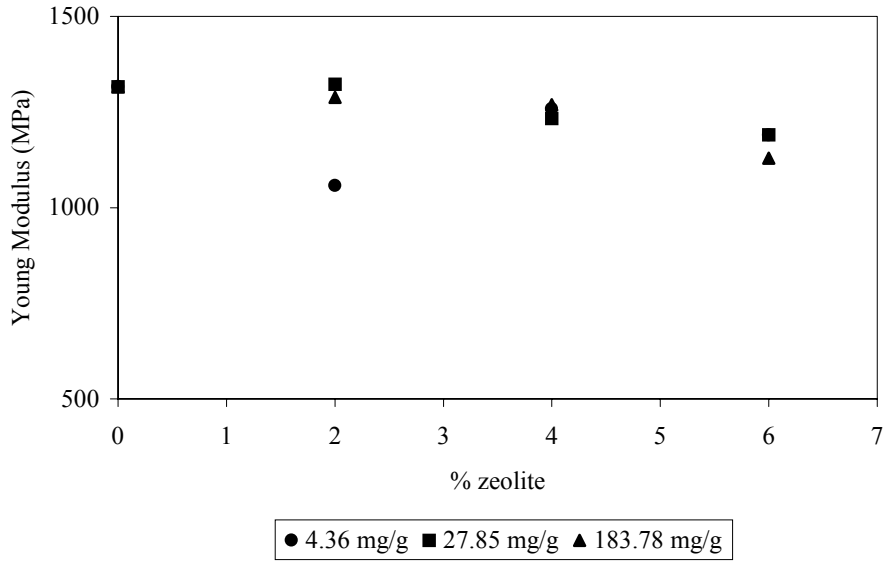


Figure 8.46.Variation of Young's Modulus with Respect to Zeolite Content for the Samples Treated with Different Silver Concentrations Prepared by Method II.

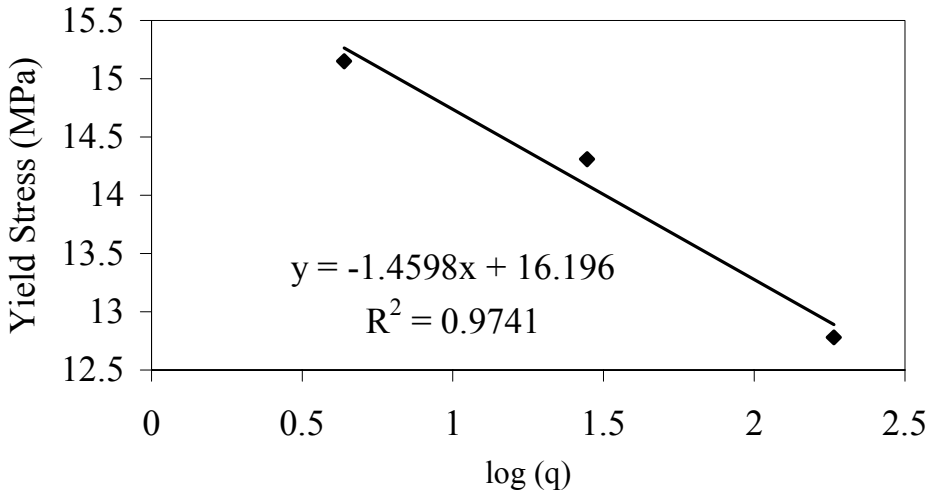


Figure 8.47.Dependence of Yield Stress on Silver Amount for 6 % wt Zeolite Containing Samples Prepared by Method II.

Figure 8.48 presents the variation of yield stress with respect to zeolite content at different silver concentrations.

As seen from Figure 8.48, Yield stress values decreased with increasing zeolite content at constant silver concentration, however, increased with the increasing silver concentration at constant zeolite loading.

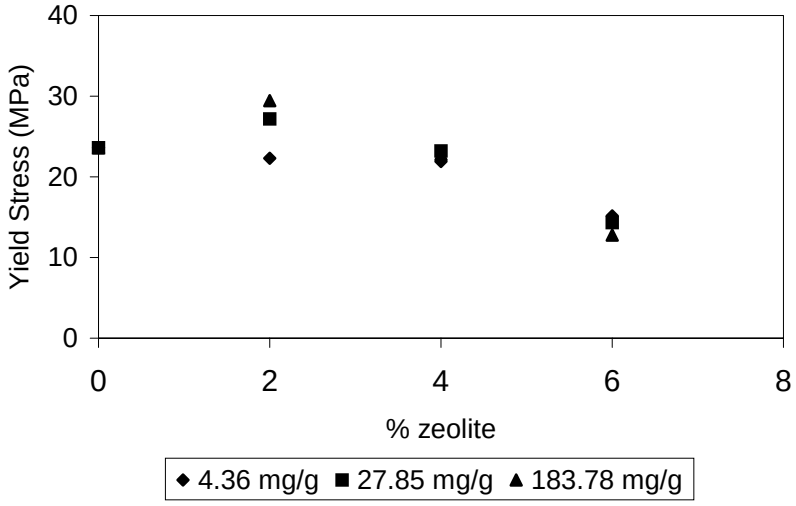


Figure 8.48.Variation of Yield Stress with Respect to Zeolite Content at Different Silver Loading for the Samples Prepared by Method II.

As tabulated in Table 8.25, 6 % wt zeolite containing samples showed a sharp decrease of the elongation at break values for all the silver concentrations compared to the 2, and 4 % wt zeolite loaded samples.

Considering these results, it is concluded that 2, and 4 % wt silver – zeolite loaded composites possess more appropriate mechanical behavior in terms of application.

The theoretical young modulus and the yield stress values were predicted using Equations 5.13 and 5.25, respectively. The measured and predicted yield stress and Young modulus values for the samples loaded with 27.85 (mg/g) silver are tabulated in Table 8.26.

The comparison of the predicted and the measured elastic modulus and yield stress are given in Figures 8.49 and 8.50 respectively. The predicted values for the young modulus showed that no adhesion was present between the filler and the matrix phases and that the theoretical model did not fit to the experimental results.

Table 8.26.Predicted and Measured Young Modulus and Yield Stress Values for the PP – Zeolite Composites Loaded with 27.85 (mg/g) Silver.

Zeolite wt %	ε	$E_{c,p}$ (Mpa)	$E_{c,m}$ (Mpa)	$\sigma_{c,p}$ (Mpa)	$\sigma_{c,m}$ (Mpa)
2	0.077	1679.282	1322.96	18.45	27.2
4	0.037	1463.077	1233.10	20.45	23.2 2
6	0.184	2549.482	1190.0	14.38	15.78

(E_c: Young modulus, σ_c: Yield stress, m: measured, p: predicted)

The predicted and measured yield stress values show a better agreement, with a decreasing trend as the zeolite loading increases.

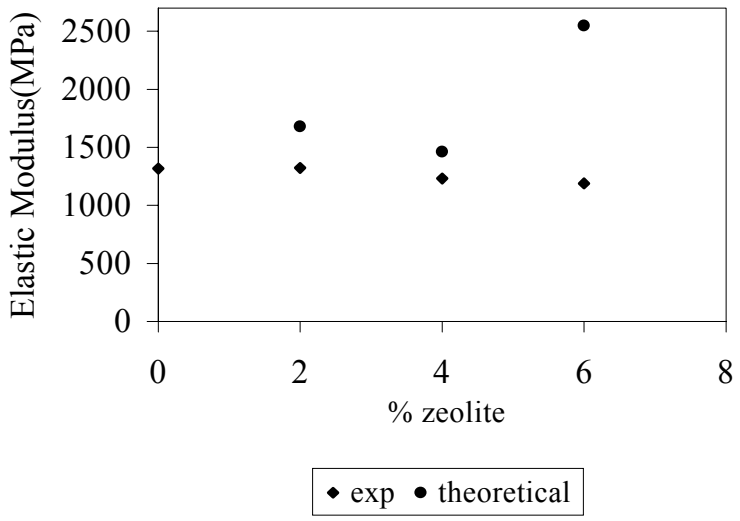


Figure 8.49.Variation of Elastic Modulus with Respect to Zeolite Content

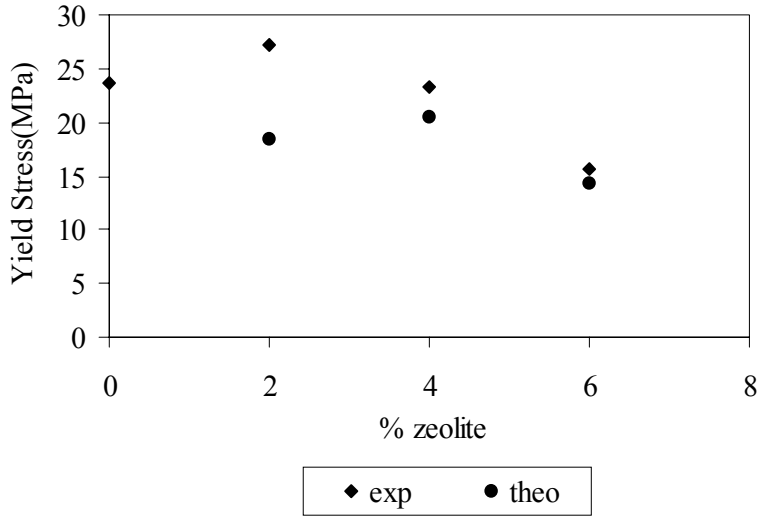


Figure 8.50.Variation of Yield Stress with Zeolite Content.

8.4.6 Microbiological Experimentation Results

Polypropylene – zeolite composite films impregnated with 50 ppm Ag^+ prepared by Methods I and II were tested for their bactericidal activity against *E. coli* with Agar Diffusion (Disc method) and Broth Dilution Methods.

It was observed that no inhibition zones were established around the test samples prepared by both of the methods for the case of disc method. However Ag^+ loaded zeolite samples in the form of pellets gave positive results against E.coli by the disc method (Top, 2001). This shows that disc method is not applicable for the present study. This might be due to the fact that silver form of zeolites entrapped in PP phase could not be as effective as the silver form of zeolites alone in the media and the film sample could not dissolve in the Agar medium. Broth Dilution Method yields considerable results for the samples prepared by method I and II. The results for both of the methods are shown in Figures 8.51 and 8.52 respectively.

As seen from the figure 8.51, 401 colonies are counted on the negative control sample. All the test samples are below this limit, however they are very close to the control sample. Only the 2 and 6 % zeolite samples of 2 micron particle size gave acceptable results, but still these experiments should have been performed for several times to be able to see the reproducibility of the results.

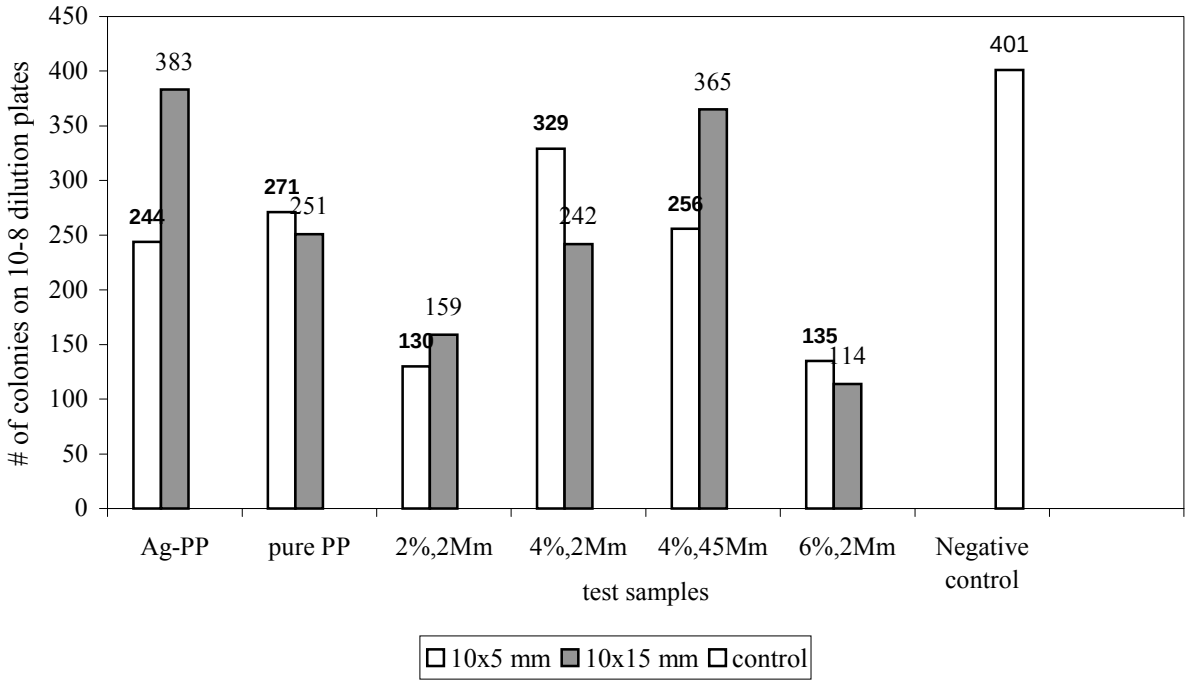


Figure 8.51.Broth Dilution Method Results for Test Samples Prepared by Method I against *E.coli*.

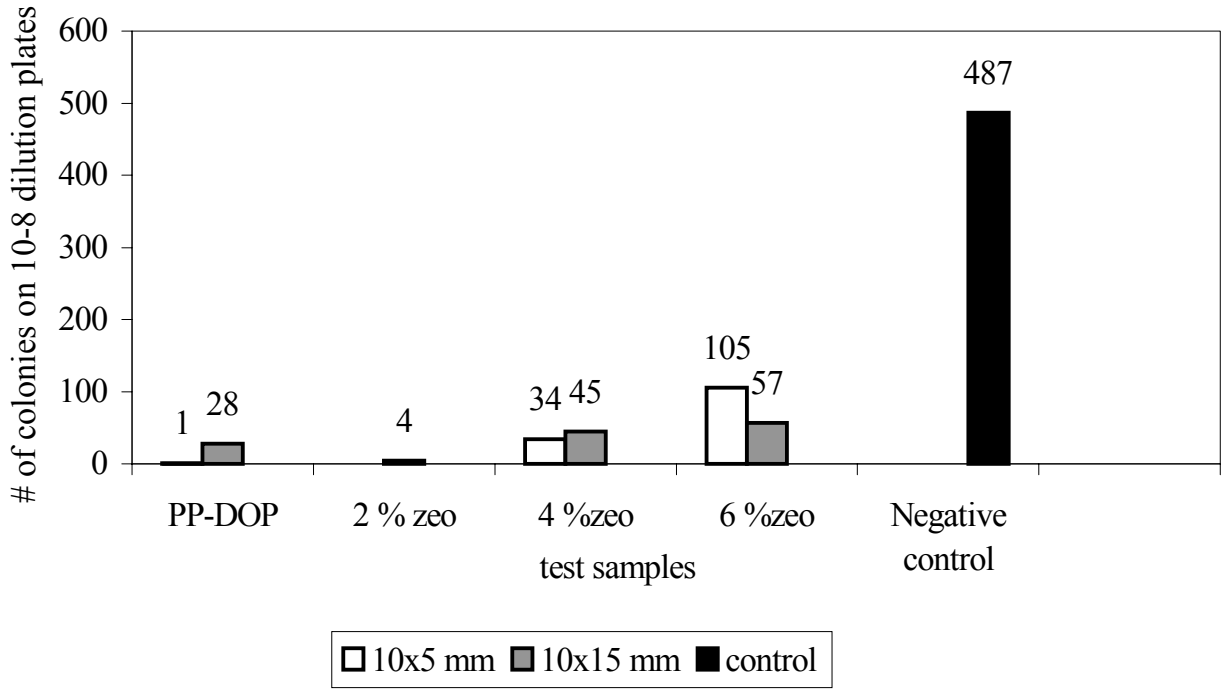


Figure 8.52.Broth Dilution Method Results for Test Samples Prepared by Method II against *E.coli*.

The samples prepared by Method II were expected to be more effective in terms of bactericidal activity, since the silver exchange was directly performed on the zeolite minerals. As expected the Broth Dilution method results showed a considerable enhancement compared with the results of Method I, but still the Agar Diffusion method did not respond with the Ag-zeolite – PP composites as shown in Figure 8.53.

(a) (b)

Figure 8.53.Disc method results of Method II against (a) *P.auroginosa* (b) *E.coli*

The pictures of the 6 % wt zeolite samples loaded with (4.36 mg/g) silver prepared by Method II with the control sample against *E.coli* is presented in Figure 8.54. As observed from the pictures, the same sample with a larger surface area yields better results in terms of the number of bacteria that keeps surviving.

(a) (b) (c)

Figure 8.54. Pictures of (a) 6 % wt zeolite sample (5x10cm) (b) 6 % wt zeolite (10x15 cm) (c) control sample (bacteria alone).

As a result of the microbiological experiments conducted against *E.coli,* it was observed that Ag – zeolite PP composites prevented the bacterial colony formation, however it was also seen that the PP matrix itself prevents the formation of bacterial colonies as well. This might be due to the additives present in the MH 418 PP acting perhaps as an antibacterial agent.

It was expected to see a decrease in the number of bacterial colonies reproduced in the samples with respect to zeolite content, however it was not the case. Uneven zeolite distribution throughout the composites prevented this situation.

When the two methods are to be compared in terms of efficiency, Method II gave better results due to the fact that silver penetration into the zeolite phase was easier. In Method I, the penetration of the silver ions from the solution to the zeolite entrapped in the PP matrix was relatively harder.

8.4.7 Discoloration Parameters

Silver, copper, or zinc ion exchanged zeolites have some disadvantages of discoloring actions. During the blending of the ion-exchanged zeolite with the polymer, the ion exchanged zeolite leads to discoloration of the composition under the influence of heat and ultraviolet light such as sunshine. Since the discoloring actions are important in terms of the final product quality, the discoloration parameters for the silver – zeolite – PP composites must be considered.

The discoloration parameters consist of three different measures which are the L, a and b values. L changes between 0 and 100, designating the color transition from black to white. The a and b values show the transition between green to red, and blue to yellow, respectively.

The discoloration parameters of the samples prepared by Method I and II were measured using Minolta 2600 D (using D 65 rays) colorometer. The results are in the form of difference values with respect to the reference sample. The reference sample is taken as the pure polypropylene film free of both silver and zeolite. The results obtained using this apparatus are tabulated in Table 8.27.

The results for the samples prepared by Method I are very similar with the reference sample. The first method was only conducted with the minimum initial silver concentration of 50 ppm. However the discoloration results of the second method for the initial concentration 50 ppm are higher than that of the method I. This means that

second method has more discoloring action on the composite films. This arises from the difference of the two methods. In the first method, the pp-zeolite composite films were treated with silver containing solutions, and the silver exchange between the solution and the zeolite embedded in the composites was limited. However in the second case, the silver exchange to zeolite minerals was performed prior to the molding process. Therefore the extent of the ion exchange processes was not of the same magnitude. Thus the amount of silver present in the films affected the discoloration parameters as expected.

Table 8.27.Discoloration Test Results of PP-Zeolite Composite Films

Method	Zeolite %	Initial $AgNO_3$ Conc. (ppm)	ΔL	Δa	Δb
I	2	50	0.35	-0.13	-0.04
I	4	50	0.72	-0.01	-0.16
I	6	50	-0.11	-0.07	0.62
II	2	50	-1.19	-0.41	1.81
II	4	50	-2.02	-0.57	-2.65
II	6	50	-3.71	-0.63	3.96
II	2	500	-2.67	-1.19	6.72
II	4	500	-5.16	-2.16	14.5
II	6	500	-9.93	-2.50	25.3
II	2	5000	-6.39	-0.82	12.6
II	4	5000	-10.8	-1.6	23.6
II	6	5000	-16.3	-1.34	28.8

As the silver concentration is increased, the discoloration parameters of the samples change from white to black, red to green, and blue to yellow for L, a, and b values respectively. ‘L’ and ‘b’ parameters changed a lot with the increasing silver concentration compared to the ‘a’ values. The higher the silver concentration, the more the pronounced discoloring effect was obtained (Niira, 1990).

Chapter 9

CONCLUSIONS AND RECOMMENDATIONS

In the scope of this study, development of an antibacterial resin composition comprising of PP and silver form of clinoptilolite rich natural zeolite by the extrusion technique was investigated.

Sorption studies indicated that, with the addition of zeolite, PP a hydrophobic polymer attained the property of water sorption due to the porous structure of the composite films with effective diffusivity values changing between 0.3 – 9.9 X 10^{-10}, and 0.1 – 3.3 X10^{-12} cm^2/ s for the hot press and extruded films, respectively. This was the desired fact since the silver exchange process would be conducted in an aqueous media. Silver loading to the PP – zeolite composites was performed by two different methods. In Method I, PP - zeolite composite films were treated with a variety of silver ion containing solutions (5 to 50 ppm $AgNO_3$ solution), whereas in Method II silver exchanged zeolite minerals (with initial $AgNO_3$ concentrations of 50, 500, and 5000 ppm) were molded with PP in the presence of DOP (Dioctyl Phthalate). The amounts of Ag^+ loaded per gram of zeolite for initial $AgNO_3$ concentrations of 50, 500, and 5000 ppm were determined as 4.36, 27.85, and 183.78 mg, respectively. In both of the methods, the extent of ion exchange was determined by analyzing the liquid phase. As expected the extent of the ion exchange with Method II was considerably larger than that of Method I because of the direct contact between the zeolite minerals and the silver ions. However, in Method I the penetration of silver ions into the zeolite phase was prevented by the PP phase.

In the FTIR studies it was observed that silver loading did not affect significantly the peaks corresponding to both PP and zeolite. Yet the presence of zeolite and high concentration of silver ions might have caused catalytic degradation of DOP thereby lowering the absorbance of its characteristic peak (1750 cm^{-1}).

Increase in zeolite content with the presence of silver ions for the samples prepared by Method I led to a slight increase in the crystallinity values of the composites. For the composites prepared by Method II, the increase in the heat of melting and degradation values, and consequently the % crystallinity was more significant especially with the increasing silver concentration. When the two methods

are compared in terms of the activation energies for their thermal decomposition reactions, the activation energy for Method I was considerably higher than that of Method II, and hence the onset of degradation values were higher. The addition of silver accelerates the decomposition reactions.

Although the zeolite minerals were surface modified with PEG 4000 and DOP was used as a plasticizer during the extrusion process, still the interface incompatibility between the matrix and the filler could not be totally eliminated. However, from the optical micrographs of the tensile tested films, it is clearly seen that stretching along the machine direction showed a considerable enhancement in the distribution of zeolite particles.

The experimental densities of the composites were lower than the theoretical densities except for the 6 % wt zeolite samples indicating the formation of voids in the composites. When the tensile tested samples are under consideration, the densities came out to be even lower, which shows that the stretching along the machine direction yields better agreement with the commercially desired values that is around 0.6 – 0.65 g /cm^3.

Mechanical tests indicated that the addition of zeolite tended to decrease the Yield stress values while a slight decrease was observed for Young moduli. The effect of silver on the Young Modulus values of the composites is not quite significant, however the Yield Stress values increased considerably with the increasing silver concentration from 23.6 to 29.5 MPa. The fluctuations obtained in the mechanical tests emphasized the uneven zeolite distribution in the PP matrix as observed in the thermal analyses, the optical micrographs, and the density measurements.

The discoloring actions of the samples prepared by Method I was almost negligible. However, the samples prepared by Method II showed very sharp increases with both the ‘L’ and the ‘b’ values with the increasing silver concentration going from white to black, and from blue to yellow respectively. Therefore, while using silver as an antibacterial agent, discoloring agents are absolutely necessary in order to avoid this discoloring action and provide a commercially valuable product.

The microbiological experiments suggest that silver – zeolite – PP composite films may be an appropriate composition to be used in different applications seeking for antibacterial activity. However, PP matrix itself was also determined to prevent the formation of bacterial colonies. This might be due to the additives present in the MH 418 PP acting perhaps as an antibacterial agent. Comparing the two methods, it was concluded that the method of Agar Diffusion was not suitable for the silver zeolite

loaded films whereas the Broth Dilution Method eliminated almost all of the pathogenic organisms with the samples loaded with 4.36 mg Ag^{+}/ g zeolite prepared by Method II. In order to reach a reliable conclusion however, a series of experiments should be conducted to see the reproducibility of the results and determine the optimum experimental conditions such as the silver concentration, pH, or the medium temperature.

The most critical problem in this study was the interface incompatibility between the filler and the matrix phases. Beyond this, the mixing process within the extruder was not sufficient. The information obtained from TGA about the zeolite content of the samples did never match with the actual amount of zeolite present in the composites. If the zeolite particles and the polypropylene beads could have been thoroughly mixed and their masterbatch forms could be obtained following a biaxial orientation of the resultant film, the problem of uneven zeolite distribution could probably be solved. Another problem was the discoloring action of silver. Especially at high silver concentrations, the discoloring effect is even more significant. Various discoloring agents being proposed recently may be used to avoid this action and prepare colorless films.

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