

Water and Water Vapor Sorption Studies in Polypropylene–Zeolite Composites

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ABSTRACT: Water and water vapor sorption to porous polypropylene–zeolite composites prepared by hot pressing have been studied as a function of zeolite loading. This work presents the first report on the effect of the zeolite as a filler on the water-sorption properties of PP composites. Water swelling experiments were conducted at 25°C using pure PP and PP–zeolite films samples having different zeolite loadings (6–40 wt %). Because PP is a hydrophobic polymer, it does not sorp any water, but the composites having 10, 20, 30, and 40% zeolites have sorbed 0.63, 1.00, 1.72 and 3.74% water, respectively. The zeolite itself at the same conditions sorbed 24.5% water. As the filler loading in the composites increased, equilibrium uptake values increased also. On the other hand, water vapor sorption and kinetics has been studied using a Cahn 2000 gravimetric sorption system.

Within in the range of 0.35–0.95% water vapor was adsorbed by the composites containing 10–40 wt % zeolites. Experimental effective water vapor diffusivities of the composite films was about one order of magnitude higher (10-fold) than the experimental water diffusion coefficient in composites. The transport of water in composites was slower than that in the liquid water due to the longer diffusion pathway and adsorption on the surface of the composites. Although the liquid water may fill all the voids in the composite, water vapor is adsorbed on the surface of the zeolite only. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3069–3075, 2003

Key words: zeolites; composites; poly(propylene) (PP)

INTRODUCTION

Polypropylene is among the most widely exploited thermoplastic polymers, and is of increasing practical importance because of its good comprehensive use, low cost, ease of processing, and recycling. It has various application areas such as packaging, protective coating, automobile, electrical, and furniture industries. However, the applications are limited by some drawbacks. To produce tailor-made properties for special applications, appropriate filler is added into the polymer matrix. The addition of fillers to the polymers is a fast and cheap method to modify the properties of the base polymer. Among the mineral fillers for PP, mica, calcium carbonate, and talc are the most often used.^{1–6} Each filler bring its own characteristic to the matrice, and as a consequence, the properties of the composite. Recently, zeolites are also being employed as particulate fillers into the polymer matrix.^{7,8} Because the zeolite is a hydrophilic and PP is a hydrophobic material, the addition of zeolite into PP matrix change the water and water vapor sorption

properties of PP and makes PP as a water and water vapor-sorbing material. In this case, the PP–zeolite composite can be used where a dessicating packaging material is needed.

In many of the applications of the PP and its composites, the material is exposed to the water and atmospheric moisture for a long time. This can lead to the loss of adhesive strength by weakening the product at the interface. This damage results from the diffusion of water molecules throughout the polymer chains causing plasticization, chain rupture, and chemical degradation. Therefore, the knowledge of water and water vapor sorption in composites and in polymer matrices is recognized to be of utmost importance.

Various techniques exist to measure the sorption equilibrium and kinetics data in the polymer system. Of these, gravimetric methods are the most frequently used. They rely on bulk equilibrium, and hence, are more time extensive, but on the other hand, the technique is very accurate and reliable. The Cahn electromicrobalance technique, which is an gravimetric one, can be used to obtain these data, and has been used by many researchers to measure the water vapor sorption isotherms.^{9–11} There are also many studies done previously in polymer composite systems. Ulutan and Balköse¹⁰ have studied the water and water vapor sorption on PVC–silica membranes using a Cahn Gravimetric sorption system. Water vapor solu-

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bility, diffusivity, and permeability in membranes have been measured and found as $4.23\text{--}7.74 \text{ cm}^3 / (\text{cm}^3 \text{ cm} \cdot \text{Hg})$, $2.0\text{--}3.5 \times 10^{-13} \text{ m}^2/\text{s}$, and $1.6\text{--}7.3 \times 10^{-6} [(\text{cm}^2/\text{s})(\text{cm}^2 \text{ cmHg})] \text{ cm}$ of water vapor, respectively. They observed the Case II transport during adsorption, which was attributed to the plasticization effect of water.

Because the composite materials are exposed to the water and humidity in their daily use, attack of water and water vapor at the interface weaken the product. Therefore, it is necessary to improve the interface by using the coupling agents. Ulutan and her coworkers¹² investigated the enhancement of PVC–silica composite interface using γ -aminopropyltrimethoxysilane on silica and its effect on the liquid water and water vapor sorption. Silane application resulted in diminishing liquid water and water vapor sorption by about 24 and 12%, respectively.

Sorption and transport of water in nylon 6,6 films as a function of relative humidity and temperature have been studied by Lim et al.¹³ They studied the moisture sorption kinetics gravimetrically using a Cahn Microbalances at three different temperatures. Water vapor transmission rates were enhanced above the intermediate RH due to the changes related to the glass transition. Measurements showed that water acted as an effective plasticizer in lowering T_g . Recent studies have been also done in the water vapor sorption of polyimides^{14,15} and sulfonated polyimide membranes, which have excellent applications for the microelectronic industry and proton exchange membranes for fuel cells, respectively.^{16,17}

Metayer and coworkers¹⁸ have determined the diffusion coefficient of water in five different pure polymer films (LLPE, PET, PI, PES, unsaturated polyester resin) based on permeation measurements. By testing various polymers, different behaviours with respect to different polymer have been observed, particularly with low density polyethylene, which shows significant hydrophobic properties. Shtanko and et al.¹⁹ studied water permeability of the modified PP membranes by radiation-induced graft polymerization of thermosensitive poly-*N*-isopropylacrylamide. They controlled pore structure by monitoring the temperature change.

Although an extensive amount of work has been done in water sorption of many pure polymers and polymeric composite systems, not much information is found in the literature about water or water vapor sorption in pure polypropylene and its composites. Özmihçi and coworkers²⁰ have been the only ones to study the permeability of PP–zeolite composite film but at low zeolite loadings (up to 6% zeolite). Therefore, in this work, water and water vapor sorption of polypropylene–zeolite composites has been studied as a function of zeolite loading (6–40%). This work presents the first report on the effect of the zeolite as a

filler on the water sorption properties of PP composites.

EXPERIMENTAL

Material

Polypropylene (PP) in powder form with a particle size range of $2.63\text{--}100 \mu\text{m}$, Aldrich; zeolite, Clinoptilolite, Gördes region, Turkey, particle size: $2 \mu\text{m}$; were used in the composite preparation. Polyethyleneglycol (PEG 4000), was supplied by Aldrich, and used for the surface treatment of the zeolite. In the modification of the zeolites, zeolites were treated with 50% alcoholic solution having 10% PEG 4000 and at zeolite/solution ratio 1 : 0.3 on weight/volume basis. The mixture was kneed at 40°C and then dried in a vacuum oven at 110°C under 400 mbar pressure for 3 h.

Preparation of PP composites

Polypropylene and zeolite compounds were compression molded by a dry sintering process at 200°C and 100 bar pressure. The composites were prepared at five different zeolite loadings, 6, 10, 20, 30, and 40 wt %, respectively.

Characterization of composites

The density of composites were measured by Archimede's principle with a density kit of Sartorius YDK01 balance. The weight of the sample and the weight of the water displayed by the sample were measured.

Electronmicrographs of gold-plated fracture surfaces of composites were taken with a JEOL Scanning electronmicroscope.

Liquid water sorption studies

Water swelling experiments were conducted at 25°C using pure PP and PP–zeolite films having different zeolite loadings (6–40 wt %). The weights of the samples were recorded by periodically removing them from the swelling media, blotting with absorbent tissue and weighing. The experiments were conducted until the samples reached equilibrium uptake. The water uptakes were plotted as a function of time. Two different runs were done for each sample. The results were given as the average of two runs.

Water vapor adsorption studies

A Cahn 2000 microelectrobalance instrument shown in Figure 1 was used in the gravimetric sorption experiments. The gravimetric set up consisted of a Cahn 2000 electronic microbalance, a rotary vacuum pump,

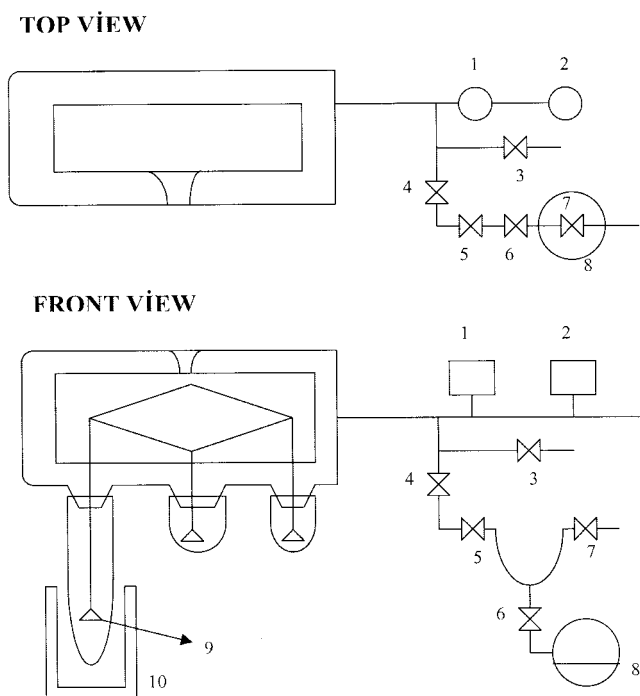


Figure 1 Cahn 2000 electromicrobalance set up for water vapor sorption: 1, 2: pressure transducers, 3, 5, 6, 7: valves; 4: needle valve; 8: water vapor supply; 9: sample; 10: oven.

an oil diffusion pump, pressure transducers, a PID temperature-controlled furnace, and a water bath. Samples (80–100 mg) were used in the experiments. The samples were dried at about 10^{-3} mbar and 100°C . Water vapor then was let into the system as doses by opening the Edwards BRV 10 K needle valve. The pressure and weight data were recorded during the adsorption of water vapor by the sample. Experiments were conducted until the weight of the sample no longer changed at each pressure level. Using the simultaneous pressure and weight increase data, the adsorption isotherms were obtained for the PP-zeolite composite films at 25°C .

Thermal gravimetric analysis

For thermogravimetric studies, a Shimadzu TGA 50 equipment was used. The samples, which were kept in liquid water for swelling experiments, were equilibrated with the air having 75% relative humidity. Experiments were carried out with 10-mg PP-zeolite films having 40% zeolite at a heating rate of 5, 10, and $20^{\circ}\text{C}/\text{min}$, respectively in a N_2 atmosphere. The composites having 6–40% zeolite content were conditioned in the same atmosphere and then analyzed at the same conditions.

RESULTS AND DISCUSSION

Characterization of porous structure of composites

The void volume fractions of composites were found to be in the range of 0.05 to 0.16 for 10 to 40% zeolite

containing samples by using their measured densities and eqs. (1) and (2), and they are reported in Table I.

$$D_{c,t} = \frac{\sum M_i}{\sum (M_i/d_i)} = (M_1 + M_2)/(M_1/d_1 + M_2/d_2) \quad (1)$$

where $D_{c,t}$ = the theoretical density of composite 1 and 2 zeolite and polypropylene, respectively; $d_1 = 1.8 \text{ g/cm}^3$; $d_2 = 0.89 \text{ g/cm}^3$.

$$d_{c,e} = (1 - \epsilon)d_{c,t} \quad (2)$$

where $d_{c,e}$ = experimental density of the composite, and ϵ = void volume fraction of composite.

The micrograph of the fracture surface of the samples in Figure 2(a) also indicated void space around zeolite particles explaining their lower density than predicted by eq. (1). As seen in the Figure 2(a), voids grew around the particles, but void formations are not even in the Figure 2(b). Figure 2(b) showed plastic deformation of the PP-rich phase during fracture of the composites. Thus, the films were not in a homogeneous structure because both brittle [Fig. 2(a)] and plastic [Fig. 2(b)] fracture surfaces were present in the same sample.

Liquid water sorption

The equilibrium uptake of liquid water was investigated with respect to the amount of filler (zeolite). Figure 3 shows the water uptake of the composites containing 0–40 wt % zeolites. Oscillatory behavior in water uptake of the composites was observed. This can be due to the migration of zeolite particles from the surface into the aqueous phase causing weight loss. Because PP is a hydrophobic polymer, it does not sorp any water, but as seen in Figure 3, the composites having 10, 20, 30, and 40% zeolites have sorbed 0.63, 1.00, 1.72, and 3.74% water, respectively. The zeolite itself at the same conditions sorbed 24.5% water. As the filler loading in the composites increased, equilibrium uptake values increased also.

TABLE I
Comparison of Experimental and Theoretical Densities of the PP-Zeolite Composites as Function of Zeolite Loading

Zeolite loading, %	Predicted density	Experimental density	Void volume fraction
0	0.89	0.9	0
10	0.98	0.93	0.05
20	1.1	0.97	0.11
30	1.2	1.03	0.15
40	1.3	1.01	0.16



(a)



(b)

Figure 2 Scanning electron micrograph of the PP-zeolite composites. (a) $\times 3600$ magnified composite film; (b) $\times 360$ magnified composite film.

Theoretical water sorption capacities of the composites were calculated using eq. (3), taking into account the additivity of matrix and filler phases on the sorption capacity^{10,21}

$$X = X_1W_1 + X_2W_2 \quad (3)$$

where X is the sorption capacity of the composite (% water g/g), W is the weight fraction, and 1 and 2 represents the matrix and filler phases, respectively. Table II shows the experimental and theoretical water sorption capacity of the composites. As seen in Table II, if 10, 20, 30, and 40 wt % zeolite in the composites were fully saturated with water, they would sorp 2.45, 4.9, 7.35, and 9.8 wt %, liquid water, respectively. The experimental sorption capacity of zeolites in composites was lower than the theoretical one. This is due to the fact that water does not reach the zeolite phases easily because the PP matrix phase and the void space around the particles were not connected to each other. This prevented water sorption of zeolites with full capacity.

The sorption process can be modeled to determine the concentration in the sample as a function of time and position using one dimensional diffusion equation.²² For the short times, the solutions can be approximated as:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \sqrt{\left(\frac{Dt}{\Pi}\right)} \quad (4)$$

where M_t and M_∞ are defined as the weight pickups at time t and infinity, and l is the thickness of the polymer film sample or length of the transport path, D is the effective diffusion coefficient, and t is the time.

By constructing a sorption curve (M_t/M_∞ vs \sqrt{t}), the effective diffusion coefficient can be calculated from the initial slope R_i , and the final equilibrium state of the curve using the following relation:

$$D = \frac{\Pi}{16} R_i^2 l^2 \quad (5)$$

The average effective water diffusivities of the PP-zeolite composite films for two different runs were

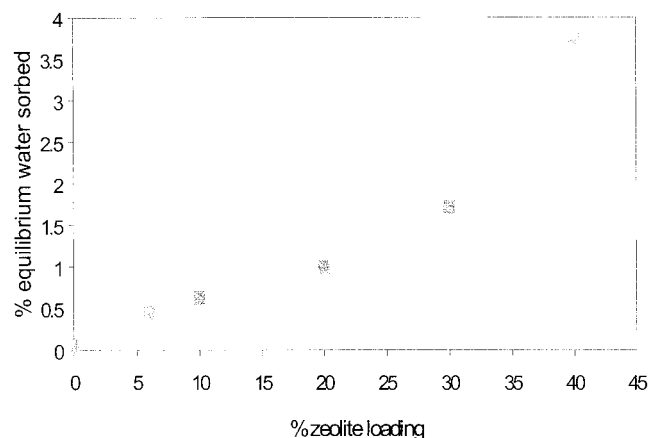


Figure 3 The water uptake of the composites containing 0–40 wt % zeolites.

TABLE II
Water and Water Vapor Uptake and Diffusion Results

Zeolite loading %	Experimental equilibrium water uptake %	Theoretical equilibrium water uptake %	$D_e \times 10^{10}$ cm ² /s Liquid water	Experimental water vapor sorption %	Theoretical water vapor sorption %
6	0.45	1.53	1.76	—	—
10	0.63	2.50	6.40	0.35	1.35
20	1.00	4.95	1.59	0.37	2.70
30	1.72	7.40	3.60	0.63	4.05
40	3.74	9.84	2.95	0.93	5.40

given in Table II. As seen from the results in Table II, diffusivity values of the composites increases with the increase of zeolite loading in the composites except for the 40% zeolite-loaded composites. This can be due to the nonhomogenous distribution of the zeolites in the composites, and void spaces around particles are not connected to each other with the same manner in each sample.

The water sorption uptake was also analyzed by the following equation, which has been derived for an infinite slab with a constant surface concentration:²²

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left[-\frac{D(2n + 1)^2\pi^2 t}{l^2}\right] \quad (6)$$

The results were compared with the experimental data as shown in Figure 4 for the first set of the 40 wt % zeolite-containing film. The symbols in the figure show the experimental data, the lines are the analytical solution of eq. (6). Sequential increases of initial slope of the M_t/M_∞ with respect to the amount of zeolite was observed in Figure 5. 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. Again, the symbols are the experimental data and the lines are the analytical solutions.

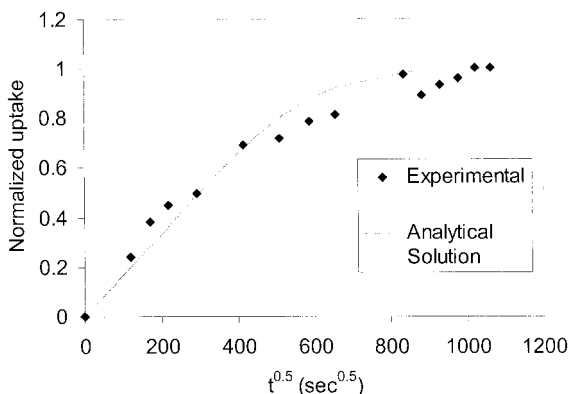


Figure 4 Comparison of the experimental and theoretical water uptake of the composites containing 40 wt % zeolites.

Water vapor sorption

The sorption isotherms of water vapor on PP composites containing 10–40 wt % zeolites were measured. Figure 6 illustrates the sorption isotherms of water vapor in composites as % water in composites vs relative pressure (P/P_0). As seen in Figure 6, experimental isotherm of the highest zeolite-loaded (40 wt %) PP composite film gives the maximum sorption capacity. The experimental data indicates that the higher the amount of zeolite in the composites, the higher the sorption capacity. Although the neat PP does not sorp water, 10–40 wt % zeolite containing PP at 5 mmHg pressure adsorbs 0.35–0.95% water. Zeolite, which was used in this study adsorbs 13.5% water vapor even at 0.5 mmHg pressure.

The lines in the Figure 6 show the prediction of the experimental sorption isotherm data. The sorption isotherms for the composite films having 10 and 20 wt % zeolite were predicted using the Langmuir isotherm equation ($y = 2.032x/(1+2.032x)$ for 10 wt % zeolite containing film); $y = 1.685x/(1+1.685x)$ for 20 wt % zeolite-containing film). The 30 and 40 wt % zeolite-containing films were predicted using the Freundlich ($y = 0.178x^{(1/2.72)}$) and BET isotherm ($x/y(1-x) = -3.11+0.072x$) equations, respectively.²³

The equilibrium uptake of water vapor was investigated with respect to the amount of filler (zeolite).

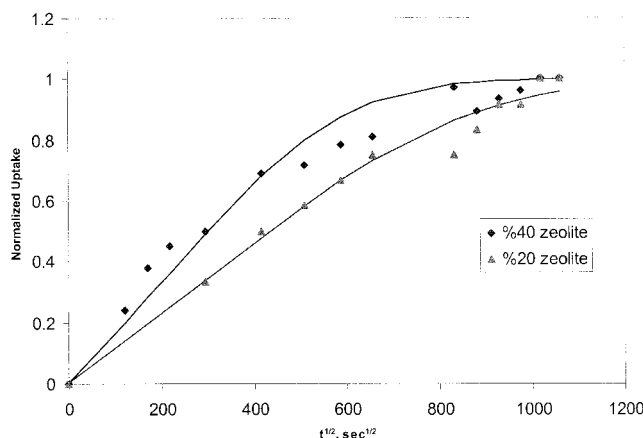


Figure 5 Comparison of the water uptake as a function of amount of zeolite into the PP matrix.

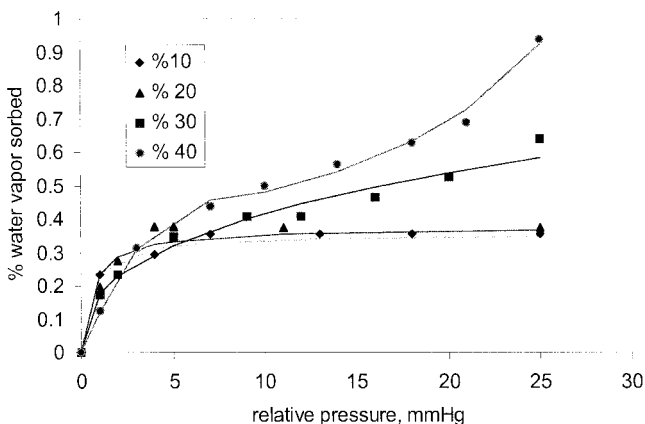


Figure 6 The sorption isotherms of water vapor in composites, as % water in composites versus relative pressure (P/P_0).

Figure 7 shows the comparison of liquid water and water vapor equilibrium uptake of the composites containing 0–40 wt % zeolites. The theoretical water vapor sorption capacity was predicted using eq. (3). As shown in Table II, the theoretical sorption capacity of water vapor is also higher than the experimental one.

The experimental water vapor sorption uptake of 30% zeolite composites as a function of M_t/M_∞ vs $t^{1/2}$ was shown in Figure 8. Fickian behavior has been observed. Experimental effective water vapor diffusivities of 30 wt % zeolite film was found from the sorption data. The water vapor diffusivity value found to be $2.8 \times 10^{-8} \text{ cm}^2/\text{s}$. The water vapor diffusion coefficient in the composites is about one order of magnitude higher (10-fold) than the water diffusion coefficient in composites. The transport of water in composites is slower than that in the liquid water due to the longer diffusion pathway and adsorption on the surface of the composites. Although the liquid water

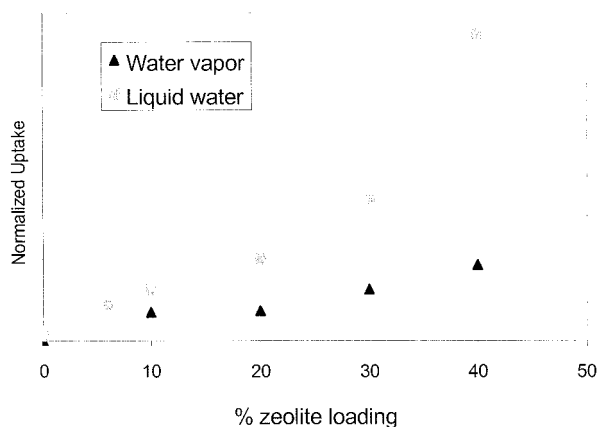


Figure 7 The comparison of liquid water and water vapor equilibrium uptake of the composites containing 0–40 wt % zeolites.

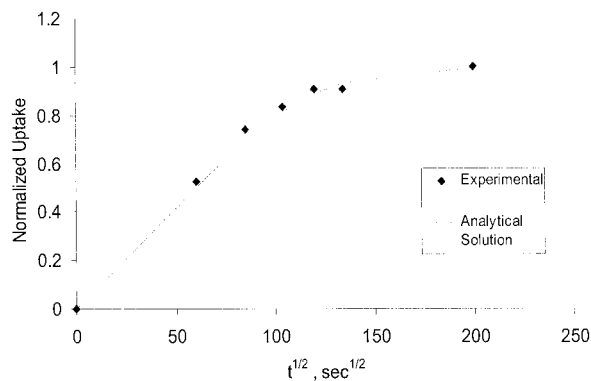


Figure 8 The experimental water vapor sorption uptake of 30% zeolite composites as a function of M_t/M_∞ vs $t^{1/2}$.

may fill all the voids in the composite, water vapor is adsorbed on the surface of the zeolite only.

Thermal gravimetric analysis

Figure 9 shows the TGA curve of the first experiment set of the 40 wt % zeolite composite film that had highest water uptake. This figure shows the weight loss vs temperature data at three different heating rates of 5, 10, 15°C/min, respectively. From the TGA analysis, it was seen that water evaporated until 150°C, PP started to degrade thermally at 260°C and completed degradation process around at 450°C. The amount of zeolite in the composite was found from the weight loss data, which is at 600°C. TGA showed that 3.5% weight loss was obtained from the 40 wt % zeolite-loaded composite film at all heating rates at 150°C. The weight left at 600°C is related to the amount of zeolite in the composite films. As it was expected the remaining weight in the composite was to be 40%. But we observed lower values at all three heating rates. The remaining weight in the composites was found at 20, 28, 30% at 5, 10, and 20°C/min, respectively. This is because of the unhomogenous

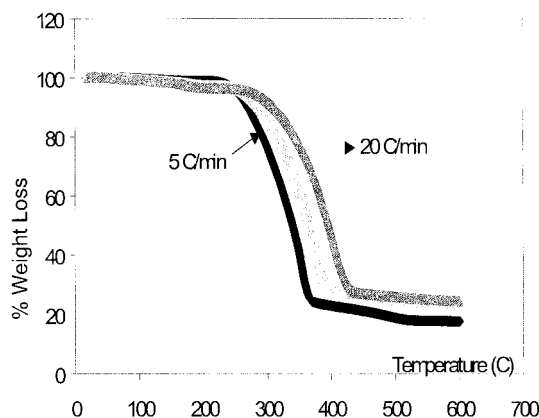


Figure 9 TGA curves of the 40 wt % zeolite composite film at different heating rates.

distribution of zeolite through the PP phase using compression moulding (hot press) method. The difference in particle size of PP (2.65–100 μm) and zeolite (2 μm), agglomeration tendency of zeolite and the difference in density also caused uneven distribution of zeolite and empty spaces between zeolites in composites.

CONCLUSION

In this work, water and water vapor sorption and transport in PP-zeolite composite films have been investigated as a function of filler amount. Because the zeolite is a hydrophilic and PP is a hydrophobic material, the addition of zeolite into PP matrix change the water and water vapor sorption properties of PP and makes PP as a water and water vapor sorbing material. In this case, the PP-zeolite composite can be used where a desiccating packaging material is needed.

It was observed that equilibrium uptake values for both water and water vapor with respect to the amount filler (zeolite) were increased. PP, a hydrophobic polymer, does not sorp any water at its pure state; however, the composites having 6, 10, 20, 30, and 40 wt % zeolites have sorbed 0.45, 0.63, 1.00, 1.72, and 3.74% liquid water, respectively. The zeolite used in this study itself at the same conditions sorbed 24.5% liquid water.

As the filler loading in the composites increased, equilibrium uptake values increased also. For water vapor sorption, the composites having 6–40 wt % zeolites have sorbed in the range of 0.35–0.95 wt % water vapor. It was found that the water vapor diffusion coefficient in the composites was about one order of magnitude higher (10-fold) than the water diffusion coefficient in composites. The transport of water in composites was slower than that in the liquid water due to the longer diffusion pathway and adsorption on the surface of the composites. Although the liquid water may fill all the voids in the composite, water vapor is adsorbed on the surface of the zeolite only. If

more efficient mixing of zeolite and PP could be satisfied, the composites would have better distribution of fillers and void spaces around fillers.

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