Castor Oil-Based Polyurethane–Polyester Nonwoven Fabric Composites: Mechanical Properties, Chemical Resistance, and Water Sorption Behavior at Different Temperatures

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ABSTRACT: Castor oil-based polyurethane (PU)–polyester nonwoven fabric composites were fabricated by impregnating the polyester nonwoven fabric in a composition containing castor oil and diisocyanate. The effects of different diisocyanates such as toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) on the mechanical properties have been studied for neat PU sheets and their composites with polyester nonwoven fabric. Chemical resistance of the PU composites has been assessed by exposing the specimens to different chemical environments. Percentage water absorption of composites and neat PU sheets has been determined both at room temperature and in boiling water. Both TDI- and HMDI-based PU composites showed a marginal improvement in tensile strength retention at 100°C heat ageing. Water sorption studies were carried out at different temperatures, viz, 30, 50, and 70°C, based on immersion weight gain method. From the sorption results, the diffusion (D) and permeation (P) coefficients of water penetrant have been calculated. Attempts were made to estimate the empirical parameters such as n, which suggests the mode of transport (non-Fickian), and K, a constant which depends on the structural characteristics of the polymer in addition to its interaction in boiling water. The temperature dependence of the transport coefficients has been used to estimate the activation energy parameters for diffusion (E_D) and permeation (E_p) processes from Arrhenius plots. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3153–3161, 2007

Key words: polyester nonwoven fabric; polyurethane (PU); composite; mechanical properties; sorption; diffusion

INTRODUCTION

Polyurethane (PU) elastomers have a wide range of industrial applications, and they are well-known for their mechanical performance. The main ingredients of these elastomers are a long-chain polyol and a diisocyanate. A lot of work has been carried out to develop PU for different applications using renewable resource such as castor oil. Castor oil is a naturally occurring material containing triglyceride of ricinoleic acid with three hydroxyl groups. The hydroxyl functionality can be used to form polyester or polyurethane network by a step-growth polymerization.[1]

Fiber-reinforced composites are of tremendous importance both in end-use applications and in the areas of research and development. These composites can be designed to exhibit both soft and stiff behavior. Textile composites are superior to other materials on strength-to-weight ratio and stiffness-to-weight basis, making them especially suitable for the applications where weight saving is an important issue.[2]

Nonwoven textile materials will gain an importance in future because of their properties and numerous advantages, such as higher production rate in comparison with traditional processes. To meet the demands of modern market, almost all types of fibers (natural and man-made), as well as various textile technologies are used in the production of technical textile materials.[3–5] Because of excellent mechanical properties and resistance to chemicals, polyester staple [polyethylene terephthalate (PET)] fiber is widely used in making nonwoven fabrics.

The mechanical properties of nonwoven fabric are insufficient to some nonstructural applications because of their highly soft nature. The strength of the nonwoven fabric can be enhanced significantly with the incorporation of polymeric binders/resins commonly called as matrix in the field of composites.[6–12] Nonwoven fabric as a textile material finds its place as a material or a part of composite. Light-weight composites are of great interest to the automotive industry because of their positive impact on fuel economy and environmental benefits. Although the particular fiber/binder combination and web-type will govern the ultimate physical properties achievable in a nonwoven fabric, the amount of binder taken up by the

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nonwoven substrate and the uniformity with which the binding agent is dispersed throughout the nonwoven fabric will also influence in achieving the optimum properties.

Generally resins and fibers are bonded together to form the fiber-reinforced composites. During the use, fibers in composite are primarily responsible for load bearing, and the resin assists to hold the fibers together. As the long-range mechanical performance of the polymer composites depends up on their stability in varying environmental condition, the sorption and diffusion of low-molecular-weight substances such as water into polymer composites is very important. Water is often sensitive to any change in segmental mobility of polymer chains.[13]

Many researchers have reported the synthesis and characterization of the castor oil-based PU.[14–19] Although there are few reports available on the nonwoven fabric-reinforced polymer composites,[20–24] there is a scarcity in the literature for study on castor oil-based PU–polyester nonwoven fabric composites. In this study, we have fabricated the composites by impregnating the needle-punched polyester nonwoven fabric in a composition containing castor oil and different diisocyanates, viz, toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). The fabricated composites have been studied for mechanical properties, chemical resistance and water sorption behavior.

EXPERIMENTAL

Materials

Needle-punched polyester nonwoven fabric (400 g/m^2) having density of 0.2 g/cc and burst strength of 1.8 MPa was procured from local supplier in India. The fiber used to make the fabric has 3 denier × 64 mm length. Castor oil was procured from the local market. Its average molecular weight (M_n) is 930, and hydroxyl group per molecule is 2.24. Toluene-2,4-diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and dibutyl tin dilaurate (DBTL) were obtained from Sigma (USA), and were used as received. The organic solvent methyl ethyl ketone (MEK) is of AR grade, and was distilled before use.

Fabrication of composites

Castor oil (0.001M) was dissolved in 50 mL of MEK in a 250-mL beaker. To this, diisocyanate (0.0022M) was added followed by two to three drops of DBTL as a catalyst. The reactants were stirred continuously until homogeneous solution was obtained. This mixture was poured into a stainless-steel tray coated with silicone releasing agent. Polyester nonwoven fabric having the dimensions of 150 mm length, 120 mm width, and 2.0 mm thickness was impregnated in the reactant mixture containing castor oil and diisocyanate. The dipped fabric is squeezed in a two-roll squeezer to obtain the pickup ratio of 1:3.5 (polyester nonwoven fabric to the PU composition). The calculation of PU pickup by the fabric was made using simple gravimetric method, where the MEK was considered as evaporating medium. The maintained solid content of the impregnating composition was 50%. A portion of the PU reactant mixture was poured into the glass molds coated with silicone-releasing agent to cast the neat PU sheets. The reaction mixture was allowed to polymerize for 24 h at room temperature and another 24 h at 80°C.

TECHNIQUES

Mechanical properties

The tensile strength of composites and polyester nonwoven fabric was measured at 23°C and 50% RH using 4302 model Hounsfield universal testing machine (UK). The width of the specimens maintained was 50 mm as described elsewhere.[8] Polyester-PU composites were tested for stiffness and stitch tear strength according to BSI 3748 and IS:5867–1970 methods, respectively. Surface hardness was measured using a Shore A durometer. Percentage compressiblity and recovery of composites have been determined as per ASTM F 36 method. The void content (%) of the composite was determined as per ASTM D 2734-91 using the following equation:

$$V_p = 100 - M_d[r/d_r + g/d_g] \qquad (1)$$

where M_d is the measured density of the composite (g/cm^3), which is measured using mass by volume elation, r is resin content (wt %), d_r is resin density, d_g is fiber density, and g is fiber content (wt %).

Chemical resistance

The chemical resistance of castor oil-based polyester–PU nonwoven fabric composites was studied as per ASTM D 543-87 method. Specimens were immersed in 15% hydrochloric acid, 25% acetic acid, 5% sodium hydroxide, potassium permanganate, methyl acetate, and distilled water. In each case, 10 dried specimens were exposed into different chemical environments for 7 days at room temperature. After 7 days, the samples were removed, washed with distilled water, and pressed between the soft filter paper to remove the water present on the surface. The samples were then subjected to tensile strength measurement. The percentage loss in the tensile strength was calculated using the following equation:

$$\mathrm{PLTS} = \frac{(T_{us} - T_{es})}{T_{us}} \times 100 \qquad (2)$$

where T_{us} is the tensile strength of unexposed specimen and T_{es} is the tensile strength after exposed to different chemical environment.

Water soaking and thickness swelling tests

Specimens of size 50×50 mm^2 were cut from the neat PU sheet and PU–polyester nonwoven fabric composites. Percentage water absorption and thickness swelling were measured in both boiling water (2 h immersion) and at room temperature (24 h immersion).

Water sorption study

Neat PU sheets and PU–polyester nonwoven fabric composites were cut circularly (diameter = 1.5 cm) using a sharp-edged steel die. Sorption experiments at 30, 50, and 70°C were performed by immersing the composite specimens in distilled water in the metal-capped bottles maintained at the desired constant temperature (± 0.5°C) in a thermostatically controlled oven. At specified intervals of time, specimens were removed from the containers, and surfaces were dried in between soft filter paper and weighed immediately using analytical balance having ± 0.1 mg accuracy. The weighing of the specimens was continued until the equilibrium values were reached.

The percentage weight gain (Q_t) of the immersed composite specimen was calculated as follows:

$$Q_t = \frac{(M_t - M_i)}{M_i} \times 100 \qquad (3)$$

where M_i is the initial weight of the composite specimen and M_t is the weight of the specimen at time t.

RESULTS AND DISCUSSION

The measured mechanical properties such as density, tensile strength, percentage elongation at break, stiffness, tear strength, surface hardness, void content, percentage compressibility, and recovery of neat PU and its composites are given in Table I. The theoretical density of the composites was calculated using volume additive principle, which states that [$d = W_1 d_1 + W_2 d_2$], where d is the density of the composite, W_1 and W_2 are the weight fractions of the constituents in the composite, and d_1 and d_2 are the corresponding densities of the composites, respectively. The experimental density of HMDI-based composite is higher compared with that of TDI-based composite. This may be due to slightly lower

TABLE I
Mechanical Properties of Castor Oil-Based PU and PU–Polyester Nonwoven Fabric Composites

Details	Density (g/cc) Theo.	Density (g/cc) Exp.	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Taber stiffness in arbitrary units	Stitch tear strength (N)	Hardness (Shore A)	Void content (%)	Compressiblity (%)	Recovery (%)
TDI-composite	0.924	0.60	5.46	40	12.6	645	40.30	85	18	9.95	72.7
TDI-PU	—	1.015	1.25	125	1.42	Flexible	6.50	80	—	—	—
HMDI-composite	0.95	0.75	8.35	105	22	990	49.45	88	16	12.9	67.4
HMDI-PU	—	1.03	1.16	138	1.25	Flexible	7.40	75	—	—	—

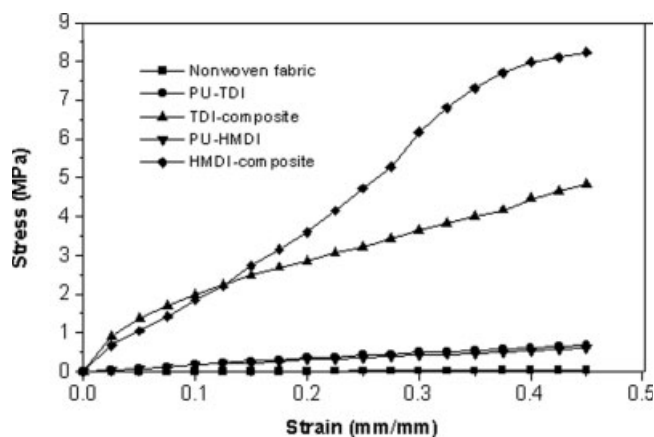**Figure 1** Stress–strain curves of polyester nonwoven fabric, TDI- and HMDI-based neat PUs and their corresponding composites.

TABLE II
Chemical Resistance of Castor Oil-Based PUs and PU–Polyester Nonwoven Fabric Composites

Chemical reagent	Percentage loss in tensile strength of the composites after exposed into chemical environment	
	TDI-based	HMDI-based
15% HCl	0	0
25% CH_3COOH	2.5	1.5
5% NaOH	9.0	8.9
10% $KMnO_4$	10.9	11.0
Methyl acetate	25	16
Distilled water	0	0

void content in the HMDI-based composite (Table I). The stress–strain curves of polyester nonwoven fabric, neat PU sheets and PU–polyester nonwoven fabric composites (TDI and HMDI base) are shown in Figure 1. Polyester nonwoven fabric exhibited high strain (147%) with low stress (0.59 MPa), indicating poor mechanical strength. Generally, the nonwoven fabric has poor mechanical properties, and polymeric binding materials are required to improve the strength properties.[7,8,25,26] In the present study, a significant increase in the tensile strength and tensile modulus of the polyester nonwoven fabric was noticed after incorporating either TDI- or HMDI-based PU. The tensile strength and tensile modulus of TDI-based neat PU is slightly higher compared with that of HMDI-based neat PU, but a reverse trend is noticed in case of their corresponding composites with polyester nonwoven fabric. The increase in tensile modulus and tensile strength in case of TDI-based neat PU sheet compared with that of HMDI-based neat PU sheet could be due to aromatic nature of TDI. The reduction in mechanical properties in case of TDI-based PU–polyester nonwoven fabric composite could be due to the brittle and hard nature of TDI.[27] The percentage elongation of neat PU with HMDI is relatively higher compared with that with TDI. HMDI-based PU–polyester nonwoven composite showed significantly higher percentage of elongation compared with that of TDI-based PU–polyester nonwoven fabric composite.

The Taber stiffness, which plays an important role in the application where the composites must stand upright during the use, is higher in case of HMDI-based composite compared with that of TDI-based composite. Stitch tear strength of the composites indicates that the force required to pull a loop of wire through the composite material when the two ends of the loop are first inserted through adjacent

holes drilled through the sheet. This test evaluates the ability of the composites to hold the stitches when it is being used with the other materials to cover the surface to impart good esthetics. Higher stitch tear strength in HMDI-based PU sheet and its composite was noticed when compared with that in TDI-based PU and its composite. Compressibility and recovery of composites are the characteristic property in selecting the suitable composite material for cushioning/seating applications. An increase in the percentage compressibility and decrease in the percentage recovery was noticed for HMDI-based composite, and a reverse trend was noticed for TDI-based composite. The void content of HMDI-based composite is lower compared with that of TDI-based composite. The surface hardness value of the TDI-based neat PU sheet is higher compared with that of HMDI-based neat PU sheet. HMDI-based PU–polyester nonwoven fabric composite exhibited higher surface hardness when compared with TDI base. The increased mechanical properties in case of HMDI-based composite can be attributed to the strong interfacial bonding between PU and fiber. As a result of interfacial bonding, the HMDI-based PU forms a continuous network in the composite, and hence the increased mechanical properties.

The influence of chemical reagent on TDI- and HMDI-based PU–polyester nonwoven fabric composites were evaluated by measuring the tensile strength after exposing the specimens to different

TABLE III
Percentage Loss or Improvement in Tensile Strength of Castor Oil-Based PU–Polyester Nonwoven Composites after Heat Ageing at 100 and 200°C

Parameters	Percentage loss or improvement in tensile strength			
	TDI-based composite		HMDI-based composite	
	100°C	200°C	100°C	200°C
Tensile strength (MPa)	+37.56	−27.32	+13.34	−13.33
Elongation at break (%)	−17.64	−48.23	−7.62	−36.24

TABLE VI
Percentage Change in Thickness and Water Absorption of TDI- and HMDI-Based PUs and Their Corresponding Composites with Polyester Nonwoven Fabric at Room Temperature for 24 h

Composition	Water absorption (%)	Thickness swelling (%)
TDI-composite	5.49	7.48
TDI-PU	0.195	7.18
HMDI-composite	5.2	5.66
HMDI-PU	0.34	8.83

chemical environments, and the results were compared with the tensile strength of unexposed specimen. The calculated percentage loss in tensile strength of the composite after exposing to different chemical reagents is given in Table II. There was no significant change in the physical appearance of composites after exposure to different chemical reagents and solvents under investigation, but considerable swelling in methyl acetate was noticed. From the table, it can be noticed that the composites are less resistant to alkali, but more resistant to acids. HMDI-based polyester nonwoven fabric composite in acetic acid and methyl acetate showed better chemical resistance when compared with TDI-based polyester nonwoven fabric composite.

The percentage loss or improvement in tensile strength and percentage elongation at break of the TDI- and HMDI-based composites after heat ageing at 100 and 200°C are given in Table III. From the table, it can be observed that the tensile strength of the composites have been increased with the reduction in percentage elongation after heat ageing at 100°C. At 200°C ageing, both TDI- and HMDI-based composites have shown a significant decrease in the tensile strength and percentage elongation. The improved tensile strength at 100°C may be due to the extended crosslinking of PU. The thermal instability of PU at 200°C for prolonged ageing (48 h) could be the reason for tensile strength loss. A significant discoloration was noticed for TDI-based composites aged at 200°C. This may be due to slow oxidation process of aromatic diisocyanate such as TDI.[28] The oxidation causes the decomposition of urethane bond, leading to the for-

TABLE V
Percentage Change in Thickness and Water Absorption of TDI- and HMDI-Based PUs and Their Corresponding Composites with Polyester Nonwoven Fabric in Boiling Water for 2 h

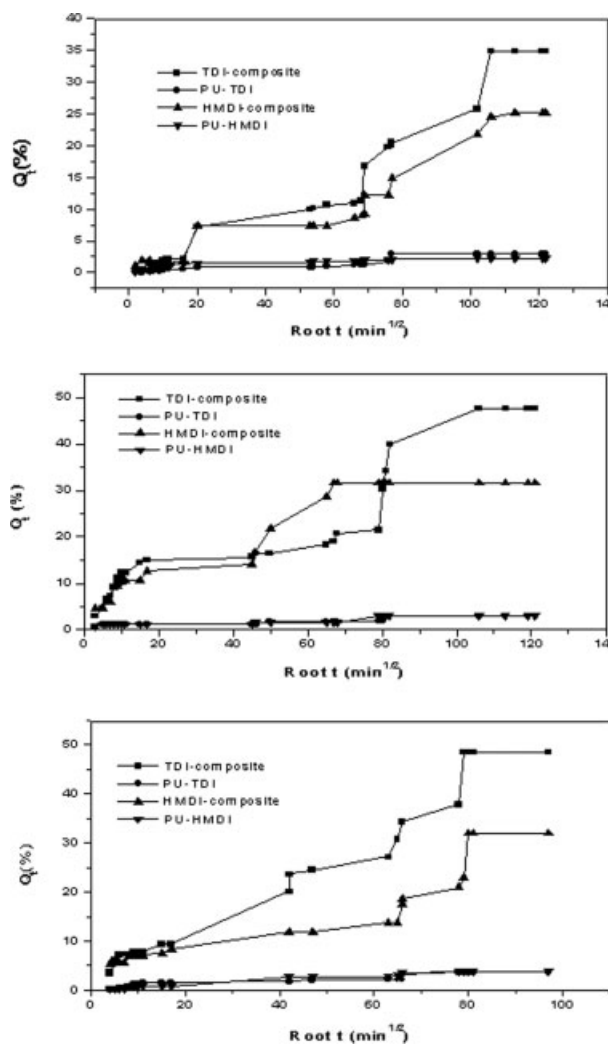| Composition	Water absorption (%)	Thickness swelling (%)
TDI-composite	5.5	0.39
TDI-PU	0.931	0.37
HMDI-composite	5.20	0.15
HMDI-PU	1.46	0.40

Figure 2 Percent mass uptake (Q_t) of TDI- and HMDI-based neat PUs and their corresponding composites with polyester nonwoven fabric at different temperatures, viz, 30, 50, and 70°C.

mation of primary amine/olefin or the formation of secondary amine and carbon dioxide.[29,30]

Water absorption and thickness swelling of TDI- and HMDI-based neat PU sheets and its composites were determined by immersing the individual samples for 24 h in water at room temperature and for 2 h in boiling water. The obtained results for water absorption and thickness swelling are given in Table IV and V respectively. It is evident from these tables that the percentage water absorption and thickness swelling of the HMDI-based PU is higher compared with that of TDI-based PU. But, the HMDI-based composites exhibit lower percentage water absorption and thickness swelling when compared with the TDI-based composite. These results support the assumption of good interfacial bond in case of HMDI-based PU with polyester nonwoven fabric. A similar behavior was noticed in boiling water. Generally, the water
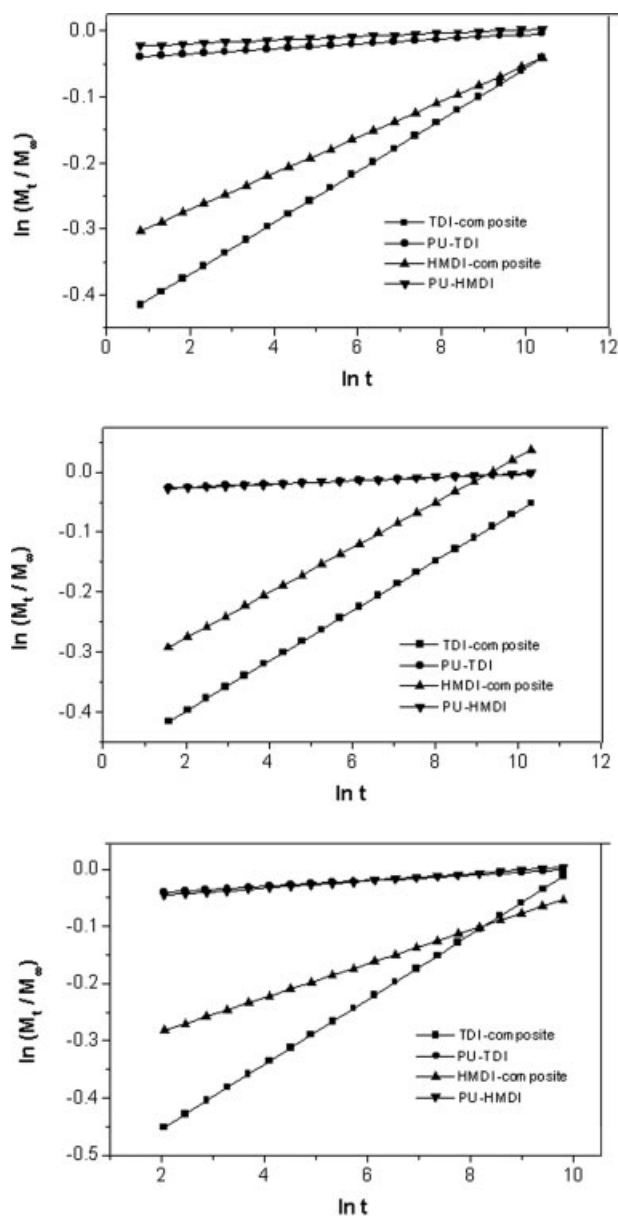
Figure 3 The plot of ln M_t/M_∞ versus ln t for TDI- and HMDI-based neat PUs and their corresponding composites with polyester nonwoven fabric.

absorption and thickness swelling increases in boiling water compared with that at room temperature.[31] The observed water absorption in boiling water is almost same as that in room temperature, and the observed thickness swelling is significantly low in boiling water compared with that in room temparature. This can be attributed to the extended curing of PU in boiling water (nearly 100°C), and this indicates the improved dimensional stability of the composites at 100°C.

The percentage mass uptake (Q_t) of water (of TDI- and HMDI-based neat PU sheets and their corresponding composites with polyester nonwoven fabric) versus square root of time is shown in Figure 2.

In all the samples, the initial portion of the water absorption curve is linear, after which the mechanism changes. Water diffusion in polymers was found to lead typical phenomena of composite swelling and physical relaxation. From the figure, it can be observed that the neat PU sheets exhibited lower water uptake when compared with their PU–polyester nonwoven fabric composites. The low void content inhibits the water uptake in neat PUs, whereas the presence of void content in the composites increases the water uptake. This could be the reason for higher water uptake in composites compared with that in neat PU sheets.

Figure 2 revealed the stage wise equilibrium of water uptake. According to Flory's two-stage theory, the swelled polymer chain induces increased elasticity of chain structure, and these will inhibit the further absorption of water. However, the swelled polymer chain relaxes with time and subsequently increases the water absorption, which results stagewise equilibrium of water uptake. The water uptake of neat PUs and their PU–polyester nonwoven composites have been increased with increasing the temperature.

To investigate the type of diffusion mechanism, an attempt was made to estimate the values of n and K by the following relation:

$$\ln(M_t/M_\infty) = \ln K + n \ln t \qquad (4)$$

where K and n are empirical parameters, and M_t and M_∞ are mass uptake values at time t and at equilibrium. The magnitude of n decides the transport mode, for instance, a value of $n = 0.5$ suggests the Fickian mode, and $n = 1$, the non-Fickian diffusion mode. The value of n ranging from 0.5 to 1 suggests the presence of anomalous transport mechanism.

To determine K and n, plots of $\ln(M_t/M_\infty)$ versus ln t were plotted and are shown in Figure 3. The calculated values of the empirical parameters n and K

TABLE VI
Values of n and K for Water for PUs and PU–Polyester Nonwoven Fabric Composites

Details of specimen	Temperature (°C)	n (10^3)	K (10^2 g/(g min))
TDI-composite	30	38.91	65.6
	50	41.65	70.3
	70	56.99	95.6
TDI-PU	30	3.62	54.3
	50	2.69	59.3
	70	5.13	61.5
HMDI-composite	30	27.29	62.9
	50	37.62	64.8
	70	29.56	89.6
HMDI-PU	30	2.69	55.9
	50	3.02	69.4
	70	6.34	71.4

TABLE VII
Diffusion (D), Sorption (S), and Permeation (P) Coefficients for PUs and
PU–Polyester Nonwoven Fabric Composites with Water

Composition	Temperature (°C)	Diffusion coefficient (D) (10^3 m^2/s)	Sorption coefficient (S) (10^2 g/g)	Permeability coefficient (P) (10^2 cm^2/s)
TDI-composite	30	9.43	135	1.270
	50	11.10	148	1.643
	70	20.51	148	3.035
TDI-PU	30	0.0141	103	0.00168
	50	0.0188	103	0.00193
	70	0.0675	104	0.00700
HMDI-composite	30	5.14	125	0.6425
	50	7.10	132	0.9880
	70	7.48	132	0.9372
HMDI-PU	30	0.0163	102	0.0014
	50	0.0263	103	0.0027
	70	0.1280	104	0.0133

for the composite–water systems at different temperatures are given in Table VI. The n value did not show any systematic variation with temperature. But, the increase in K value with increase in temperature revealed that the interaction of water molecules with the composite is high as the temperature increases. It is also noted that the K value is higher in case of PU–polyester nonwoven fabric composites compared with that in case of PU sheet. This may be due to higher sorption behavior of composites. The low value of n clearly indicates that the mechanism of water transport deviates from Fickian mode.

The sorption coefficients of the PU sheets and composites were computed using

$$S = M_\infty / M_i \tag{5}$$

where M_∞ and M_i represent the maximum water uptake and initial composite weight, respectively.

The ability of the water molecules to move along the polymer segments was characterized by diffusion coefficient D, which is predominantly matrix-dominated parameter and can be calculated from the following equation:

$$D = \pi \, (h\theta/4M_\infty)^2 \tag{6}$$

where θ is the slope of the linear portion of the sorption curve, h is the initial thickness of the sample, and M_∞ is the mass uptake at infinite time.

The permeability of the specimens to water molecules was related to the diffusion coefficient and equilibrium sorption of the penetrant, and it can be expressed by the equation

$$P = DS \tag{7}$$

Therefore, permeability is the net effect of sorption and diffusion. Calculated diffusion (D), sorption (S), and permeability (P) coefficient values of the water

with neat PUs and PU–polyester nonwoven composites at different temperatures are given in Table VII. From the table, it is noticed that the diffusion coefficient of the water into neat PU sheets is much lower compared with that of PU–polyester nonwoven fabric composites. It is also observed that the diffusion coefficient of the water into the TDI-based neat PU ($0.0141–0.0675 \times 10^{-3}$ cm^2/s) is lower compared with that of HMDI-based neat PU ($0.0163–0.1280 \times 10^{-3}$ cm^2/s). The diffusion coefficient values for TDI- and HMDI-based PU–polyester nonwoven fabric composites lie in the range $9.43–20.51 \times 10^{-3}$ and $5.14–7.48 \times 10^{-3}$ cm^2/s respectively. As the diffusion process is a thermally activated process, an increase in temperature was found to increase the diffusion coefficient of the water. The D value of neat PUs and PU–polyester nonwoven fabric composites has been increased with increasing the sorption test temperature. HMDI-based PU–polyester nonwoven fabric composites have showed lower D value compared with TDI-based PU–polyester nonwoven fabric composites. The increase in diffusion of water with increase in the temperature can be attributed to the development of microcracks/voids on the surface and the bulk of the materials.[32] The formation of microcavities were prominent at 50 and 70°C sorption test temparature compared to 30°C. This

TABLE VIII
Equilibrium Moisture Content of TDI- and HMDI-Based
Neat PUs and Their Corresponding Composites
with Polyester Nonwoven Fabric

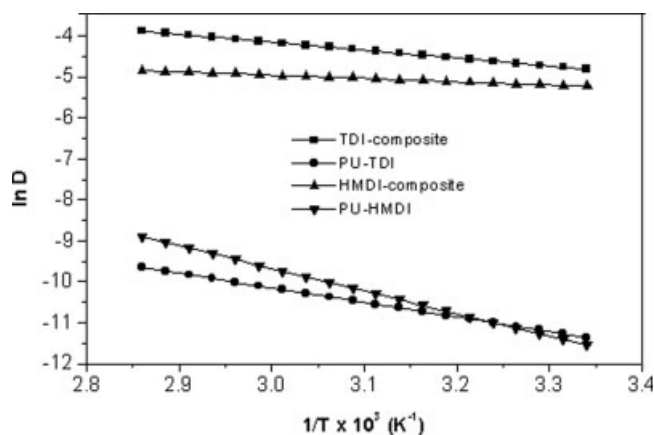| Composition	Equilibrium moisture content (M_m) (%)		
	At 30°C	At 50°C	At 70°C
TDI-composite	34.85	47.51	48.41
TDI-PU	2.96	3.11	3.76
HMDI-composite	25.19	31.68	31.94
HMDI-PU	2.13	3.11	3.88

Figure 4 The plot of ln D versus $1/T$ for TDI- and HMDI-based neat PU and their corresponding composites with polyester nonwoven fabric.

can also be supported by Henry's law mode, which states that the sorption proceeds through the creation of new sites or pores in the polymer. The sorption coefficient values of TDI- and HMDI-based neat PU at different temperatures lie correspondingly in the range 103–104 $\times$ 10^{-2} and 102–104 $\times$ 10^{-2} g/g. The sorption coefficients of HMDI-based PU–polyester nonwoven fabric composites are lower (125–132 $\times$ 10^{-2} g/g) compared with that of TDI composite (135–148 $\times$ 10^{-2} g/g). The permeability coefficient, which is the net effect of sorption and diffusion coefficient, followed a similar trend as D and S values. The P value of water in TDI-based neat PU (0.00168–0.007 $\times$ 10^{-2} cm^2/s) is lower compared to HMDI-based PU (0.00144–0.0133 $\times$ 10^{-2} cm^2/s). An opposite trend to this was noticed in PU–polyester nonwoven composites. The P value for TDI-based PU–polyester nonwoven composite (1.27–3.035 $\times$ 10^{-2} cm^2/s) is higher compared with HMDI-based PU–polyester nonwoven fabric composite (0.6245–0.9372 $\times$ 10^{-2}
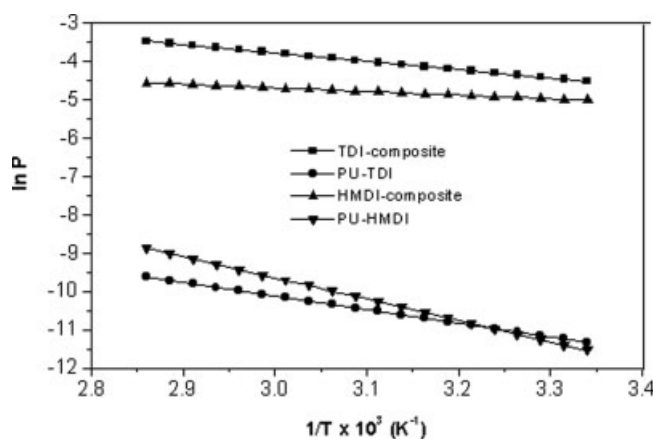
TABLE IX
Values of Activation Energy for Diffusion (E_D) and Permeation (E_p) for PUs and PU–Polyester Nonwoven Fabric Composites

Composition	E_D (kJ/mol)	E_p (kJ/mol)
TDI-composite	16.2	18.2
TDI-PU	29.6	29.8
HMDI-composite	6.7	7.9
HMDI-PU	45.9	46.4

cm^2/s). Table VIII shows the variation in equilibrium water content (M_m) of the TDI- and HMDI-based neat PUs and their corresponding composites. It is observed that the water uptake of the neat PU and PU–polyester nonwoven fabric composites increased with increase in the temperature. The water uptake at different temperatures for TDI- (2.96–3.76%) and HMDI (2.13–3.88%)-based neat PUs almost lies in the same range. But, the water uptake by HMDI-based PU–polyester nonwoven composite (25.19–31.94%) is lower compared to TDI-based composite (34.85–48.41%).

The activation energy for the process of diffusion (E_D) and for the process of permeation (E_p) is estimated from the Arrhenius relation:

$$X = X_0 \exp(-E_a/RT) \qquad (8)$$

where X_0 is pre-exponential factor, R is the molar gas constant, T is the absolute temperature, and X is the coefficient (D for diffusion process and P for permeation process). The Arrhenius plots of ln D and ln P versus $1/T$ are shown in Figures 4 and 5, respectively. The values of E_D and E_p for TDI- and HMDI-based PUs lie in the range 29.6–45.9 and 29.8–46.4 kJ/mol respectively, (Table IX). The values of E_D and E_p for TDI- and HMDI-based composites lie in the range 6.7–16.2 and 7.9–18.2 kJ/mol respectively. The PUs have shown higher activation energy than their corresponding composites. This may be due to the presence of microvoid content in the composite compared with that of PU sheets.

CONCLUSIONS

From this study, a significant improvement in the mechanical properties of nonwoven fabric composite was noticed for both TDI- and HMDI-based PUs. Despite the low tensile strength and tensile modulus of neat HMDI-based PU compared with that of TDI, the corresponding composite has showed improved tensile strength. This indicates that the good interaction between polyester fiber and HMDI. HMDI-based PU composites showed better chemical resistance test compared with TDI-based PU composite. Heat ageing experiments revealed that the ageing at 100°C is required for better performance of composites. The obtained water absorption values at room

Figure 5 The plot of ln P versus $1/T$ for TDI- and HMDI-based neat PU and their corresponding composites with polyester nonwoven fabric.

temperature and boiling water are same. The low thickness swelling in boiling water compared with that in room temparature indicates that the dimensional stability of the composites could be improved with extended drying of composites at 100°C. From the water sorption results, it is observed that PU composites have higher sorption values and lower activation energy when compared with neat PUs. This may be due to the heterogeneity and the presence of voids in the composites.

References

1. Zhang, L.; Ding, H. J Appl Polym Sci 1997, 64, 1393.
2. Parikh, D. V.; Kamath, M. G.; Bhat, G. S.; Muller, D. Int Nonwovens J 2000, Spring, 34.
3. Lawrence, C. A.; El-Jack, M.; Tebay, R. In the Proceedings of the First AUTEX Conference, Povoa de Varzim, Portugal, Autex: Portugal, 2001; Vol. 1, pp 426.
4. Rupp, J. Nonwovens Ind Text 2000, 2, 40.
5. Mark, L.; Marienfeld, M. L. TAPPI J 1995, 78, 143.
6. Attwood, B. W.; White, D. G. TAPPI J 1979, 62, 39.
7. Villalobos, J. A. TAPPI J 1981, 64, 129.
8. Rigdahl, M.; Westerlind, B.; Hollmark, H.; de Ruvo, A. J Appl Polym Sci 1983, 28, 1599.
9. Marriott, R. C. TAPPI J 1995, 78, 164.
10. Dever, M. TAPPI J 1993, 76, 181.
11. Lukic, S.; Jovanic, P. Mater Lett 2004, 58, 439.
12. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1993, 50, 863.
13. Mehta, B. S.; Dibenedetto, A. T.; Kardos, J. L. J Appl Polym Sci 1977, 21, 3111.
14. Kendagannaswamy, B. K.; Siddaramaiah. J Appl Polym Sci 2002, 84, 359.
15. Siddaramaiah; Mallu, P.; Varadarajulu, A. Polym Degrad Stab 1999, 63, 305.
16. Jeevananda, T.; Siddaramaiah. Eur Polym J 2003, 39, 569.
17. Wu, Q.; Zhang, L. J Appl Polym Sci 2001, 79, 2006.
18. Alfani, R.; Iannace, S.; Nicolais, L. J Appl Polym Sci 1998, 68, 739.
19. Mallu, P.; Siddaramaiah; Somashekar, R. Bull Mater Sci 2000, 23, 413.
20. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1995, 57, 751.
21. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1992, 45, 1693.
22. Idriss Ali, K. M.; Khan, A. M.; Balo, K. S.; Ahmad, M. U. J Appl Polym Sci 1998, 67, 79.
23. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1994, 51, 1629.
24. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1992, 46, 375.
25. Gill, R. A.; Drennen, T. J.; Swaney, E. J.; Allynar, L. TAPPI J 1972, 55, 762.
26. Athey, R. D. TAPPI J 1977, 60, 118.
27. Gum, W. F.; Riese, W.; Ulrich, H. Reaction Polymers; Hanser: New York, 1992; pp 50.
28. Duffy, R. D.; Whitman, R. D. J Cell Plast 1978, 14, 161.
29. Monteavaro, L. L.; Riegel, I. C.; Petzhold, C. L. Polímeros 2005, 15, 151.
30. Javni, I.; Petrovic, Z. S.; Guo, A.; Fuller, R. J Appl Polym Sci 2000, 77, 1723.
31. Satheesh Kumar, M. N.; Siddaramaiah. J Reinforc Plast Compos 2005, 24, 1413.
32. Zhou, J.; Lucas, J. P. Compos Sci Tech 1995, 53, 57.