

# Characterization of pure and silver exchanged natural zeolite filled polypropylene composite films

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## Abstract

In the present study, untreated and silver exchanged natural zeolite–polypropylene (PP) composites were prepared and characterized by means of different techniques (TGA, DSC, mechanical tests, density measurements, optical microscopy and colorometer). The effects of zeolite loading and silver concentration on the composite properties were investigated. The thermal characterization studies showed that the addition of the zeolite increased the crystallinity of the composites acting as a nucleating agent in PP crystallization and retarded the degradation of PP. At low silver concentrations, the zeolite behaved as a decelerating agent in PP degradation, however at higher silver concentrations, the composites degraded at a faster rate than pure PP. The experimental densities of the composites were found to be lower than the theoretical densities. When the tensile tested samples are considered, the densities were even lower indicating porous structure of the films. From the optical micrographs of the tensile tested films, it was clearly seen that the stretching along the machine direction caused hole formation around the particles. The optimum conditions obtained in this study for the PP–silver zeolite composite film production are in the range of 2–4 wt% zeolite treated with 4.36 mg Ag<sup>+</sup>/g zeolite. At higher zeolite loadings, the film becomes brittle and at higher Ag<sup>+</sup> concentrations, the film produced was discolored.

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## 1. Introduction

Particulate filled polypropylene composites are used extensively in various application fields such as; food packaging, medical delivery systems, carpets, fibers, protective coating, automobile, electrical and furniture industries. Because of their importance, these composite systems have been investigated to meet the increasing requirements of these fields and to produce tailor made properties for special applications. One way of tailoring the properties of PP is to add the appropriate particulate filler into the matrix. Talc, calcium carbonate, mica, sil-

ver and clays are the most commonly used ones as a filler in the PP matrix [1–4]. Recently, different types of zeolite minerals, either natural (clinoptilolite, mordenite, chabazite), or synthetic (A-type, X-type, Y-type), are being employed as particulate fillers into the polymer matrix [5,6].

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 [7–9]. 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 [9] has investigated the silver as a source of antiseptic agent. Silver salts appeared to meet

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the requirements to be considered as an antiseptic agent. The modification of inorganic compound by the addition of silver became attractive to protect the circumstances from the diseases originating from microorganisms. 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 [9] and as well as polymer additives in food packaging.

The original clinoptilolite, NH<sub>4</sub>-form, K-form, and Na-form of clinoptilolite were determined to take 74.0, 84.3, 86.6, and 120.7 mg Ag<sup>+</sup>/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 [10].

Hagiwara et al. [7] studied zeolite particles retaining Ag ions having antibacterial properties. They proposed a polymeric substance holding the metallic ions to be used in various fields. In their proposal, a polymer contains organic functional groups having an ion-exchange function over a complex forming function and thereby these groups retain the metal ions. Since the zeolite is more cost effective compared to the other antimicrobial agents and no toxicity to humans is reported, they are used in many manufactured goods that have antibacterial coating/ingredients, such as toothbrushes, and toothpaste, bath and toilet tiles, kitchen utensils, baby toys and recently medical instruments, especially in Japan. Hagiwara et al.'s [7] invention provides two processes for producing polymer article. 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. Silver ions are taken up by microbial cells disrupting the cells' enzymatic activity. Commercial examples of the silver exchanged zeolites include Zeomic, Apacider, AgIon, Bactekiller and Novaron.

As reported in a variety of studies [7–9,11], silver zeolite exhibits excellent antibiotic property. However, such an antibiotic zeolite suffers from the disadvantage that it gradually discolors in time. While this discoloration has no effect on antibiotic effect, depending on the nature of the product containing this antibiotic zeolite, this feature may greatly reduce their commercial value.

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 few studies were reported with zeolite as a filling material in polymer matrix. Özmihçi et al. [6] previously investigated the preparation and characterization of natural zeolite–polypropylene composites proposing natural zeolite from Gördes region as an alternative filler to CaCO<sub>3</sub>. 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 [3,12].

In the present study, the preparation and characterization of untreated and silver exchanged zeolite filled polypropylene composite system were studied. The effects of zeolite addition to the polymer matrix and silver concentration on the thermal, mechanical, and structural properties of the composites were investigated. The optimum zeolite and silver concentration based on the thermal stability, mechanical strength and discoloring properties of the composites were determined.

## 2. Experimental

### 2.1. Material

Isotactic PP (MH-418, MFI = 4–6 g/10 min, PET-KIM Co.) in pellet form with a density of 895 kg/m<sup>3</sup> was used for the matrix material and natural zeolite, clinoptilolite, from Gördes, Turkey, was used as filling material for the preparation of composites. For the surface modification of the zeolite, PEG 4000 (Aldrich) was used to prevent agglomerations and provide uniform distribution along the PP phase. The natural zeolite was characterized earlier by Akdeniz [13] and was used by Özmihçi [14] to prepare zeolite–PP films.

### 2.2. Preparation of the materials

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

AgNO<sub>3</sub> solutions with initial concentrations in the range of 5–5000 ppm were used as the ion-exchange media. Zeolite minerals placed in AgNO<sub>3</sub> solutions were kept at 25 °C for 24 h using a water bath equipped with a shaker and a top cover preventing the passage of light. At each set of experiment the solid to liquid ratio was kept constant as 1:100 (w/v). Following the ion-exchange process, by filtration, the solid and the liquid

part of the slurry was separated. The liquid phase was centrifuged for the removal of colloidal zeolite particles and was analyzed for the remaining silver ion concentration present in the solution. The solid phase was washed twice for the removal of excessive silver ions. The samples were then dried in a vacuum oven at 400 mbar and 110 °C for 3 h.

PEG 4000 was used for the surface modification of silver exchanged zeolites to provide uniform distribution of zeolites in the PP phase. Firstly, silver exchanged zeolites were mixed with 50 wt% aqueous ethanol solution containing 10 wt% PEG 4000 modifier. Then the mixture was dried in a vacuum oven at 110 °C for 3 h. Zeolite to solution ratio was taken as 1:0.3 on weight/volume basis [14].

The extent of silver exchange onto the zeolites was determined by analyzing the remaining  $\text{Ag}^+$  concentration in the liquid phase using Varian ICP-AES (inductively coupled plasma-atomic emission spectrometer). The amounts of  $\text{Ag}^+$  loaded per gram of zeolite for initial  $\text{AgNO}_3$  concentrations of 50, 500, and 5000 ppm were determined as 4.36, 27.85, and 183.78 mg, respectively.

The sorption isotherm of  $\text{Ag}^+$  on zeolite was determined and compared with the Langmuir and Freundlich isotherm equations. The experimental data and the Freundlich isotherm solution showed a better agreement with each other compared to the Langmuir isotherm. The constants,  $K$  and  $n$ , obtained from the Freundlich isotherm ( $q = KC^{1/n}$ ) are 1.73, 2.08, respectively. Czarán et al. [10] have determined the silver uptake of the clinoptilolite depending on different monocationic forms of clinoptilolite (original, K-,  $\text{NH}_4$ -, or Na-form). The uptake was between 74 and 121 mg  $\text{Ag}^+$ /g zeolite. The maximum amount of silver taken by Gördes 1 zeolite (183.78 mg  $\text{Ag}^+$ /g zeolite), in the present study, was comparable with the silver uptake in the different monocationic forms of the clinoptilolite.

### 2.3. Composite preparation

Zeolites treated with different amounts of  $\text{Ag}^+$  (50, 500, 5000 ppm) containing solutions were mixed with PP pellets by physical means. Due to the density difference between the PP and zeolite particles, the zeolites agglomerated at the bottom of the container. In order to prevent the agglomeration of particles dioctyl phthalate (DOP) was used as a plasticizer. PP pellets, 45  $\mu\text{m}$  zeolite particles (2, 4, and 6 wt%), and DOP (10% total w/v) were mixed. The zeolite dispersion in DOP coated the PP pellets evenly. And they were conditioned at 85 °C at 400 mbar pressure using a vacuum pump to ensure the displacement of the air in the pores of the zeolite with DOP for an hour before the film drawing process. The mixture was then fed to the hopper of the mini extruder (Axon BX-18) for the extrusion process.

The zone temperatures in the extruder kept constant throughout the film drawing process were in between 200 and 220 °C and the screw speed was 120 rpm. The extruder has an  $L/D$  ratio of 20, a diameter of 18 mm, and a flat die of dimensions of (50 × 1 mm). Axon two roll mill (AXON, 2R-180) with a roller speed of 90 rpm 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. Thus the films having thickness around 275  $\mu\text{m}$  and width around 18 mm were obtained.

### 2.4. Characterization and properties

Thermal analyses of the untreated and silver exchanged zeolite containing PP films 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 °C for the DSC analyses and up to 1000 °C for the TGA analyses, at heating rates of 5, 10, and 20 °C/min. The analyses were performed in a dry nitrogen atmosphere.  $\text{N}_2$  flow rate was 40 ml/min and kept constant throughout the experiments.

Mechanical tests of the extruded composite films were performed on a Instron Machine (Series IX Automated Materials Testing System). 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 max. allowable load cell of 50 kgf. Each test was repeated three times and the mean values were used.

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

XRD experiments were carried out on a Philips Powder Diffraction instrument and the data were taken using Philips X'Pert software. Cu  $\text{K}\alpha$  radiation with wavelength 0.154 nm was used. The degree of crystallinity was calculated as the ratio of total integral intensities of crystalline peaks ( $I_c$ ) to the integral intensities of amorphous and crystalline peaks ( $I_a + I_c$ ).

Densities of the films, 12 mm in diameter, were measured with the density kit of Sartorius YDK 01 balance making use of the Archimedes' Principle. For the tensile tested samples, 1 × 10 cm samples were used for density measurements. Both the sample weight and the weight of the water displaced by the sample were recorded.

To determine the discoloring effect of Ag ions on the composite films, the color of the composite films containing silver zeolite exposed to sunlight was measured by placing each sample on a white paper using Minolta color-color difference meter 2600D (using D 65 rays). The results are compared with respect to the reference sample, pure polypropylene film.

### 3. Results and discussion

#### 3.1. Morphology of the films

The microstructure of the composite materials without any treatment was examined by their transmitted optical micrographs. Fig. 1(a) shows the transmitted optical micrograph of tensile tested pure PP film. In the tensile tested samples, it is easier to see the orientation (alignment) of the PP molecules. Effect of zeolite addition to PP matrix was also examined. Fig. 1(b) shows the optical micrographs of the PP films containing 6 wt% Ag-zeolite (183.78 mg silver/g zeolite). The agglomerates of the zeolite particles, which are the spherical dark particles, could easily be seen within the aligned PP matrix phase. Although the zeolite particles were ground down to 45  $\mu\text{m}$ , due to the interface incompatibility between the matrix and the filler phases, very large agglomerates formed, leading a non-uniform zeolite distribution throughout the composite films. When same amount of zeolite loaded composite films were stretched, it was seen that void formation occurred, and voids grew around the zeolite particles as seen in Fig. 1(c). The brighter part represents the PP matrix and the dark part represents the zeolite particles. It was observed that the stretching along the machine direction can be detected as another layer, and air is entrapped around the zeolite particles.

#### 3.2. Film orientation during processing and tensile testing

##### 3.2.1. Machine direction

The polymer melt flowing from the flat die (50 mm  $\times$  1 mm) is pulled at a higher speed by the calender to obtain the film having the size of (18 mm  $\times$  0.275 mm). Since the maximum flow rate from the extruder and calender should be identical, the draw ratio of the films in machine can be calculated using the following equation:

$$\text{Draw ratio} = \frac{\text{Cross - section of the die}}{\text{Cross - section of the calender}} \quad (1)$$

Thus, the PP film is drawn with a draw ratio of 10 in the machine direction during its production.

##### 3.2.2. Cold drawing of the film in tensile test machine

The films were cold drawn during tensile testing. They were elongated 2–4 times of their original length before they were broken.

##### 3.3. Density measurements

While stretching the films, in machine or transverse directions, pores form around the filler particles, causing a decrease in the density. The theoretical densities were determined using Eq. (2) to compare with the experimental results.

$$d_c = \frac{\sum M_i}{\sum (M_i/d_i)} = \left[ \frac{(M_1 + M_2 + M_3)}{(M_1/d_1 + M_2/d_2 + M_3/d_3)} \right], \quad (2)$$

where  $d_c$  is the theoretical composite density,  $M$  is the mass,  $d$  is the density, and 1, 2, and 3 denote zeolite, PP, and DOP, respectively ( $d_{\text{zeolite}} = 1.8 \text{ g/cm}^3$ ;  $d_{\text{PP}} = 0.89 \text{ g/cm}^3$ ;  $d_{\text{DOP}} = 0.98 \text{ g/cm}^3$ ) [15].

The void fractions in the composites were determined using Eq. (3). The experimental and the theoretical densities and the void fraction values for the samples are tabulated in Table 1.

$$d_{c,e} = (1 - \varepsilon)d_{c,t}, \quad (3)$$

where  $d_{c,e}$  and  $d_{c,t}$  are the experimental and the theoretical densities of the composites respectively, and  $\varepsilon$  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 1 except for the 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 theoretical density values were also calculated using the experimental density

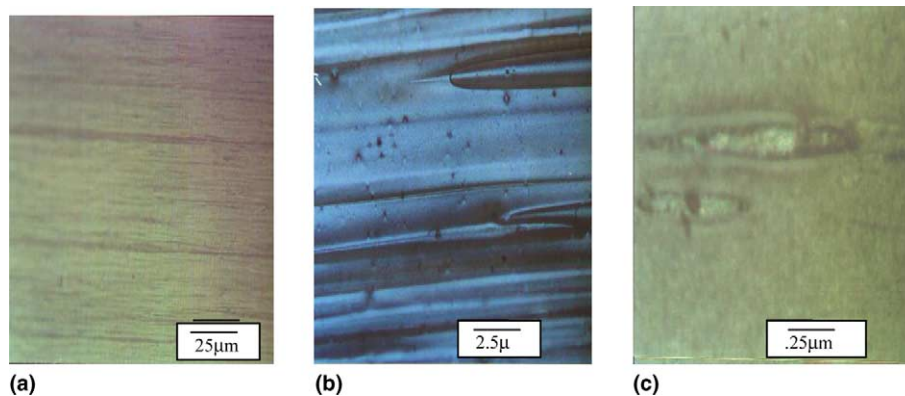


Fig. 1. Transmitted optical micrographs of 100 times magnified: (a) the tensile tested pure polypropylene film; (b) 6 wt% zeolite loaded PP composite films; (c) tensile tested 6 wt% zeolite, loaded PP composite films.

Table 1  
Density of the untreated and treated zeolite filled PP composite films

wt% Zeolite	Amount of Ag <sup>+</sup> exchanged on composite (mg/g)	DOP (w/w%)	Thickness (mm)	Theoretical density, $d_{c,t}$ (g/cm <sup>3</sup> )	Experimental density, $d_{c,e}$ (g/cm <sup>3</sup> )	Experimental density of tensile tested films (g/cm <sup>3</sup> )	Void fraction ( $\epsilon$ )
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	–	–

and crystallinity data. The relationship for a semicrystalline polymer as:

$$\rho_{PP} = \rho_{amorp}(1 - \text{crystallinity}) + \rho_{crystal} * \text{crystallinity}.$$

For isotactic PP,  $\rho_A = 0.85$  and  $\rho_c = 0.936$  were taken [16]. The crystallinity values were determined using DSC. The detail explanation related to the determination of crystallinity can be found in Section 3.6.1 and the values were given in Table 4. It was observed that the lower density values were obtained compared to the expected ones which again shows the void formation in the composites. The void fractions were in the range of 0.02–0.18 and were very close to the ones found by Özmihçı et al. [6].

### 3.4. Mechanical properties

The mechanical properties of the extruded films were given in Table 2. 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. Fig. 2 illustrates the effect of silver concentration on the Young modulus values of the PP–silver exchanged zeolite composites as a function of zeolite loading. A decrease in Young's modulus of PP–zeolite composites with an increase in zeolite loading was observed. The decrease in modulus of PP composites indicates the formation of voids around filler due to poor bonding between the zeolite particles and PP matrix. The Young modulus slightly decreases with the increasing silver concentration. Considering the variation of Young modulus values between 1100 and 1300 MPa, it is concluded that silver concentration does not quite affect the Young modulus values of the composites.

A decrease was also observed in the yield stress values with the increasing silver concentration as the zeolite loading increased especially for 6 wt% zeolite loaded composites as seen in Table 2. The elongation at break for 6 wt% zeolite containing film were lower than that of control (410.6%) films, and 2 and 4 wt% zeolite loaded composite films. The low elongation at break values indicated the presence of the brittle fracture of the films.

Table 2  
Tensile test results of the PP–zeolite composite films

Zeolite (wt%)	DOP % (v/w)	Ag <sup>+</sup> conc. (mg/g zeolite)	Yield stress (MPa)	Stress at break (MPa)	Elongation at break (%)	Modulus (MPa)
0(PP)	0	0	24.6	29.2	389	1608
0(PP)	10	0	23.6	31.3	411	1316
2	10	0	20.8	31.3	424	868
4	10	0	27.9	18.8	188	1274
6	10	0	27.6	24.1	320	1483
2	10	4.36	22.3	29.5	404	1058
4	10	4.36	21.9	21.8	382	1259
6	10	4.36	15.1	15.4	7	1189
2	10	27.85	27.2	24.4	343	1323
4	10	27.85	23.2	17.7	345	1233
6	10	27.85	14.3	15.8	6	1190
2	10	183.78	29.5	26.5	400	1288
4	10	183.78	22.8	15.7	206	1269
6	10	183.78	12.8	13.3	5	1129

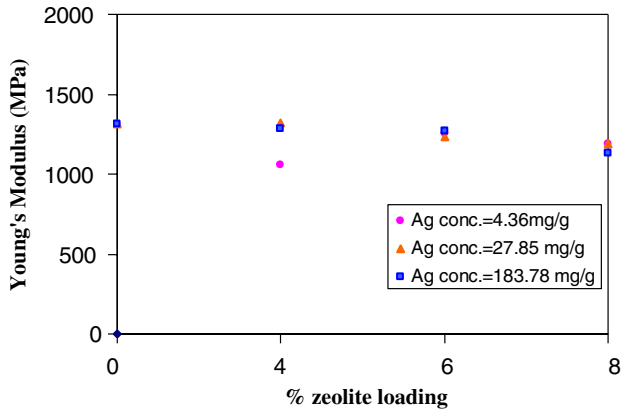


Fig. 2. The effect of zeolite loading and silver concentration on the Young's modulus of the composites.

Interfacial interaction between the polymer matrix and the filler is an important factor affecting the mechanical properties of the composites. Thus, theoretical yield strength and ultimate tensile strength of the composites are modelled to show the effect of interfacial interaction on the tensile strength of the composites. Pukanszky model describes the effects of composition and the interfacial interaction on tensile yield stress or tensile strength of particulate filled polymers is given in Eq. (4). The parameter  $B$  is an interaction parameter that is related to the macroscopic characteristics of the filler–matrix interface and interphase [17]

$$\sigma_{yc}/\sigma_{ym} = \frac{1 - \Phi_f}{1 + 2.5\Phi_f} \exp(B_{\sigma_y}\Phi_f), \quad (4)$$

Where  $\Phi_f$  is the volume fraction of the filler,  $\sigma_{yc}$  and  $\sigma_{ym}$  denote the tensile yield stress or tensile strength of composite and matrix, respectively. The first term in Eq. (4) is related to the decrease in effective load bearing cross-section, while the second one is concerned with the interfacial interaction between filler and matrix. Fig. 3 shows the comparison of the experimental tensile strength data with the Pukanszky model for PP–zeolite composites containing pure zeolite and silver exchanged zeolites, respectively. As seen in the figures, the model does not well predict the data of PP–zeolite composites very well.  $B$  parameter in the model characterizes the interaction between PP and zeolite, and the higher the  $B$  values indicate the better interaction. Results of the model prediction gave the negative  $B$  values which indicated the poor adhesion in PP–zeolite composite system. As the silver concentration were increased, the  $B$  values were even more decreased which again showed the worse interfacial adhesion.

### 3.5. Discoloration tests

The discoloration parameters consist of three measures which are  $L$ ,  $a$  and  $b$  values.  $L$  changes between 0 and 100, designating the color transition from black

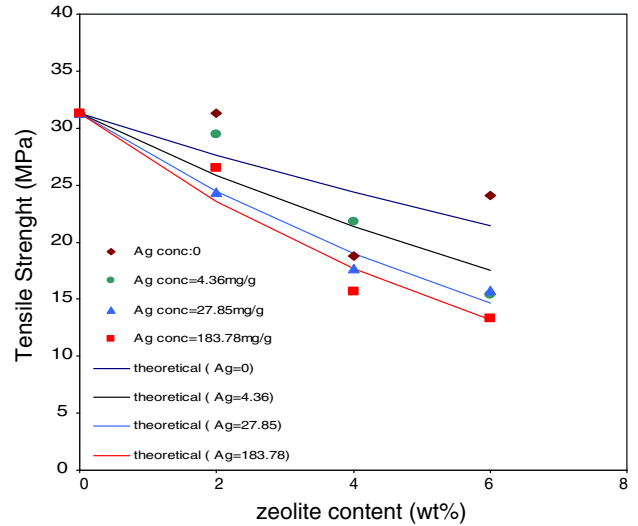


Fig. 3. The effect of zeolite loading and silver concentration on the tensile strength of PP composites.

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 were measured using Minolta Colorometer and the results given in Table 3 show the difference according to the reference sample. The reference sample taken as the pure PP film free of both silver and zeolite.

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 more compared to the “ $a$ ” values with increasing silver concentration. Fig. 4 shows the change of  $L$  parameter according to the control sample ( $\Delta L$ ) as a function of zeolite loading at three different silver concentrations. As seen in Fig. 4, the higher the silver concentration, the more pronounced discoloring effect was obtained. This effect was also seen by Niira et al. [11]. It can be said that the composites containing 2–6 wt% zeolites treated with 4.36 mg  $\text{Ag}^+$ /g zeolite show the less discoloring effect compared to the control sample.

Table 3  
Discoloration test results of PP–silver zeolite composite films

Zeolite (wt%)	$\text{Ag}^+$ conc. (mg/g zeolite)	$\Delta L$	$\Delta a$	$\Delta b$
2	4.36	−1.19	−0.41	1.81
4	4.36	−2.02	−0.57	−2.65
6	4.36	−3.71	−0.63	3.96
2	27.85	−2.67	−1.19	6.72
4	27.85	−5.16	−2.16	14.5
6	27.85	−9.93	−2.50	25.3
2	183.78	−6.39	−0.82	12.6
4	183.78	−10.8	−1.60	23.6
6	183.78	−16.3	−1.34	28.8

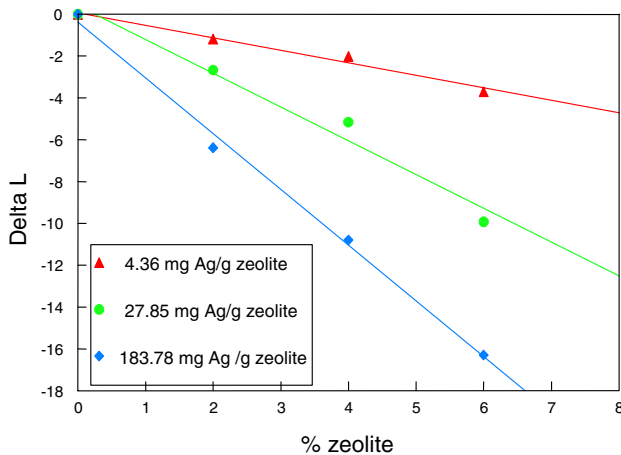


Fig. 4. Discoloring effect of zeolite and  $\text{Ag}^+$  concentration.

### 3.6. Thermal characterization studies

#### 3.6.1. DSC 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. At a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ , the quantitative information about peak temperatures for melting and degradation, enthalpy of fusion ( $\Delta H_f$ ) and enthalpy of degradation values ( $\Delta H_d$ ), and the % crystallinity values are tabulated in Table 4.

As seen in Table 4, the melting and degradation peak temperatures of the composites containing 0–6 wt% zeolite with three different silver concentrations: 4.36, 27.85, 183.78 mg  $\text{Ag}^+/\text{g}$  zeolite were found to be in the range of 161–165 and 459–466  $^\circ\text{C}$ , respectively. This shows that silver concentration and zeolite loading do not affect the peak temperatures of melting and degradation significantly. Heat of fusion ( $\Delta H_f$ ) and heat of degradation

( $\Delta H_d$ ) were determined from the melting and degradation endotherm areas, respectively. Heat of fusion and heat of degradation values showed an increasing trend with increasing zeolite loading and silver concentration except for the case of samples with 183.78 mg  $\text{Ag}^+/\text{g}$  zeolite.  $\Delta H_f$  values were found in the range of 59.6–84 kJ/kg for the 0–6% weight silver zeolite containing composites. Özmihçı et al. [6] previously found the  $\Delta H_f$  values in the range of 63.8–87 kJ/kg for the 0–6 wt% untreated zeolite containing composites.

The % crystallinity of the films was determined using the following equation:

$$\% \text{ crystallinity} = \frac{\text{Heat of fusion of the sample}}{\text{Heat of fusion of the 100\% crystalline sample}} \times 100. \quad (5)$$

The  $\Delta H_f$  value for 100% crystalline isotactic PP is cited in the literature as 209 kJ/kg [18]. This value was used to determine the % crystallinity of the composites. The higher the zeolite content, the higher the crystallinity values were obtained for the composites. As shown in Table 5, Pure PP and PP-DOP films were 28.5% and 35% crystalline, respectively, whereas the crystallinity of the composites was increased with the increasing zeolite content up to 40%. It is concluded that zeolite acts as a nucleating agent in the PP matrix. The degree of crystallinity values of the PP-DOP, 2 wt% pure zeolite (PP-DOP–%2 zeolite) and silver exchanged zeolite (PP-DOP–%2 Ag zeolite) loaded PP composite films were also calculated using XRD data as explained in Section 2.4 and shown in Fig. 5. The crystallinity values of PP-DOP, 2 wt% pure zeolite and 2 wt% silver exchanged zeolite (4.31 mg Ag/gm zeolite) loaded composite films were obtained as 38%, 31% and 33%, respectively. These results were in good agreement with DSC results given in Table 4.

The thermal degradation activation energy of the composites was determined from the DSC curves using Kissinger and Ozawa methods [19,20]. According to

Table 4  
DSC analysis results of composites

Zeolite loading (wt%)	$\text{Ag}^+$ conc. (mg/g zeolite)	Melting peak temperature ( $^\circ\text{C}$ )	Degradation peak temperature ( $^\circ\text{C}$ )	$\Delta H_f$ (kJ/kg)	$\Delta H_d$ (kJ/kg)	% Crystallinity
0	0	165.0	459.9	59.6	258.2	28.5
2	0	163.4	460.5	67.8	346.7	32.4
4	0	160.6	464.1	70.3	373.4	34.0
2	4.36	161.0	464.2	58.4	321.0	27.9
4	4.36	161.5	459.9	70.0	352.1	33.5
6	4.36	165.6	459.3	79.2	363.6	37.9
2	27.85	158.4	464.1	72.7	315.9	34.8
4	27.85	162.7	462.8	79.3	360.5	37.9
6	27.85	165.7	465.7	83.8	319.4	40.1
2	183.78	162.7	466.5	78.2	390.2	37.4
4	183.78	162.7	459.9	69.7	335.3	33.3
6	183.78	162.6	462.6	81.5	314.6	39.0

( $\Delta H_f$ : heat of fusion;  $\Delta H_d$ : heat of degradation).

Table 5  
Degradation kinetic constants of the composite films obtained from DSC and TGA

Ag <sup>+</sup> conc. (mg/g)	Zeolite (%)	DSC			TGA			
		<i>E</i> (kJ/mol)	Frequency factor	<i>k</i> (min <sup>-1</sup> ) at 450 °C	<i>E</i> (kJ/mol)	<i>L</i>	<i>A</i>	<i>k</i> (min <sup>-1</sup> ) at 450 °C
0	0	181.1	$3.5 \times 10^{12}$	0.285	56.1	5	$4.79 \times 10^3$	0.42
4.36	4	168	$4.09 \times 10^{11}$	0.297	96.5	5	$9.98 \times 10^6$	1.06
27.85	4	226	$6.2 \times 10^{15}$	0.291	56.5	4	$7.75 \times 10^3$	0.64
183.78	4	214	$8.68 \times 10^{14}$	0.299	64.6	5	$2.78 \times 10^4$	0.59

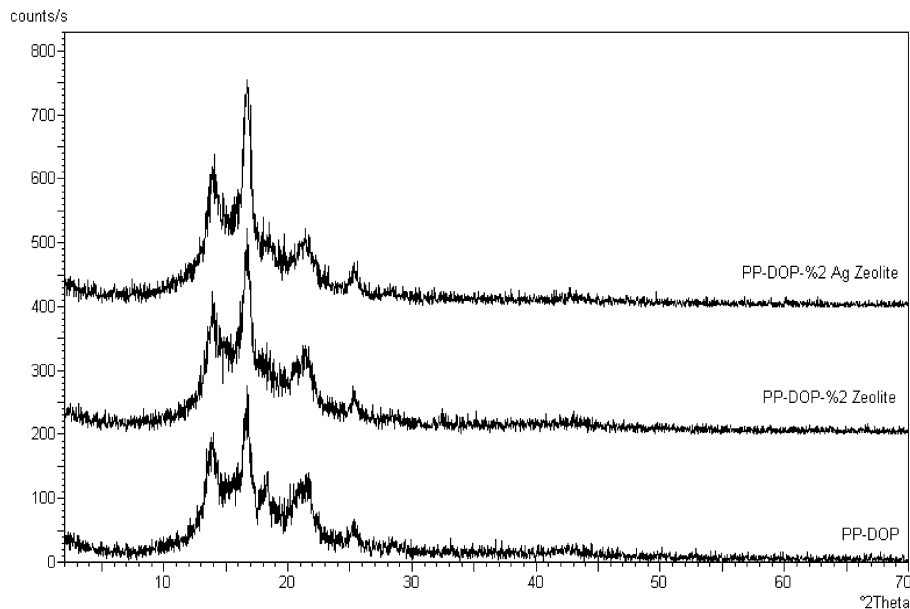


Fig. 5. X-ray diffraction patterns of PP-DOP, 2 wt% zeolite and 2 wt% silver exchanged zeolite loaded composite films.

the Kissinger method, the activation energy of the composites for the decomposition reaction is determined from the slope of the logarithmic heating rate ( $\ln \beta$ ) against  $1/T$  plot corresponding to  $-E_a/R$ :

$$\frac{d(\log \beta)}{d(1/T)} = -\frac{E_a}{R} \quad (6)$$

where  $\beta$  is the heating rate (°C/min),  $T$  is the peak maximum for degradation temperature,  $E_a$  is the activation energy, and  $R$  is the gas constant. The thermal decomposition temperature was measured from the DSC thermograms for various heating rates. The DSC thermograms of the 4 wt% zeolite loaded with 4.36 mg/g silver performed at three different heating rates are given in Fig. 6. Fig. 7 illustrates the plot of  $\ln \beta$  vs.  $1/T_d$  for the same composites. From the slope of this plot, thermal decomposition activation energy,  $E_a$ , was calculated as 170 kJ/mol.

DSC curves were also analyzed according to the Ozawa method using the kinetic analysis software of Shimadzu 50. The quantitative information obtained from the kinetic analysis of the samples performed with both the Ozawa and the Kissinger methods were tabulated in Table 5. As seen from the table, the activation energies

obtained by the two methods were in good agreement with each other.

Since the thermal decomposition occurs around 450 °C, the reaction constant  $k$  was calculated at 450 °C using the Arrhenius equation:

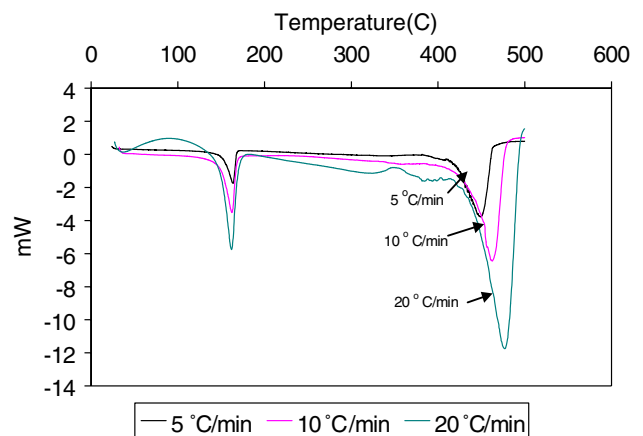


Fig. 6. DSC curves of 4 wt% zeolite composites with 4.36 mg Ag<sup>+</sup>/g zeolite at three different heating rates.



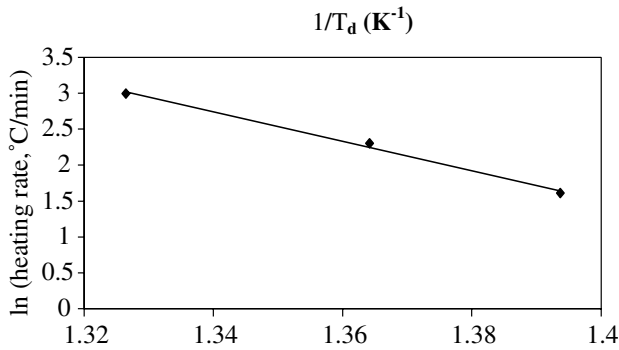


Fig. 7. Kissinger plot of 4 wt% zeolite composite film treated with 4.36 mg Ag/g zeolite.

$$k = A \exp\left(-\frac{E}{RT}\right), \quad (7)$$

where  $E$  is the activation energy (kJ/mol),  $A$  is the frequency factor ( $\text{min}^{-1}$ ),  $R$  is the gas constant, and  $T$  is the temperature (K).

It was observed that the reaction constant was not significantly affected by the increasing silver concentration, and that slight increases occurred, but zeolite addition decreased the decomposition rate.

### 3.6.2. TGA analyses

Composite films were all analyzed using TGA with a heating rate of 10 °C/min. 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. On the average, the degradation started at around 220 °C, and terminated at about 550 °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 at 550 °C came out to be 98.6%, 98.2%, and 96.9%, respectively. Although all the samples were supposed to contain 4 wt% zeolite, the TGA results indicated that the zeolite distribution along the composite films was not uniform.

The kinetic analysis was performed with heating rates of 5, 10, and 20 °C/min for the 4 wt% zeolite samples. Fig. 8 shows the TGA curves of the 4 wt% zeolite samples containing 27.85 mg/g silver. 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 °C. The Ozawa plot shows the logarithm of heating rate versus  $1/T$  at constant  $x$  values (reaction percent) for different conversions (weight losses). From the slope of the lines, the activation energy,  $E_a$ , is calculated for different weight losses

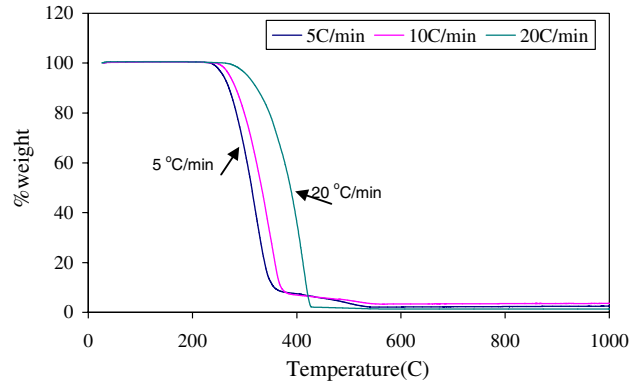


Fig. 8. TGA curves of the 4 wt% silver zeolite (27.85 mg Ag<sup>+</sup>/g zeolite) loaded composites.

and averaged by the software. The kinetic energies and the related parameters obtained for the 4 wt% zeolite containing samples are shown in Table 5.  $A$  is the frequency factor and  $L$  is the order for degradation reaction.  $L$  is a measure of minimum degree of polymerization of volatile degradation products. If the degree of polymerization of degraded polymer is lower than a critical  $L$  value, it is volatile.  $L$  was around 5 for PP [6].

Reaction rate constant for the degradation reaction was determined using Arrhenius equation at 450 °C and given in Table 5. It was observed that the 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. The  $k$  values also determined at 250 °C in this study were close to the ones found by Özmihçi et al. [6] for the films prepared by the same material but with a different extruder operating at 260 °C.

The  $E_a$  and  $A$  values found for degradation of PP by DSC and TGA were very different from each other indicating heat absorbed and evolved gaseous were not proportional.

## 4. Conclusions

In the present study, the silver exchanged natural zeolite–PP composites were prepared via extrusion technique, and the effects of zeolite loading and silver concentration were investigated on the thermal, mechanical, and structural properties of the composite films. The thermal characterization studies showed that the addition of the zeolite increased the crystallinity of the structure acting as a nucleating agent in the PP crystallization as well as retarding the degradation temperature of PP. It was found that at low silver concentrations, the zeolite

behaved as a decelerating agent in PP degradation, however at higher silver concentrations, the composites degraded at a faster rate than pure PP. As a result, PP is much more susceptible to the thermal decomposition in the presence of silver exchanged zeolite compared to the pure zeolite. This was also indicated by the discoloring and brittle fracture of the films at high  $\text{Ag}^+$  and zeolite concentration. It was also found that the addition of the zeolite into the PP matrix decreased the density of pure PP ( $0.89 \text{ g/cm}^3$ ) indicating the formation of voids confirming previous studies.

The optimum conditions obtained in this study for the silver zeolite–PP film production are 2–4 wt% zeolite treated with 4.36 mg  $\text{Ag}^+$ /g zeolite concentration. At higher zeolite loading, the film becomes brittle, and at higher Ag concentration the produced films were discolored. Since polypropylene having silver exchanged zeolite in an extruder causes thermal degradation, the treatment of PP–zeolite composite films with silver containing solution would be a better alternative for antimicrobial film preparation.

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