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# The effect of interfacial interactions on the mechanical properties of polypropylene/natural zeolite composites

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## Abstract

The effect of interfacial interactions on the mechanical properties of polypropylene (PP)/natural zeolite composites was investigated under dry and wet conditions. Interfacial interactions were modified to improve filler compatibility and mechanical properties of the composites by surface treatment of natural zeolite with a non-ionic surface modifier; 3 wt% polyethylene glycol (PEG) and three different types of silane coupling agents; 3-aminopropyltriethoxysilane (AMPTES), methyltriethoxysilane (MTES) and 3-mercaptopropyltrimethoxysilane (MPTMS), at four different concentrations (0.5–2 wt%). PP composites containing (2–6 wt%) zeolite were prepared by an extrusion technique. The tensile properties of the composites determined as a function of the filler loading and the concentration of the coupling agents were found to vary with surface treatment of zeolite. Silane treatment indicated significant improvements in the mechanical properties of the composites. According to the dry and wet tensile test results, the maximum improvement in the mechanical properties was obtained for the PP composites containing 1 wt% AMPTES treated zeolite. The improvement in the interfacial interaction was confirmed using a semi-empirical equation developed by Pukanszky. Good agreement was obtained between experimental data and the Pukanszky model prediction. Scanning electron microscopy studies also revealed better dispersion of silane treated filler particles in the PP matrix.

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**Keywords:** A, Polymer-matrix composites (PMCs); B, Adhesion; B, Interface interphase; B, Mechanical properties

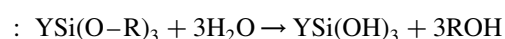
## 1. Introduction

Polypropylene (PP) is one of the most important commercial polymers due to its superior properties such as high melting temperature, high chemical resistance and low density. Moreover, PP is used in combination with other materials such as fillers or reinforcing agents to enhance its properties (stiffness, gas permeability, heat resistance, etc.), to provide functional properties to the polymer such as flame retardancy or conductivity and to reduce the cost in applications such as household, automotive and packaging. Although the addition of fillers provides many advantages, they can lead to a loss in the mechanical properties of the polymer due to incompatibility between the fillers and polymer. Since interfacial PP–filler properties strongly influence the properties of the composites, the interface can be modified to improve wettability and adhesion with

surface modifiers such as fatty acids, silane coupling agents and titanate coupling agents [1–10]. In the literature, there are many studies dealing with the characterisation of interfaces and their influence on the mechanical properties of particulate filled composites. The studies on the effects of silane coupling agents indicate that surface treatment of the fillers provide considerable improvement in the interfacial and mechanical properties of polymer composites [11–17].

Silane coupling agents have a general formula of  $YSi(OR)_3$ , where R and Y stand for a hydrolysable group (methyl or ethyl) and a non-hydrolysable organofunctional group (amino, methacrylate, mercapto or vinyl groups), capable of interaction with fillers and polymers, respectively. Surface treatment of fillers with silane coupling agents was carried out through hydrolysis and condensation reactions as follows [18–20]:

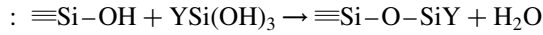
Hydrolysis reaction



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Condensation reaction



Silanol groups formed as a result of a hydrolysis reaction react with hydroxyl groups found on filler surfaces to form siloxane bonds through a condensation reaction. As a result of these reactions, silane coupling agents modify the interface by forming a link between the components [19,20].

Although fillers such as  $\text{CaCO}_3$ , talc, mica, glass fiber, etc. have been used with PP matrices, not much work was found in the literature related to the use of zeolite as a filler. Zeolites are microporous crystalline, hydrated alumina silicates of alkaline and alkaline earth elements, extensively used as catalysts, adsorbents, and also in ion exchange due to their regular pore structures and high thermal stability [21,22]. They were also employed as an additive to impart antibacterial and flame retardant properties to polymers [23–26]. However, Pehlivan [26] and Özmihçi et al. [27] reported that zeolite loading decreases the mechanical properties of PP because of poor interfacial interactions. They also concluded that natural zeolites are abundant and low-cost materials, which could be used as an alternative filler in PP composites by enhancement of interfacial interactions between PP and zeolite.

The objective of this study is, therefore, to improve the mechanical properties of the PP–zeolite composites by enhancement of the interphase and to analyse the interfacial properties of the composites quantitatively from the mechanical results.

## 2. Theory

### 2.1. Quantitative evaluation of interfacial interaction

Interfacial interaction between the fillers and matrix is an important factor affecting the mechanical properties of the composites. Thus, theoretical tensile yield strength and ultimate tensile strength of the composites are modelled for the cases of adhesion and no adhesion between the filler particles and matrix. In the case of no adhesion, the interfacial layer cannot transfer stress. The tensile strengths of the composites can be predicted using Nielsen and Nicholais–Narkis models, Eqs. (1) and (2), respectively, [28–30].

$$\sigma_c/\sigma_m = (1 - \Phi_f^{2/3})S \quad (1)$$

$$\sigma_c/\sigma_m = (1 - a\Phi_f^b) \quad (2)$$

where  $\Phi_f$ ,  $\sigma_c$  and  $\sigma_m$  are volume fraction of filler, and tensile strengths of the composite and matrix, respectively. The parameter  $S$  in Nielsen's model describes weakness in the structure due to stress concentration in the filler–matrix interphase. A value of unity means 'no stress concentration effect', whereas the lower the value the 'greater the stress

concentration effect or poorer the adhesion'. In the Nicholais and Narkis model, parameters  $a$  and  $b$  are the constants that are related to filler–matrix interaction and geometry of the filler, respectively. The value of  $a$  less than 1.21 represents good adhesion for composites containing spherical fillers. In the absence of adhesion for the composites, Eq. (2) becomes

$$\sigma_c/\sigma_m = (1 - 1.21\Phi_f^{2/3}) \quad (3)$$

The Pukanszky model, Eq. (4), describes the effects of composition and the interfacial interaction on tensile yield stress of particulate filled polymers [31].

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

The parameter  $B$  is an interaction parameter that is related to the macroscopic characteristics of the filler–matrix interface and interphase.  $\sigma_{yc}$  and  $\sigma_{ym}$  denote the tensile yield stress of composite and matrix, respectively. The first term in Eq. (4) is related to the decrease in effective load bearing cross-section, and the second one is concerned with the interfacial interaction between filler and matrix. Interfacial interaction depends on the area of the interphase, and the strength of the interaction as shown in Eq. (5).

$$B = (1 + A_f\rho_f t)\ln(\sigma_{yi}/\sigma_{ym}) \quad (5)$$

where  $t$ ,  $\sigma_{yi}$ ,  $A_f$  and  $\rho_f$  are the thickness of the interface, strength of interaction, the specific surface area and density of the filler [12,31], respectively.

## 3. Experimental

### 3.1. Materials

MH-418 PP in pellet form, supplied by PETKİM Petrochemical Co., and clinoptilolite rich natural zeolite from Gördes 1 mine (Western Anatolia) were used. Natural zeolite was characterised by Akdeniz [32] in 1999. Natural zeolite particles less than  $1 \mu\text{m}$  in size were obtained by grinding in a ball-mill, sieving and sedimentation in water for 35 h. Particles of  $1.5 \mu\text{m}$  mean size were obtained by drying the suspension at  $110^\circ\text{C}$ .

Zeolite particles were modified using four different types of surface modifiers to improve compatibility of zeolite with the hydrophobic PP. The surface modifiers were: polyethylene glycol (PEG-4000), 3-aminopropyltriethoxysilane (AMPTES), 3-mercaptopropyltrimethoxysilane (MPTMS) and methyltriethoxysilane (MTES) and details are given in Table 1. These silane agents require no external acid or base catalysts for the hydrolysis reaction. Additionally, MTES was used for investigating the effect of functional groups of silane coupling agents.

Table 1  
Chemical structures of surface modifiers

Surface modifier	Chemical formula	Producer
PEG	$\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$	Aldrich
AMPTES	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si-(O-CH}_2\text{-CH}_3)_3$	Fluka
MPTMS	$\text{SH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si-(O-CH}_3)_3$	Merck
MTES	$\text{CH}_3\text{-Si-(O-CH}_2\text{-CH}_3)_3$	Merck

### 3.2. Surface modification of zeolite

Surface modification of zeolite with a non-ionic surface modifier, PEG and a silane coupling agent was performed by two different methods. In the first, the zeolite surface was modified during the grinding process: zeolite was blended with 3 wt% PEG for 5 h at 100 rpm in the ball mill.

In the second method, surface modification of ground zeolite with silane coupling agents was carried out in solution. Zeolite was added to the solution of silane agent (0.5, 1, 1.5 and 2 wt%) in 50 v% aqueous ethanol solution. The zeolite to solution ratio was taken as 1:1 on weight/volume basis. The slurry was stirred for 2 h by a magnetic stirrer and then kept for 1 h at room temperature. The surface treatment of the zeolite with the silane was completed after drying the slurry in a vacuum oven at 110 °C and 400 mbar pressure for 4 h.

### 3.3. Composite preparation

PP composites containing 2, 4 and 6 wt% untreated or treated zeolite were prepared using an Axon BX-18 single screw extruder and an Axon 2R-180 two roll mill. Before the extrusion process, surface treated or untreated forms of zeolite (2, 4 and 6 wt%) were mixed with PP pellets and a plasticiser. Epoxidised soybean oil (EPSO) plasticiser was used at a rate of 5 v/w% of total weight of the PP and zeolite to improve processability in the extruder. The mixtures were conditioned in a vacuum oven at 80 °C under 400 mbar pressure for an hour to ensure replacement of air in the pores of zeolite with EPSO. Conditioned compositions containing a pre-mix of PP, zeolite and plasticiser were fed into the extruder having L/D of 20, and a diameter of 18 mm, and flat die dimensions of (50 × 1 mm<sup>2</sup>). The zone temperatures of the extruder was kept constant at 200 and 220 °C for the first zone and the other five zones, respectively. The PP composite cast film taken from the flat die was quenched using a polished drum cooled by tap water and then stretched between casting rolls in the calender.

### 3.4. Characterisation studies

#### 3.4.1. Contact angle measurements

The effect of silane treatment on the zeolite surface was investigated by measurement of the contact angle. After the zeolite surface was polished using silicon carbide papers, it was treated with different silane coupling agents according

to the surface modification method. The contact angle of water on the zeolite surface was measured with a Krüss-G10 goniometer. The mean contact angle of untreated and treated zeolite samples was obtained from five different measurements for each zeolite sample.

#### 3.4.2. Mechanical properties

Tensile tests of PP–zeolite composites in dry and wet conditions were performed on an Instron Universal Testing Machine Model 4411 with a 50 kgf load cell, a cross-head speed of 500 mm/min and a gauge length of 50 mm. Wet samples were obtained by immersing PP–zeolite composites in distilled water for 24 h at room conditions. Tensile tests were carried out at 23 °C and 50% relative humidity. Tensile test specimens were prepared as strips 0.5 cm in width according to ASTM D-882. At least three specimens were tested for each PP composite and the mean values reported.

#### 3.4.3. Morphology

Scanning electron microscopy was used to examine the morphology of PP–zeolite composites. Fracture surfaces of tensile tested composites containing 4 wt% untreated and treated zeolite with 1 wt% AMPTES, 1 wt% MTES and 0.5 wt% MPTMS were observed with a Philips XL-30S FEG scanning electron microscope (SEM). Samples were coated with gold and palladium prior to scanning to minimise problems such as radiation damage and charging.

## 4. Results and discussions

### 4.1. Characterisation of zeolite surface

Contact angles of untreated zeolite (UZ) and zeolite treated with silane coupling agents (AMPTES, MTES and MPTMS) were measured to investigate the effects of silane treatment on the zeolite surface and the wettability between PP and zeolite. The mean contact angles of untreated and treated zeolites as a function of silane type and concentration are listed in Table 2. The surface modification was conducted in order to obtain hydrophobic zeolite with a lower tendency to form agglomerates. The contact angle of UZ, 0°, indicates strong hydrophilicity of the zeolite. As seen in Table 2, the contact angles of the treated zeolites

Table 2  
Contact angle measurements

Surface modifier	Surface modifier concentration			
	0.5	1	1.5	2
–	0	0	0	0
AMPTES	33.0	39.0	34.2	30.4
MPTMS	90.0	85.0	78.2	75.0
MTES	27.0	30.6	37.2	30.0

were dependent on the silane type and its concentration. The contact angles of amino functional and mercapto silane coupling agents having terminal functional groups such as  $H_2N-$  and  $HS-$  are higher than that of MTES, which has no functional group, because the introduction of a polar terminal functional group causes the formation of more ordered layers around the filler [33].

The contact angles of zeolites were increased by silane treatment. The increase in contact angle of water on the filler shows the increase in hydrophobicity of the filler. The mean contact angles of the silane treated zeolites were measured as 39, 30.6 and  $90^\circ$  for 1 wt% AMPTES, 1 wt% MTES and 0.5 wt% MPTMS, respectively. It was found that the hydrophobicity of zeolite was significantly increased by surface modification and 0.5 wt% MPTMS was determined as the most effective coupling agent for hydrophobisation of the zeolite.

PP being an organic material, exhibits no tendency to wet and cover the surface of inorganic zeolite particles during film production in the extruder. This problem can be overcome by the improvement of PP–zeolite compatibility. The increase in hydrophobicity of zeolite with surface modification causes an improvement in compatibility between apolar PP and polar zeolite. As a result, the wettability between hydrophobic PP and hydrophilic zeolite improves with the increase in hydrophobicity of zeolite using silane coupling agents due to the enhancement of compatibility between PP and zeolite.

#### 4.2. Mechanical properties

Tensile tests of PP–zeolite composites were conducted to determine how mechanical properties were influenced by the presence of surface modifiers (PEG, AMPTES, MTES or MPTMS). In addition, tensile tests of wet samples were carried out to determine the interfacial strengths of the composites. Young's modulus, yield stress, tensile stress at break and elongation at break of PP–zeolite composites were investigated as a function of zeolite loading, type of surface modifier, and surface modifier concentration in dry and wet conditions.

##### 4.2.1. Young's modulus

In this study, Young's modulus of the composites increased as the filler content increased. The increase in Young's modulus of the zeolite-filled composites indicates an increase in the rigidity of PP related to the restriction of the mobility in PP matrix due to the presence of fillers [29,34]. Conversely, Özmihçi et al. [27] and Pehlivan [26] observed a decrease in Young's modulus of PP–zeolite composites with an increase in zeolite loading. 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 in the absence of a coupling agent.

Figs. 1 and 2 show the influence of the surface treatment concentration of silane coupling agents (0.5, 1, 1.5 and

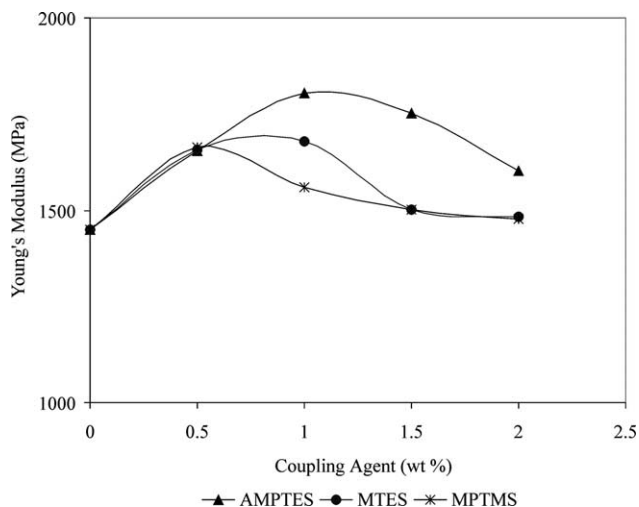


Fig. 1. Effect of silane coupling agents on the Young's modulus of PP composites containing 6 wt% zeolite in dry conditions.

2 wt%) on Young's modulus of the composites containing 6 wt% zeolite in dry and wet conditions, respectively. As seen in the figures, silane treatment leads to an increase in Young's modulus due to improvement of adhesion between zeolite and PP matrix. Thus, the maximum Young's modulus values indicate the maximum strength of interaction between zeolite and PP matrix. Young's modulus decreases with increase in silane concentration after 1 wt% concentration for AMPTES and MTES and 0.5 wt% for MPTMS. The decrease in modulus can be explained by the plasticising effect of the surface modifier.

Young's modulus of composites containing 4 wt% untreated and treated zeolite in dry and wet conditions is illustrated in Fig. 3. Young's modulus of composites containing 4 wt% zeolite treated with PEG, 1 wt% AMPTES and MTES and 0.5 wt% MPTMS corresponding to respective optimum silane concentrations, increased by 8.7, 17.3, 10.3 and 9.2% as compared to the 4 wt% UZ filled

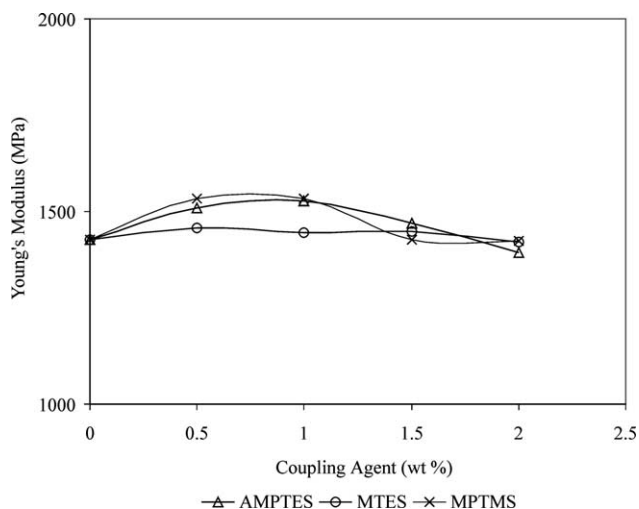


Fig. 2. Effect of silane coupling agents on the Young's modulus of PP composites containing 6 wt% zeolite in wet conditions.



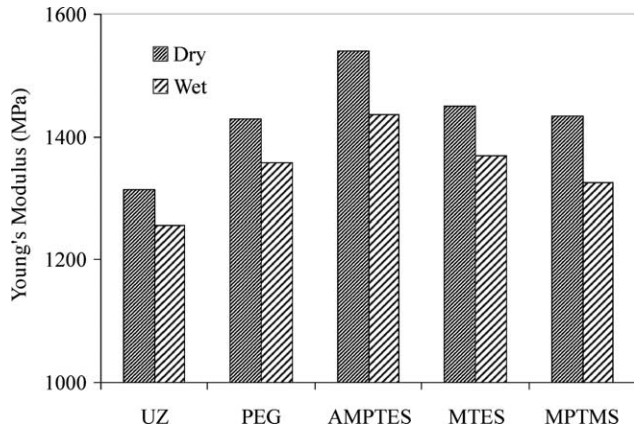


Fig. 3. The Young's modulus of PP composites containing 4 wt% untreated (UZ) and treated zeolite with 3 wt% PEG, 1 wt% AMPTES, 1 wt% MTES, and 0.5 wt% MPTMS in dry and wet conditions.

PP composites in dry conditions, respectively. In the case of wet conditions, the increase in Young's modulus values of the composites containing 4 wt% zeolite treated with PEG, 1 wt% AMPTES and MTES and 0.5 wt% MPTMS were found as 8.2, 14.3, 9.1 and 5.5% compared to the 4 wt% UZ filled PP composites, respectively. Although dry and wet tensile moduli of the silane treated composites are higher than those of the untreated and PEG treated composites, wet tensile modulus of all composites was lower than their dry modulus owing to the water absorption. Pehlivan et al. [35] investigated the water and water vapour sorption of PP–zeolite composites. Water absorption may lead to a reduction in the bond strength at the interface. The adhesion between matrix and filler can be very weak under wet conditions. The decrease in wet modulus of silane treated composites indicates that there is no perfect interfacial adhesion between the zeolite and PP matrix. However, PP composites containing 1 wt% AMPTES treated zeolite in dry and wet conditions have higher modulus values than the others at the constant zeolite loading. This indicates that the better interfacial adhesion between PP matrix and zeolite particles was obtained by surface treatment of zeolite with 1 wt% AMPTES.

#### 4.2.2. Tensile yield stress

The effect of various coupling agents on dry and wet yield stress of the composites is shown in Fig. 4 with respect to the concentration of coupling agent. The yield stress of the composites containing treated filler with silane coupling agents increased similarly to the Young's modulus. As seen in the figure, the addition of a small amount of silane coupling agent leads to a sharp increase in the tensile yield strength of the composites. The increase in the yield stress values of the composites indicates that the strength of PP–zeolite composite is improved by a silane coupling agent. Maximum values in the yield stress were observed at the coupling agent concentration of 1 wt% for AMPTES and MTES and 0.5 wt% for MPTMS, respectively. These levels for each

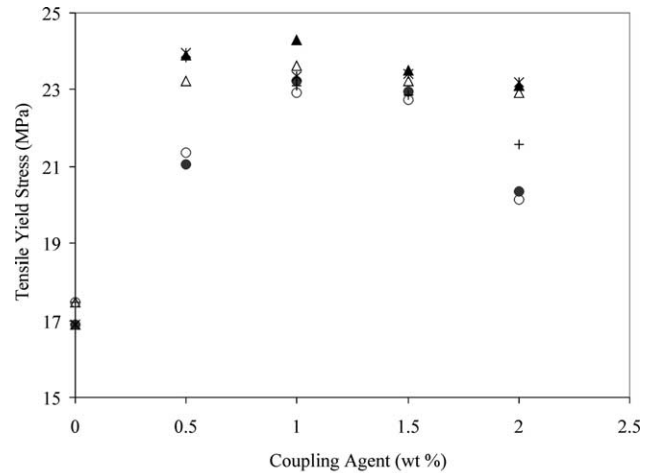


Fig. 4. Effect of silane coupling agents on the tensile yield stress of PP composites containing 6 wt% zeolite in dry and wet conditions.

silane coupling agent are the optimum, which reflect the highest strength of interaction between the zeolite and PP matrix. Demjen and coworkers [11,12] also observed this type of behaviour for PP–CaCO<sub>3</sub> composites. A maximum for the tensile properties of the composites was found by Demjen and coworkers around 1 wt% silane concentration for various silane coupling agents such as (3-methacryloxypropyl)-trimethoxysilane and aminopropyltriethoxysilane.

Fig. 5a and b illustrates the dry and wet tensile yield stress values of PP composites containing untreated and PEG treated zeolite and zeolite treated with silane coupling agents at optimum silane concentration, as a function of zeolite content, respectively. All coupling agents used at optimum concentration show a reactive coupling effect that results in higher yield stresses compared to the untreated ones.

Fig. 6 shows the dry and wet tensile yield stress values of composites containing 4 wt% untreated and treated zeolite. Dry tensile yield stress values of the composites containing 4 wt% zeolite treated with PEG, 1 wt% AMPTES and MTES and 0.5 wt% MPTMS increased by –1.3, 18.9, 14.9 and 18.4% compared to the dry yield stress of 4 wt% UZ filled composite, respectively. Also, the increase in tensile yield stress of these composites under wet conditions was found as 9.7, 23.4, 19.8 and 22.8% compared to the yield stress of UZ filled composites, respectively. As seen in the figures, only a slight difference was observed between dry and wet yield stress values of the composites containing silane treated zeolite. It is evident that interfacial adhesion between zeolite and PP was improved by silane coupling agents. The maximum improvement in tensile yield stress values was observed in the case of AMPTES treated composites under dry and wet conditions.

Fig. 5a and b also shows the comparison of the experimental data with the Pukanszky model for dry and wet tensile yield stress values of PP–zeolite composites,

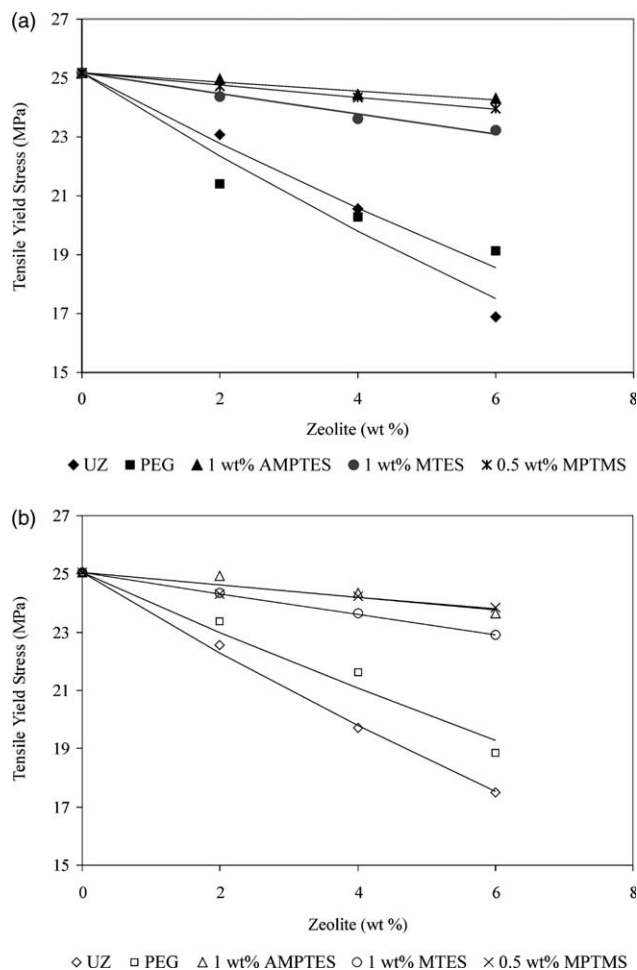


Fig. 5. (a) Effect of surface treatment and zeolite content on the experimental and theoretical tensile yield stress of composites in dry conditions. Lines represent the fit of the data with Pukanszky model. (b) Effect of surface treatment and zeolite content on the experimental and theoretical tensile yield stress of composites in wet conditions. Lines represent the fit of the data with Pukanszky model.

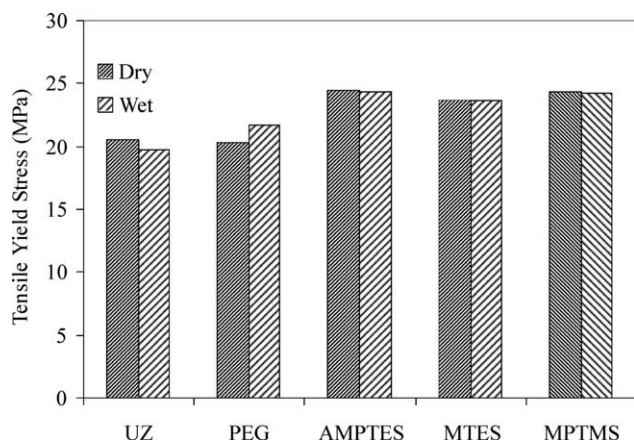


Fig. 6. The tensile yield stress values of PP composites containing 4 wt% untreated (UZ) and treated zeolite with 3 wt% PEG, 1 wt% AMPTES, 1 wt% MTES, and 0.5 wt% MPTMS in dry and wet conditions.

Table 3

$B$  values of the Pukanszky model for PP–zeolite composites in dry and wet conditions

Surface modifier	Dry $B$	Wet $B$
–	–9	–8.8
3 wt% PEG	–6.99	–5.53
1 wt% AMPTES	2.15	1.67
1 wt% MTES	0.47	0.38
0.5 wt% MPTMS	1.7	1.71

respectively. As seen in the figures, the model predicts the data of PP–silane treated zeolite composites very well. Parameter  $B$  in the model characterises the interaction between PP and zeolite, and the higher the  $B$  values indicate the better interaction. Parameter  $B$  can be effectively used as a quantitative measure of the efficiency of surface treatments on each filler–matrix interface [12,31].  $B$  values of the Pukanszky model for the composites in dry and wet conditions were found using experimental yield data and Eq. (4) and reported in Table 3. Compared to the dry yield stress of the composites,  $B$  values of the PP–EPS composites containing untreated and PEG treated zeolites and zeolite treated with silane coupling agents at optimum silane concentrations: 1 wt% AMPTES, 1 wt% MTES and 0.5 wt% MPTMS were changed by –9, –6.99, 2.15, 0.47 and 1.7, respectively. The respective  $B$  values of these composites were found as –8.8, –5.53, 1.67, 0.38, and 1.71 for the wet tensile test results. Negative  $B$  values could be an indication of the non-homogeneous distribution of the zeolite particles in the composites and result from weak adhesion at the interface of polymer and particle. As seen in Table 3, AMPTES has the highest  $B$  value with the strongest strength of interaction compared to the others. Similarly, in the study of Demjen et al. [12], where eight different silane coupling agents were used in PP–CaCO<sub>3</sub> composites, the treatment with amino functional silane (AMPTEs) yielded the maximum  $B$  value of 2, indicating the strongest interaction. Thus, the maximum  $B$  value for AMPTEs treated zeolite composites in the current study, 2.15, was found to be in good agreement with the results of Demjen and coworkers for PP–CaCO<sub>3</sub> composites.

#### 4.2.3. Tensile stress at break

The tensile stress at break of the composites gives information about the final break of the composite. Fig. 7a and b shows the effect of surface treatment and the composition dependence of tensile stress at break for dry and wet conditions. Fig. 7a illustrates the tensile stress at break values for the composites containing 6 wt% zeolite. As seen in Fig. 7a, maximum tensile stress values were obtained at the coupling agent concentrations of 1 wt% for AMPTEs and MTES and 0.5 wt% for MPTMS, similar to the tensile yield stress behaviour. The tensile stress at break values of the composites show a decreasing trend as the zeolite loading increases. The reduction in the tensile stress

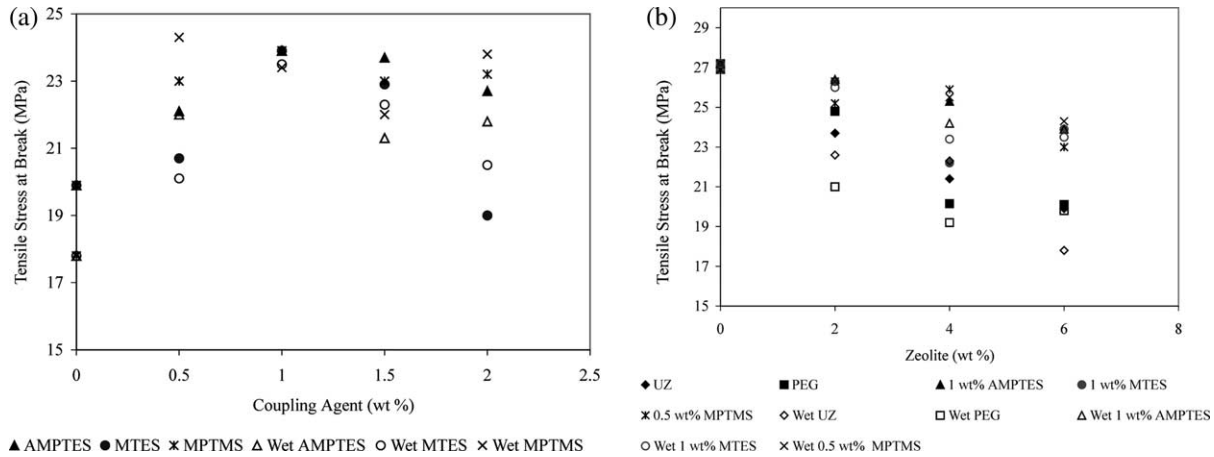


Fig. 7. (a) Effect of surface treatment on the dry and wet tensile stress at break values of composites containing 6 wt% zeolite. (b) Effect of zeolite content on the dry and wet tensile stress at break values of composites.

with an increase of filler content can be explained by the reduction in the effective matrix cross-section and formation of voids in the matrix. However, the reduction in the tensile strength of PP composites has been decreased by silane coupling agents as in the case of tensile yield stress of the composites. As seen in the figures, although tensile stress values of the composites containing untreated and PEG treated zeolites were decreased significantly under wet conditions, no significant difference between wet and dry stress values of the composites was obtained by silane treatment. This result indicates that interfacial enhancement between zeolite and PP matrix was achieved by silane coupling agents.

4.2.4. Elongation at break

The effect of silane coupling agents and zeolite content on the elongation at break of the dry and wet composites is shown in Fig. 8. Fig. 8a illustrates the dry and wet elongation at break values of composites having 4 wt%

zeolite. Although dry and wet elongation at break values show some fluctuations due to the uneven distribution of zeolite particles in the matrix, there was no significant difference between dry and wet elongation values. Elongation at break values increase with an increase in coupling agent concentration at constant zeolite loading and decrease with an increase in zeolite loading. The increase in deformability of polymer composites with an increase in coupling agent concentration indicates that silane coupling agents probably provide a plasticising/lubricating effect because of the formation of physisorbed layers in the interphase [11,29].

As shown in Fig. 8b, the elongation at break values for all composites decrease with increase in zeolite content. This decrease indicates that the composites become brittle with increase in zeolite loading owing to the stress concentration effect of zeolite. The decrease in the elongation at break of the composites in the presence of coupling agents was expected due to the enhancement of adhesion between PP and zeolite.

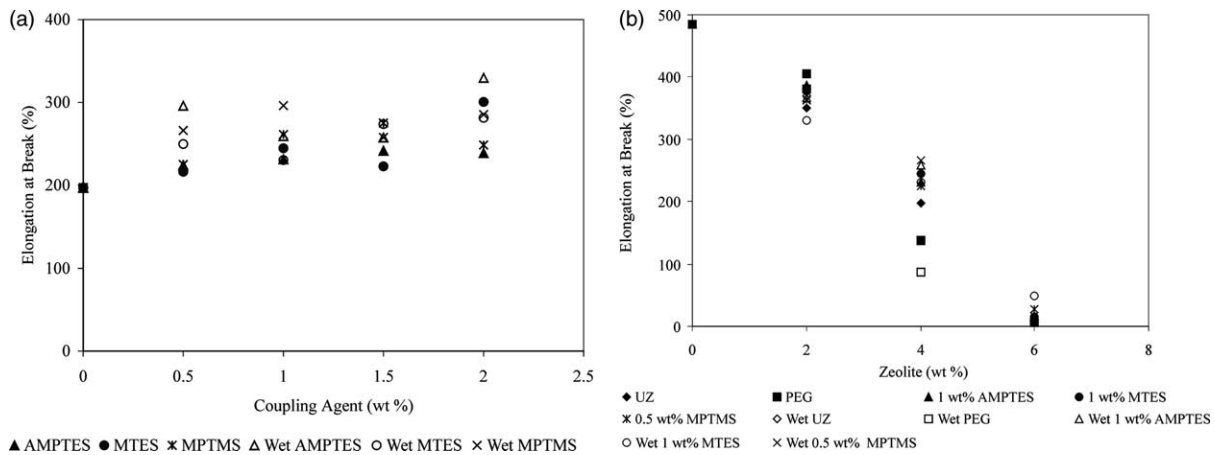


Fig. 8. (a) Effect of surface treatment on the dry and wet elongation at break values of composites containing 4 wt% zeolite. (b) Effect of zeolite content on the dry and wet elongation at break values of composites.



However, the elongation at break values of the composites increase with the silane coupling agent treatment compared to the untreated case at the constant loading due to the plasticiser effect of silane coupling agents and EPSO.

#### 4.3. Morphology

Morphology of the fracture surfaces of the composites depends on the interfacial structure due to load transfer between zeolite and PP matrix. The effect of surface treatment on the interface between PP and zeolite was studied by examining the fracture surfaces of tensile tested composites with a SEM. Fig. 9a–d illustrates the 5000 times magnified electron micrographs of fracture surfaces of PP composites containing 4 wt% untreated and treated zeolite with 1 wt% AMPTES and MTES and 0.5 wt% MPTMS, respectively. The weak interface between UZ and PP matrix can be clearly observed from the SEM micrograph in Fig. 9a. As indicated by arrows in Fig. 9a, the micrograph of PP composites containing 4 wt% UZ shows the clean surface of UZ particles at the fracture surface and the separation of some zeolite particles from the PP matrix. These indicate that zeolite particles can be pulled out completely from the PP matrix by breaking the interface due to the poor adhesion between zeolite and PP. The reason for poor adhesion between UZ and the polymer is the difference in surface free

energy (or polarity) between zeolite and PP as shown by contact angle measurement.

SEM micrographs of the composites containing treated zeolites are significantly different from that of the composite containing UZ. The micrographs show the enhanced modification of silane treated composite's interface compared to the UZ composite. The elongation at break values of the composites containing 4 wt% UZ and silane treated zeolites were in the range of 190–260%. Although ductile fracture and fibrillar formation of the fracture surface were expected in all cases, brittle fracture was seen in Fig. 9a and c. However, the fibrillar formation indicating ductile fracture was observed in the micrographs of the composites containing AMPTES and MPTMS treated zeolite as demonstrated by the arrows in Fig. 9b and d. It is clear that the plastic deformation of the composites indicating ductile fracture is higher than that of the others. As seen on Fig. 9b and d, zeolite particles were embedded into the polymer matrix by the wetting of zeolite particles with the matrix. Consequently, better dispersion of the zeolite particles in the PP matrix and the enhancement of the interface between PP and zeolite were obtained. The enhancement of the interface can be explained by the decrease in surface energy of the filler with silane coupling agents, which leads to the improvement of compatibility between zeolite and

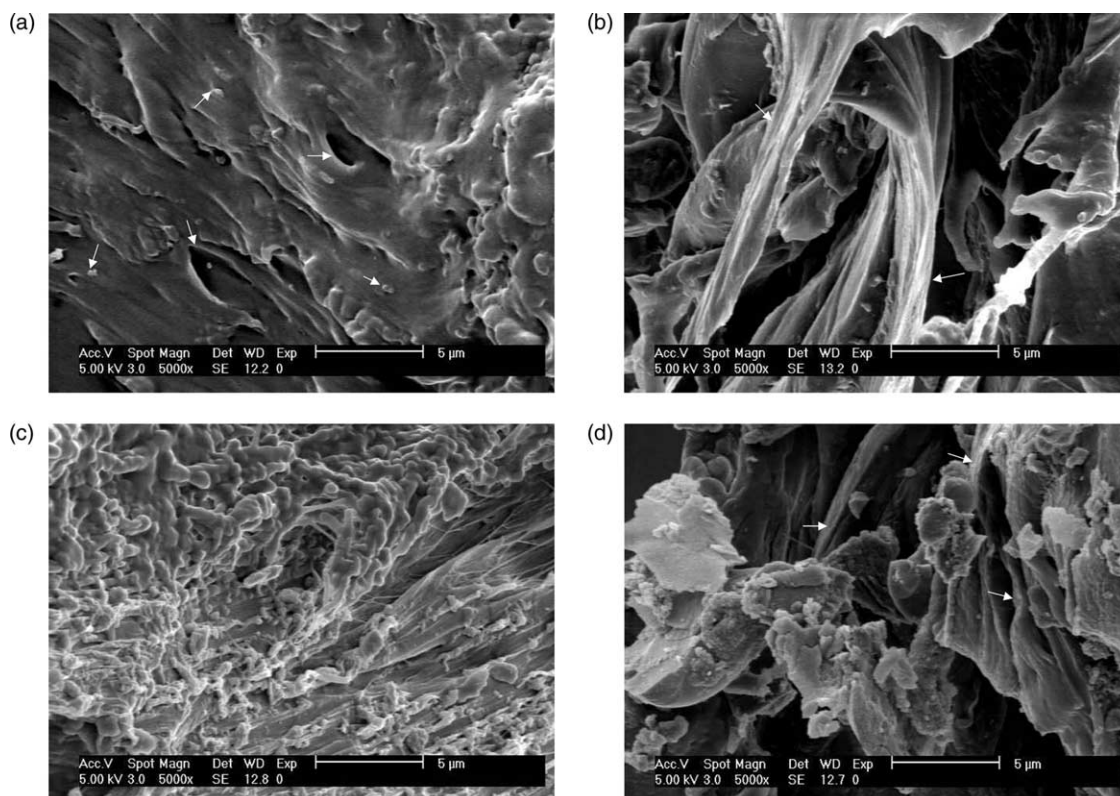


Fig. 9. SEM micrographs of the fracture surfaces of PP composites containing 4 wt% (a) untreated zeolite and treated zeolite with (b) 1 wt% AMPTES, (c) 1 wt% MTES and (d) 0.5 wt% MPTMS.



PP. The improvement of adhesion between zeolite particles and PP led to the higher elastic moduli and yield strengths of the composites as found in the mechanical test results.

## 5. Conclusions

In the present study, the effect of zeolite loading and surface treatment of zeolite with PEG and silane coupling agents on the mechanical and structural properties of the PP–natural zeolite composites was investigated. It was found that composites containing silane treated zeolite showed a significant improvement in the mechanical properties compared to composites containing UZs due to the enhancement of adhesion and compatibility between PP and silane treated zeolite. The improvement in adhesion between zeolite and PP with silane coupling agents was in agreement with the Pukanszky model and shown by SEM studies. Although the mechanical properties of the composites under wet conditions decreased, depending on zeolite loading and surface treatment, no significant difference in tensile yield stress and tensile stress at break for the composites containing silane treated zeolite was observed. According to the dry and wet tensile test results, the maximum improvement in the mechanical properties of the composites was observed in the PP composites containing 1 wt% AMPTES treated zeolite.

Consequently, mechanical test results and scanning electron micrographs of the composites indicated that PP composites containing 1 wt% AMPTES treated zeolite had improved compatibility and interfacial adhesion between zeolite particles and PP matrix.

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