Thermogravimetric Analysis and Morphological Behavior of Castor Oil Based Polyurethane–Polyester Nonwoven Fabric Composites

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ABSTRACT: Castor oil (CO) based polyurethane (PU)–polyester nonwoven fabric composites were fabricated by impregnating the polyester nonwoven fabric in a reactive composition containing CO and diisocyanate. Composites were fabricated with two different isocyanates such as toluene-2, 4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). Thermogravimetric analysis (TGA) studies of the composites were performed to establish the thermal stability and their mode of thermal degradation. It was found that degradation of neat PU takes place in two steps and that of polyester nonwoven fabric reinforced PU composites takes place in three steps. From the TGA thermograms, a little improvement in thermal stability incase of polyester nonwoven fabric reinforced PU composites were noticed compared to unreinforced PUs. Degradation kinetic parameters were obtained for the composites using Broido, Coats and Redfern, and Horowitz and Metzger methods. Tensile fractured composite specimens were used to analyze the morphology of the composites by scanning electron microscopic technique. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3521–3528, 2007

Key words: polyester nonwoven fabric; castor oil PU; composites; TGA; kinetic parameter; thermal stability

INTRODUCTION

Thermogravimetric analysis (TGA) has proved to be a suitable method to investigate the thermal stability of polymeric systems.[1] Thermal degradation and mode of decomposition under the influence of heat is highly recommended in the processing optimization. The threshold decomposition temperature gives an indication of the highest processing temperature that can be used, whereas the study of the kinetics of the different decomposition processes helps in the identification of the degradation mechanisms.

Nonwoven fabric is one of the popularly used materials in the fabrication of composites for many applications since they possess a good blend of strength, light weight, and flexibility compared to conventional materials.[2] As the nonwoven fabric alone does not have the load carrying ability,[3] the use of polymeric binders is essential for more number of various applications. A thorough literature survey revealed that the fabrication of polyester nonwoven fabric composites using reactive composition of castor oil (CO) and diisocyanate has not yet been carried out. Hence the authors have selected the CO based PU as the binder for the present research work. Several researchers have reported on the binders for the fabrication of nonwoven composites.[4–7]

The versatility of the CO, which has two reactive sites, the double bond of the unsaturated fatty acid and the carboxyl group, linking the acid to the glycerol made several researchers to develop polyurethane (PU) materials using these renewable resources like CO. PU elastomers have a wide range of industrial applications, and they are well known for their mechanical properties. Considerable efforts have been put to develop PU materials using renewable resources like CO.[8–13] Many researchers have characterized the PU composites using TGA techniques to know the thermal stability and kinetics of thermal degradation.[14–15] Yang et al.[16] showed that the degradation of urethanes based on 4,4′-diphenylmethane diisocyanate and 1,4-butane diol gives isocyanates and alcohol at elevated temperatures. Schollenberger et al.[17] have also reported that the urethane linkages may be broken because of the high shear and stress at the elevated processing temperature. Kinetic parameters of the degradation reaction of short fiber polyester fiber reinforced thermoplastic PU were studied by Ronald et al.[18] Agi et al.[19] estimated the kinetic parameters for thermal degradation of PU elastomers based on poly (ether polyol) soft segment and aromatic-type

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diisocyanates. The kinetic parameters studied by Mothe et al. for PU/bagasse composites revealed that the incorporation of 5% by weight of bagasse increased the activation energy of the PU composites.[20] Thermal decomposition and combustion reactions of polyether-PU and polyester-PU in air and nitrogen atmospheres investigated by Shufen et al.[21] Rein et al. described the application of TGA to determine the kinetics of PU in smoldering combustion.[22] Kutty and coworkers[23] studied the thermal degradation of short kevlar fiber-thermoplastic polyurethane (TPU) composites using TGA. The incorporation of kevlar fiber enhanced the thermal stability of the TPU-kevlar composites.

In the earlier communications authors have studied the physico-mechanical properties, water sorption behavior, heat ageing, and transport behavior of *n*-alkanes into fabricated PU-polyester nonwoven fabric composites.[24,25] In the present research article, authors have fabricated the composites by impregnating the needle punched nonwoven fabric in a reactive composition containing CO and isocyanates to facilitate the formation of PU in the polyester nonwoven fibrous structures. The fabricated composites were characterized by TGA and SEM methods to understand the thermal and morphological behavior.

EXPERIMENTAL

Materials

Needle punched polyester nonwoven fabric (400 g/m^2) having density of 0.2 g/cm^3 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. CO was procured from the local market. Its average molecular weight ($\overline{M}_n$) 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 distilled before use.

Fabrication of composites

CO (0.001 mol) was dissolved in 50 mL of MEK in a 250-mL beaker. To this, diisocyanate (0.0022 mol) 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 dimension of 150 mm length, 120 mm width, and 2.0 mm thickness was impregnated in the reactant mixture containing CO 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 an 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

The TGA thermograms were obtained using Waters TA thermal analyzer 2950 TGA at a heating rate of 10°C/min in air media. The TGA profiles were taken over a temperature range of 30–600°C. The weight of the sample used was about 6–8 mg in all the cases. The integral procedural decomposition temperature (IPDT) is defined as a means of summing up the whole shape of the normalized data curve. IPDT is an index of thermal stability, was determined from the thermogram area using the method reported in the literature.[26] The oxidation index (OI) was calculated based on the weight of carbonaceous char (CR) as related by the empirical equation:

$$OI \times 100 = 17.5 \times 0.4CR \quad (1)$$

The thermal degradation kinetic parameters were determined for polyester nonwoven fabric, TDI, and HMDI based PUs and their corresponding composites using Broido (BR),[27] Coats and Redfern,[28] and Horowitz and Metzger[29] methods which provide overall kinetic data. For the sake of calculations and to know the nature of the decomposition, the complete thermogram was divided into distinct sections according to their degradation processes. The activation energy for the thermal degradation process was evaluated using Broido equation:

$$\ln[-\ln(1-\alpha)] = -\frac{E_a}{RT} + \text{Const} \quad (2)$$

where α is the $(w_0 - w_t)/(w_0 - w_\infty)$ in which $w_0, w_t,$ and w_∞ are the weights of the sample before degradation, at time t and after total conversion respectively. R is gas constant, T the temperature (in K), and E_a is the energy of activation can be obtained from the plot of ln [−ln (1 − α)] versus 1/T.

Coats-Redfern (CR) equation is as follows:

$$\ln\left[-\ln(1-\alpha)/T^2\right] =$$
$$\log ZR/\beta E(1 - 2RT/E) - E/RT \quad (3)$$
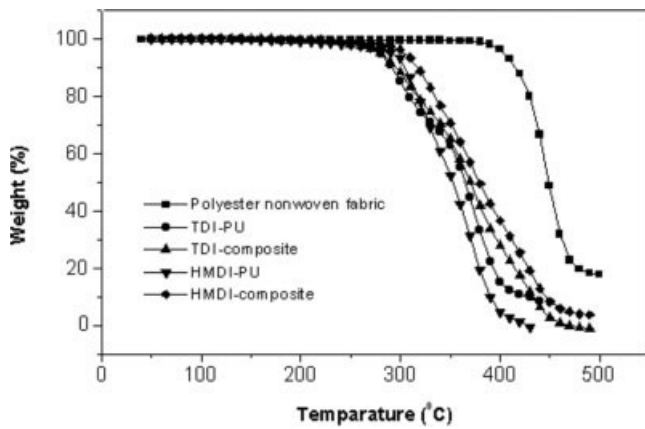
Figure 1 TGA thermograms of polyester nonwoven fabric, TDI-PU, TDI-composite, HMDI-PU, and HMDI-composite.

where Z is the frequency factor, β the heating rate, and E_a the activation energy. A plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$ gives the slope for the evaluation of activation energy most appropriately.

Horowitz-Metzger (HM) suggested the following equation to calculate the energy of activation:

$$\ln[-\ln(1-\alpha)] = E_a\theta\Big/RT_m \qquad (4)$$

where θ is the variable auxiliary temperature defined as $\theta = T - T_m$ in which T_m is the temperature of maximum degradation. Plot of $\ln[-\ln(1-\alpha)]$ versus θ should give a straight line whose slope is E_a/RT_m.

Scanning electron microscopy (SEM) studies were conducted (Jeol-JSM, 840A, Japan) to study the morphology of the composites.
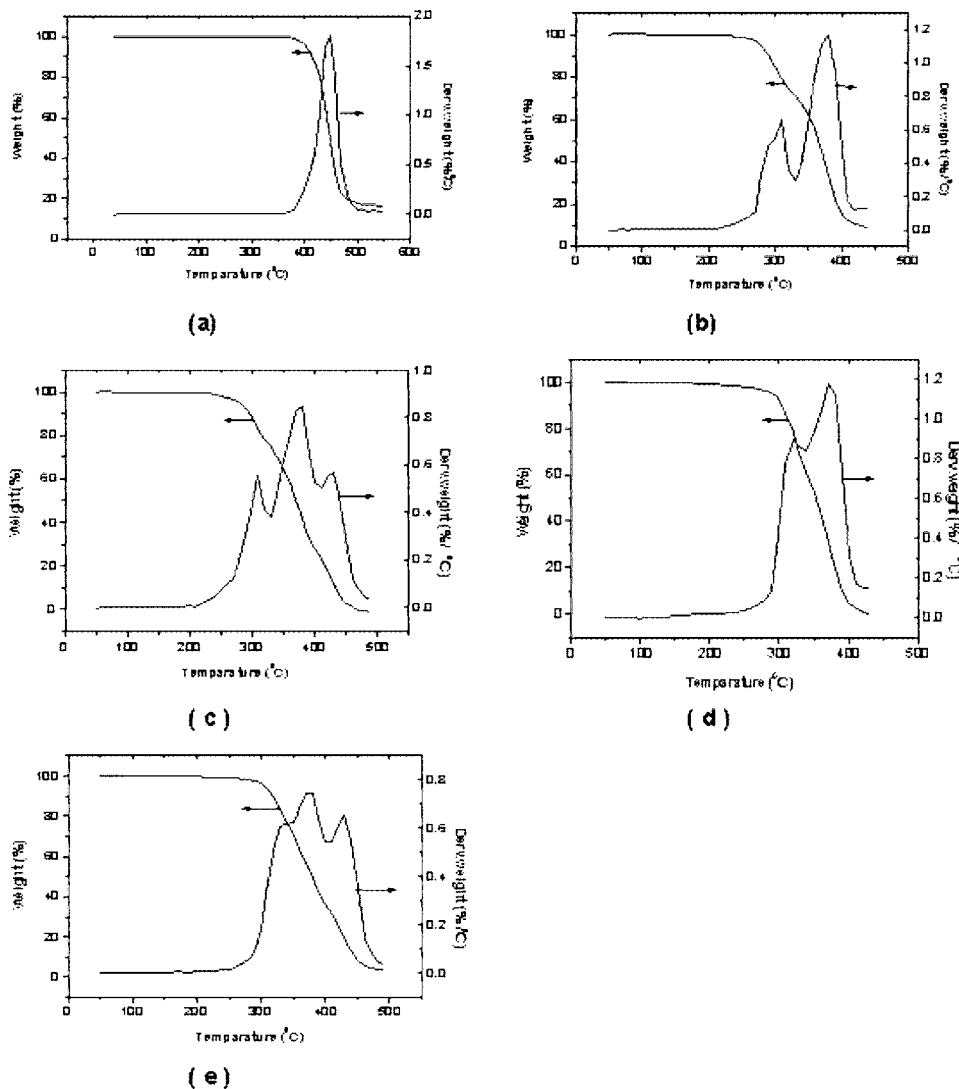
Figure 2 TGA and its derivative thermograms of (a) polyester nonwoven fabric, (b) TDI-PU, (c) TDI-composite, (d) HMDI-PU, and (e) HMDI-composite.

TABLE I
Data Obtained Form TGA Analysis of Polyester Nonwoven Fabric, TDI and HMDI Based PUs and Their Corresponding Composites with Polyester Nonwoven Fabric

Samples	Process	Transition range ± 2 (°C)[a]			Weight loss (%)
		T_i	T_d	T_c	
Polyester	1	390	439	490	83
nonwoven fabric	Ash	–	–	–	17
TDI-PU	1	229	310	330	29
	2	331	380	428	63
	Ash				8
TDI-composite	1	230	310	331	25
	2	332	370	410	52
	3	411	430	470	22.5
	Ash				0.5
HMDI-PU	1	270	320	340	38
	2	341	370	420	61
	Ash				1.0
HMDI-composite	1	281	340	354	33
	2	355	375	403	30
	3	404	430	480	33
	Ash				4.0

[a] T_i, temperature at which decomposition starts; T_d, temperature at which decomposition rate is maximum; T_c, temperature at which decomposition is completed.

RESULTS AND DISCUSSION

TGA thermograms for polyester nonwoven fabric, TDI, and HMDI based PUs and their corresponding composites with polyester nonwoven fabric are given in Figure 1. From the thermograms, it is found that the polyester nonwoven fabric undergoes single step degradation and stable upto 390°C. The maximum degradation occurred was at 490°C. Schwenker and Beck[30] made a similar observation for polyester fiber (Dacron) textile and other high polymeric materials by using differential thermal analysis (DTA) technique. The TGA and its derivative thermograms (DTG) for polyester nonwoven fabric, TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric are given in

Figure 2. Both TDI and HMDI based PUs showed two-step degradation. The first step degradation for TDI and HMDI PUs occurs in the range 229–330°C and 270–340°C respectively. The second step degradation occurs in the range 331–428°C and 341–420°C for TDI and HMDI based PUs respectively. This is in agreement with the reported values elsewhere.[31–33] The first stage weight loss is due to the breaking of urethane links, and starts at 260°C leading to the formation of CO_2, alcohols, amines, aldehydes, CO, etc.,[34,35] and the second stage may be due to the polyol decomposition. Since polyols used in this study are based on CO, the main chain may result in the formation of 10-undecanoic acid and heptanal as evident by the thermal degradation of Ricinoleic acid,[36] which is the main constituent of CO. Polyester nonwoven fabric reinforced TDI and HMDI based PU composites has shown three step degradation process. In case of HMDI based PU-polyester nonwoven fabric composites, the first step weight loss occurs in the temperature range 281–354°C with a mass loss of 33% can be attributed to the base PU present in the composite.[9] The second step weight loss occurs in the range 355–403°C with a weight loss of 30% can be attributed to partial degradation of polyester fiber. The third and final step weight loss occurs in the temperature range 404–480°C with a weight loss of 33% could be due to the complete decomposition of both PU and polyester fiber. The onset degradation of PU-polyester nonwoven fabric composite is slightly higher than that of neat PUs (Table I). This can be attributed to the presence of polyester nonwoven fabric, which has relatively higher thermal stability than PU.

The temperature range of decomposition, the percentage weight loss in each step and the percentage ash content for polyester nonwoven fabric, TDI, and HMDI based neat PUs and their corresponding composites with polyester nonwoven fabric are given in Table I. From Table I, it can be observed that, the polyester nonwoven fabric reinforced PU-polyester nonwoven composites (both TDI and HMDI based) showed an increased onset degradation values com-

TABLE II
Data Obtained Form TGA Analysis of Polyester Nonwoven Fabric, TDI and HMDI Based PUs and Their Corresponding Composites with Polyester Nonwoven Fabric

Samples	Temperature at different weight loss ± 2 (°C)[a]					IPDT	Oxygen index (OI)
	T_0	T_{10}	T_{20}	T_{50}	T_{max}		
Polyester nonwoven fabric	205	412	419	436	545	598	1.19
TDI-PU	187	291	312	366	438	620	0.56
TDI-composite	209	299	317	369	472	645	0.04
HMDI-PU	185	308	322	352	428	625	0.07
HMDI-composite	239	321	338	380	487	695	0.28

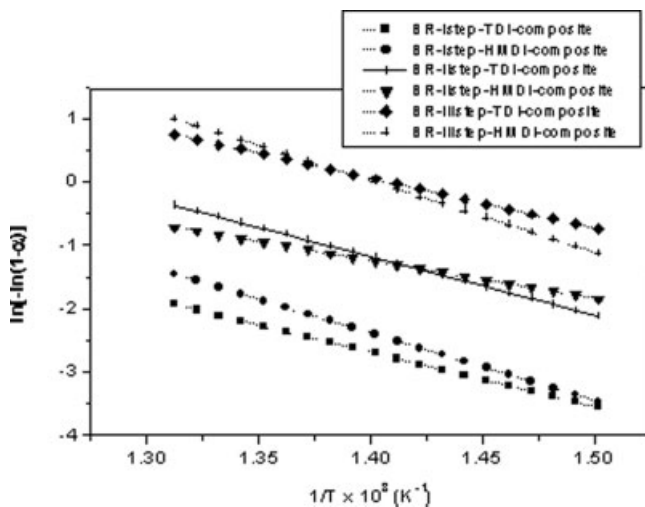[a] T_0, temperature of onset decomposition; T_{10}, temperature of 10% weight loss; T_{20}, temperature of 20% weight loss; T_{50}, temperature of 50% weight loss; T_{max}, temperature at which decomposition is completed.
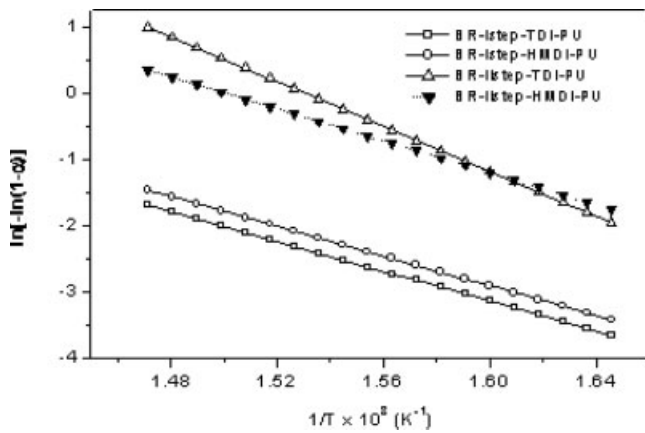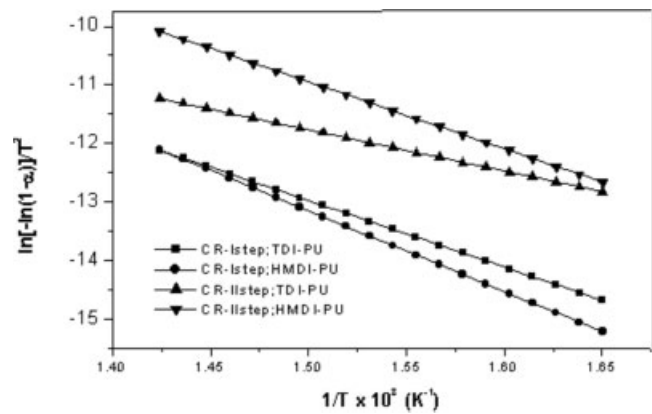
Figure 3 Typical Broido (BR) plot for the determination of activation energies for first and second step weight loss for TDI and HMDI based neat PUs.

Figure 5 Typical Coats-Redfern (CR) plot for the determination of activation energies for first and second steps weight loss for TDI and HMDI based neat PUs.

pared to that of neat PUs. This can be attributed to the synergistic effect of fiber and matrix present in the composite. The obtained percentage ash content is higher in polyester nonwoven fabric (17%) compared to neat PUs and their composites. The low ash content in the case of neat PUs could be due to the fact that, the CO present in the PU contains more oxygen units and hence PU undergoes combustion leaving less residue or ash. Pielichowski et al.[37] noticed similar trend for the thermal degradation of PU obtained from MDI and different polyols.

The thermograms obtained during the TGA scans were analyzed to give the percentage weight loss as a function of temperature. T_0 (temperature of onset decomposition), T_{10} (temperature for 10% weight loss), and T_{max} (temperature for maximum weight loss) are the main criteria to indicate their thermal

stability of the composites. The relative thermal stability of composites was evaluated by comparing decomposition temperatures at various percentage weight loss and IPDT values are given in Table II. IPDT values represent the overall nature of the thermogram over the entire range of the TGA curves. From the Table II, it can be observed that the thermal stability of the polyester nonwoven fabric reinforced PU composites is high compared to neat PUs. The IPDT values of composites are higher compared to their constituents. On the basis of the OI values, it can be concluded that the polyester nonwoven fabric reinforced PU composites are not good flame-retardants.

Kinetic parameters were evaluated from the TGA curves using the plots of BR, CR, and HM methods. To know the activation energy of the TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric, the complete thermogram was divided into distinct sections according to
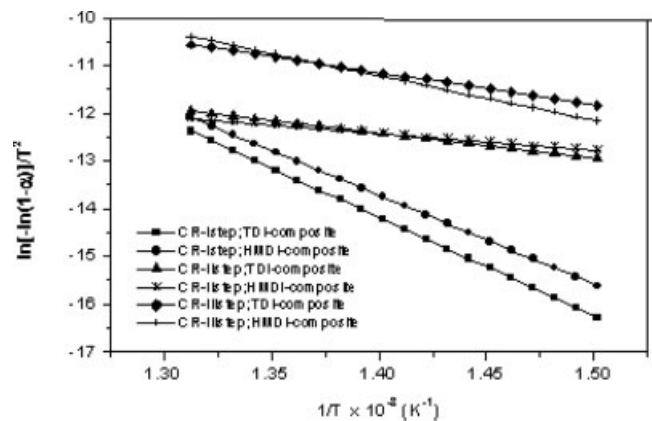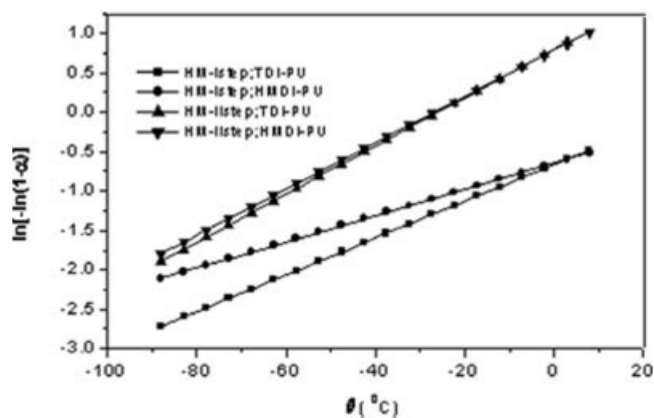

Figure 4 Typical Broido (BR) plot for the determination of activation energies for first, second, and third steps weight loss for TDI and HMDI based PU-polyester nonwoven fabric composites.
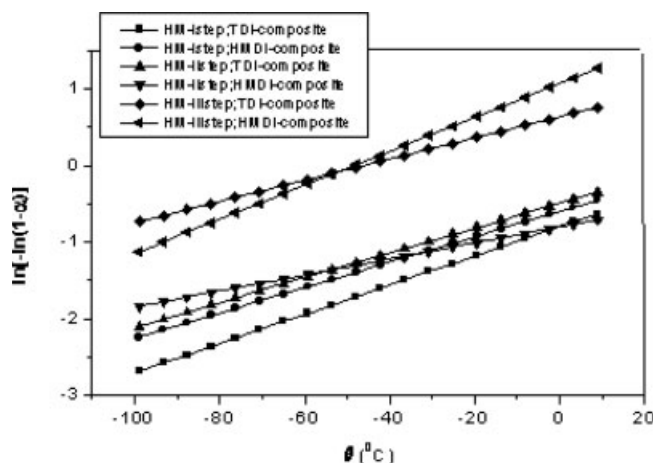

Figure 6 Typical Coats-Redfern (CR) plot for the determination of activation energies for first, second, and third steps weight loss for TDI and HMDI based PU-polyester nonwoven fabric composites.

Figure 7 Typical Horowitz-Metzger (HM) plot for the determination of activation energies for first and second steps weight loss for TDI and HMDI based neat PUs.

their degradation steps/processes. The plots of ln $[-\ln(1 - \alpha)]$ versus $1/T$, $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$ and $\ln[-\ln(1-\alpha)]$ versus θ for different degradation processes of TDI and HMDI based neat PUs and their corresponding composites with polyester nonwoven fabric are given in Figures 3–8 respectively, for BR, CR, and HM methods respectively. Regression analysis carried out for all the plots. The mechanism of R^2 close to unity was chosen. The regression analysis gives the results of slopes, constants and R^2 values corresponding to thermal degradation for the selected temperature range. The R^2 values and calculated activation energy (E_a) for each thermal degradation process and for each method are tabulated in Table III. BR and HM methods have shown almost identical values of E_a. The values of R^2 less than 0.98 shows that the CR method is less precise and supports the conclusion presented by

Figure 8 Typical Horowitz-Metzger (HM) plot for the determination of activation energies for first, second, and third steps weight loss for TDI and HMDI based PU-polyester nonwoven fabric composites.

TABLE III
Activation Energies Calculated by Broido (BR), Coats-Redfern (CR), and Horowitz-Metzger (HM) Methods for Polyester Nonwoven Fabric, TDI, and HMDI Based PUs and Their Corresponding Composites with Polyester Nonwoven Fabric

| Samples	Degradation step	Activation energies ± 2 (kJ/mol)					
		BR	R^2	CR	R^2	HM	R^2
TDI-PU	I	41	0.952	98	0.978	51	0.994
	II	90	0.994	90	0.996	90	0.993
TDI-composite	I	34	0.957	54	0.998	48	0.996
	II	63	0.998	82	0.995	62	0.998
	III	104	0.986	88	0.980	96	0.988
HMDI-PU	I	65	0.963	95	0.981	55	0.989
	II	100	0.995	103	0.991	94	0.997
HMDI-composite	I	62	0.984	63	0.993	56	0.993
	II	66	0.999	79	0.999	63	0.996
	III	112	0.992	107	0.989	102	0.995

other author.[38] The lowest E_a values were observed for the initial thermal degradation compared to final degradation for all the methods. This is due to the lower energy required to remove low molecular materials present in PU. Higher E_a values were observed for second step, because higher energies are required for bond scission and unzipping of polymer chains.

Morphological behavior

The SEM of tensile fractured nonwoven fabric [Fig. 9(a)] revealed that the fibers are curled, randomly arranged, and deformed indicating the poor stress transfer characteristics. The morphology of tensile fractured HMDI based PU and its composite with polyester nonwoven fabric is given in Figure 9 (b,c) respectively. The SEM micrograph of HMDI based showed layers and cavities because of fractured surface. The morphology of tensile fractured HMDI based PU-polyester nonwoven fabric composite [Fig. 9(c)] showed the skin formation and PU-fiber bonding. The close packing can be observed compared to the bare nonwoven fabric.

CONCLUSIONS

TGA of TDI and HMDI based neat PUs and their composites with polyester nonwoven fabric revealed that the incorporation of reactive composition of di-isocyanate and CO into fibrous nonwoven structures increases the thermal stability of composites compared to neat PU. Lowest activation energy (E_a) observed for all the samples for the first-step thermal degradation as compared to second and third step. This may be due to the fact that, the less energy is
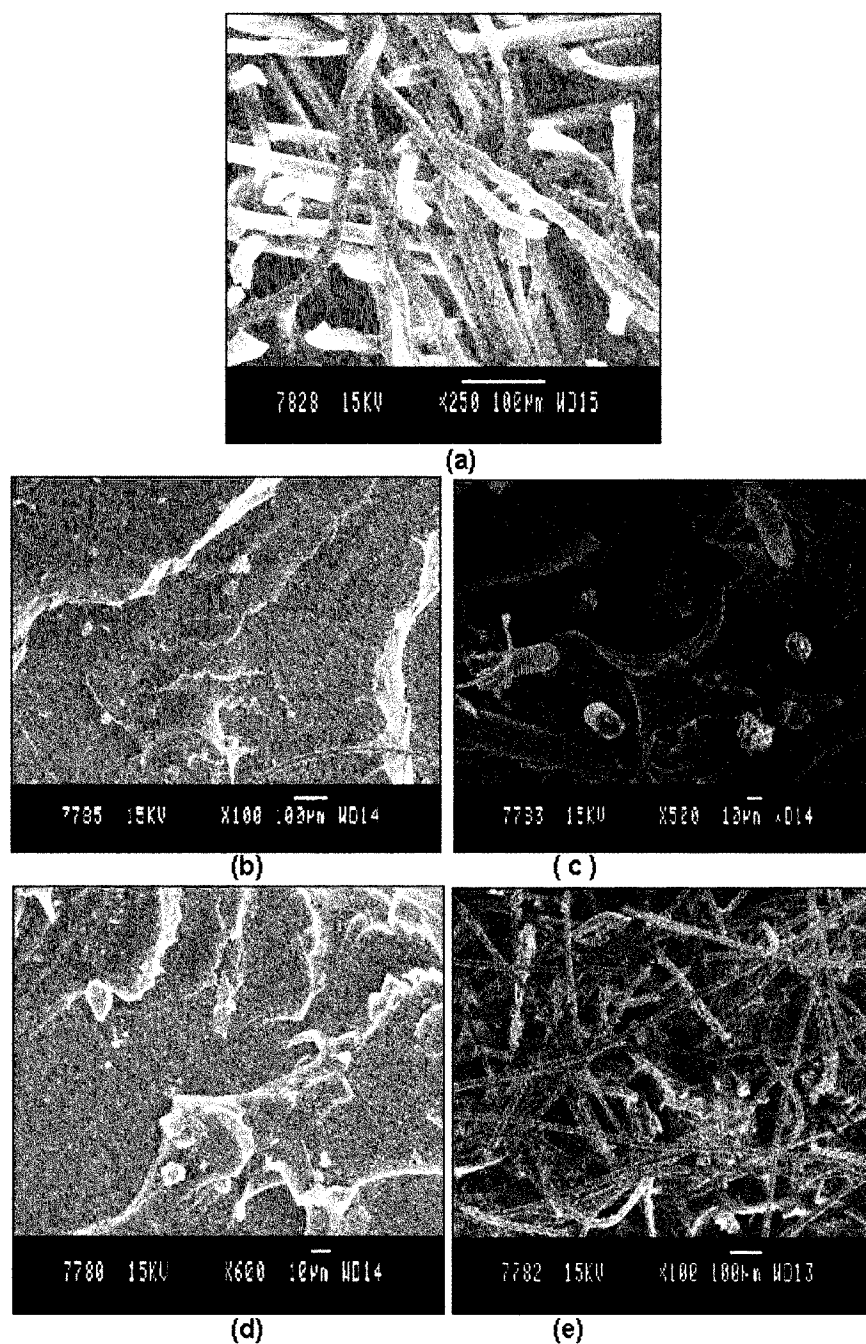
Figure 9 Scanning electron micrographs of (a) polyester nonwoven fabric, (b) TDI-PU, (c) TDI-composite, (d) HMDI-PU, and (e) HMDI-composite.

sufficient to remove the low molecular weight impurities. The SEM images indicates the embedded polyester nonwoven fabric in the PU matrix. The number of contact points between the fiber and matrix was relatively more in HMDI based composites compared to TDI based composite.

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