Thermogravimetric Analysis and Morphological Behavior of Melamine-Formaldehyde Filled Polyvinyl Acetate—polyester Nonwoven Fabric Composites

M. N. Satheesh Kumar,[1] Siddaramaiah[2]

[1]Research and Innovation Center, Raman Boards Limited, Thandavapura, Mysore-571 325, India
[2]Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, Mysore-570 006, India

ABSTRACT: The objective of the present research work is to study the effect of different amounts of melamine-formaldehyde (MF) viz., 0–20 parts by dry weight on the thermal stability of polyvinyl acetate (PVAc) latex impregnated polyester nonwoven fabric composites. From the thermogravimetric analysis, the improvement in thermal stability of the composites was noticed with increase in the MF content. Composites fabricated with five parts MF-incorporated PVAc showed a drastic increase in the onset degradation temperature when compared with unfilled composites. It was found that the degradation of MF-loaded PVAc-polyester nonwoven fabric composites takes place in two steps. Degradation kinetic parameters were calculated for the composites using Broido and Horowitz-Metzger methods. The tensile fractured composite specimens were analyzed using scanning electron microscope to know the morphological behavior. The increased percentage ash content also supports for the increased thermal stability of the composites with increasing the MF content in the system. The adhesion between the fiber and matrix can be seen from scanning electron microphotographs. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1165–1171, 2009

Key words: polyester nonwoven fabric; PVAc/MF; composites; TGA; kinetic parameter

INTRODUCTION

The textile-based nonwoven fabric has several potential applications for disposable applications. Among the various types, needle punched nonwoven fabric has the advantages of low cost and flexibility.[1–3] The mechanical properties of nonwoven fabric are insufficient even for nonstructural applications because of poor stress transfer characteristics. The strength of the nonwoven fabric can be enhanced significantly by the incorporation of polymeric binders/resins.[1–7] The polymer binder/resin-incorporated nonwoven fabric composites has the several advantages like high delamination resistance, light in weight, and high strength to weight ratio. The polyvinyl acetate (PVAc) is well known for higher bond strength and better film properties as compared with styrene-based polymers.[8] However, the mechanical resistance of PVAc decreases with increasing the temperature.[9,10] As the PVAc offers free hydroxyl groups,[11–13] the incorporation of melamine-formaldehyde (MF) into PVAc gives crosslinked polymer networks, which

are more rigid and also have better moisture and heat resistance. In the present research, MF incorporated PVAc is selected as the binder for the fabrication of polyester nonwoven fabric composites.

Considerable efforts have been made to study the thermal degradation of fiber-polymer composites using thermogravimetric analysis (TGA), because it analyzes the degradation response and determines the upper temperature limit of use and durability. The onset of mass loss defines the upper limit of stability, above which the composites degrades appreciably. Few researchers have reported on PVAc/MF blends. Thermal stability and viscoelastic properties of MF/PVAc hybrid resins were studied by Kim and Kim.[14] Qaio and coworkers[15] discussed the improvement in the water resistance of PVAc with the incorporation of MF. Kim and Kim[16] discussed the initial tack and viscoelastic properties of PVAc/MF blends on decorative veneer and plywood surfaces using texture analyzer and dynamic mechanical thermal analysis. Iwata et al.[17] was investigated the application of PVAc/MF blend as adhesive for large laminated timber. Although few reports available on PVAc/MF blend, there is a scarcity in the literature on the studies of MF incorporated PVAc-polyester nonwoven fabric composites. In the previous

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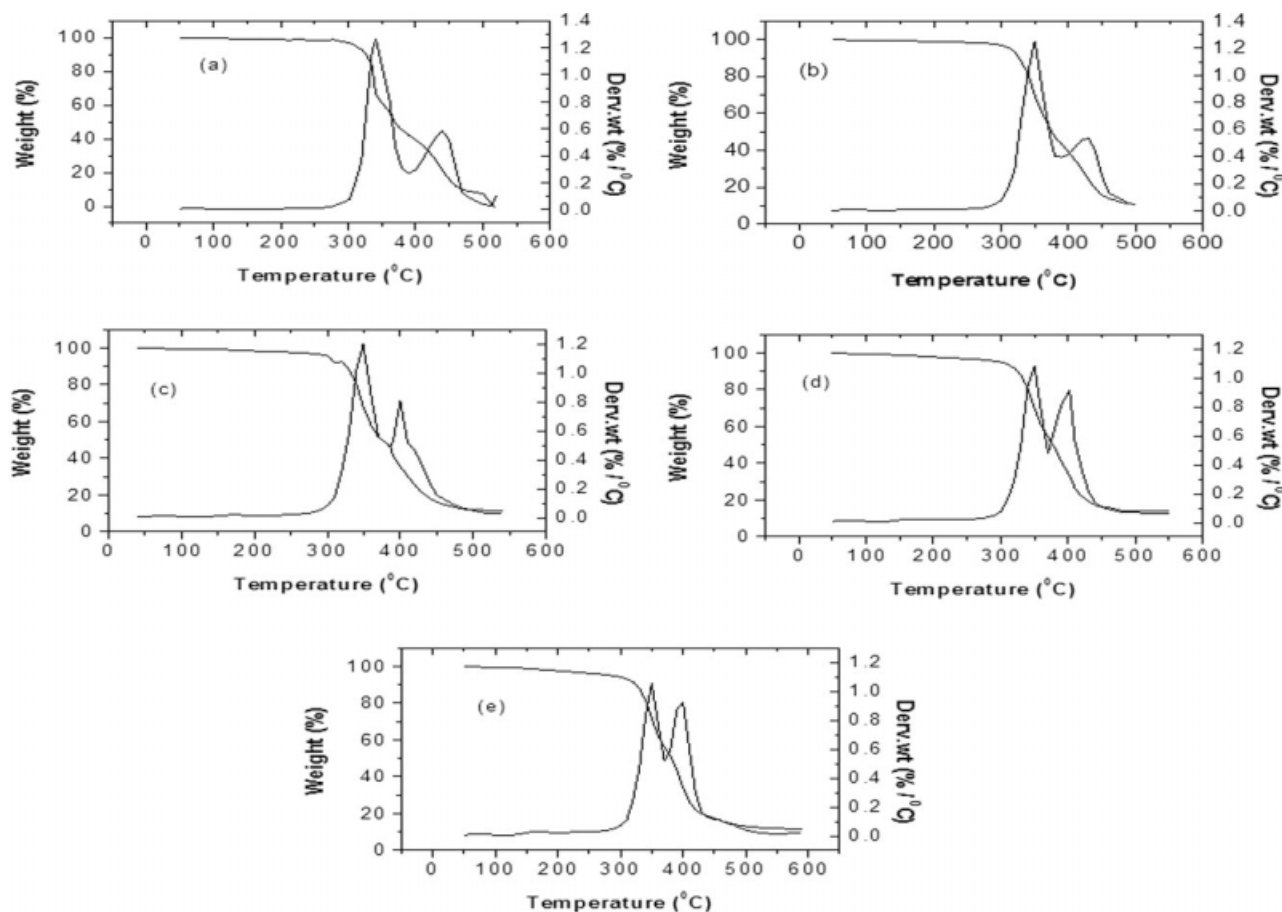*Correspondence to:* Siddaramaiah (siddaramaiah@yahoo.com).

Figure 1 TGA and its derivative thermograms of different amounts of MF-loaded PVAc-polyester nonwoven fabric composites weight by weight viz., (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20.

communications, the authors have studied the effect of MF on the physicomechanical and water sorption behavior of the composites.[18,19] In the present research article, authors have reported the effect of MF contents on the thermal stability of PVAc-polyester nonwoven fabric composites using TGA and on the material morphology using scanning electron microscope (SEM).

EXPERIMENTAL

Materials

Needle punched polyester nonwoven fabric (400 g/m²) 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. Aqueous PVAc latex was procured from a local supplier and its molecular weight (M_n) was 102 × 10³. Aqueous MF resin (Pidifix 361) having a solid content of 62% and viscosity of 180 cP was procured from M/s Pidilite Industries Limited, Mumbai.

Fabrication of composites

Polyester nonwoven fabric having 400 g/m² was impregnated in bath-containing MF-loaded PVAc latex. The impregnated fabric was squeezed in a two-roll squeezer to adjust the desired optimized pickup of latex to fabric (3.2 : 1). After the desired amount of latex was adjusted, the impregnated fabric was dried in hot air oven at 60°C for 8 h and cured at 150°C for 30 min. Composites were fabricated by varying the amounts of MF in PVAc latex viz., 0/100/, 5/100, 10/100, 15/100, and 20/100 weight-by-weight on dry-to-dry basis.

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 used for estimating the inherent thermal stability of the composites. IPDT data was calculated

TABLE I
Data Obtained from TGA Thermograms of Different Amounts of MF-Loaded PVAc-Polyester Nonwoven Fabric Composites

PVAc/MF ratio (%, wt/wt)	Process	Transition temp. range ± 2 (°C)[a]			Weight loss (%)
		T_i	T_d	T_c	
100/0	1	290	342	390	58
	2	391	440	510	35
	Ash	–	–	–	7
100/5	1	293	350	391	57
	2	392	440	520	32
	Ash	–	–	–	11
100/10	1	295	350	401	54
	2	396	410	540	34.5
	Ash	–	–	–	11.5
100/15	1	298	350	370	46
	2	396	402	550	40.9
	Ash	–	–	–	13.1
100/20	1	300	352	370	44
	2	398	400	591	43
	Ash	–	–	–	13

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

from the thermogram area applying the method reported in the literature.[20] The oxidation index (OI) was calculated based on the weight of carbonaceous char as related by the empirical equation;

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

The thermal degradation kinetic parameters were determined for different amounts of MF incorporated PVAc-polyester nonwoven fabric composites using Broido[21] and Horowitz-Metzger[22] methods. For the sake of calculations and to know the nature and mechanism of decomposition, the complete thermogram was divided into distinct region according to their degradation processes. The activation energy for the thermal degradation process was evaluated using Broido equation;

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

where, $\alpha = (w_0 - w_t)/(w_0 - w_\infty)$ 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 the gas constant, T is the temperature (in K), and E_a is the energy of activation can be obtained from the plot of $\ln[-\ln(1 - \alpha)]$ versus $1/T$.

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

$$\ln[-\ln(1 - \alpha)] = E_a\theta/RT_m \quad (3)$$

where, θ is the auxiliary temperature variable 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.

SEM studies were conducted (Jeol-JSM, 840A, Japan) to study the morphology of the composites. The tensile fractured samples were gold sputtered before

TABLE II
Transition Temperature, IPDT, and OI Data Obtained from TGA Curves for PVAc/MF-Nonwoven Fabric Reinforced Composites

PVAc/MF ratio (%, wt/wt)	Temperature at different weight loss ± 2 (°C)[a]					IPDT (°C) ± 2.0	OI ± 1.5%
	T_0	T_{10}	T_{20}	T_{50}	T_{max}		
100/0	180	326	337	370	510	590	0.49
100/5	220	327	342	375	520	640	0.77
100/10	230	330	342	372	540	680	0.81
100/15	240	330	343	380	550	710	0.91
100/20	242	330	346	385	591	735	0.91

[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; and T_{max}, temperature at which decomposition is completed.
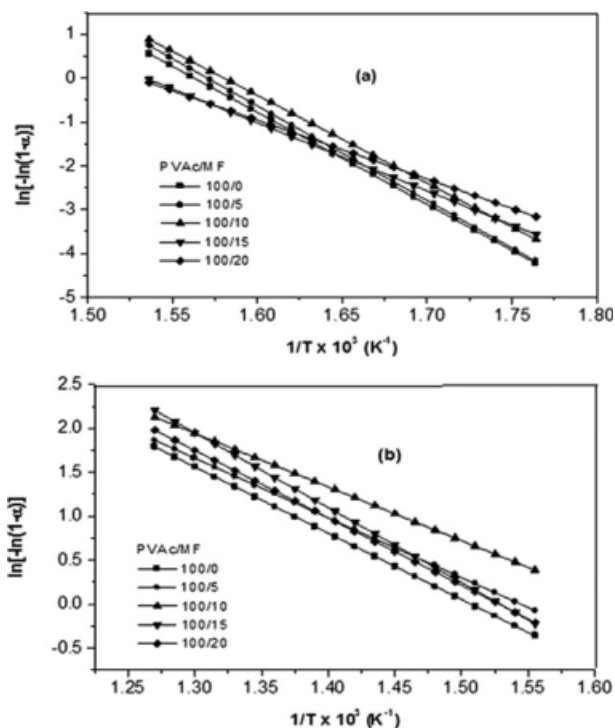
Figure 2 Typical Broido (BR) plots for the determination of activation energies for; (a) first step and (b) second step weight loss for different amount of MF-incorporated PVAc-polyester nonwoven fabric composites.

viewing under the microscope. The magnification and the voltage are displayed on the microphotographs of the samples.

RESULTS AND DISCUSSION

TGA is of the widely used tool to probe the thermal stability and thermal degradation mechanism of the polymeric matrix. TGA and its derivative thermograms for different amounts of MF-incorporated PVAc-polyester nonwoven fabric composites are shown in Figure 1(a–e). From the thermograms, it is found that all the samples undergone two-step degradation processes. Kim and Kim[16] made a similar observation in their study on the MF/PVAc blends for use as adhesives in engineered flooring. The first stage thermal degradation process is occurred at the temperature range 290–401°C, could be due to loss of alkyl chain and ether linkage present in the MF. At higher temperatures, the oxidation of activated methylene of the N—CH_2—O— may most likely occur via the formation of hydroperoxide.[23] The second stage degradation occurred in the temperature range 391–591°C may be due to the complete decomposition of fiber and matrix. With increase in the MF content, the thermal decomposition temperature of the composites shifted slightly towards higher temperature range than that of one without MF. This

may be due to the crosslinked polymer network in the composite.[24]

The temperature range of decomposition, the percentage weight loss in each step and the percentage ash content for different amounts of MF-incorporated PVAc-polyester nonwoven fabric composites are given in Table I. From Table I, it can be observed that, the onset degradation temperature of the composites increased with increase in the MF content. This can be attributed to the formation of hydrogen bond between the PVAc and MF resin. The percentage ash content of the composites increases with increasing the MF content in the system. This increased percentage ash content is also an indication for the enhancement of thermal stability of the composites. The nitrogen-containing units present in the MF resin do not allow the composite for more combustion and hence the ash content increases with increase in the MF content in the system.

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 were evaluated by comparing decomposition temperatures at various percentage weight loss and IPDT values, given in Table II. IPDT values represent the overall nature of the
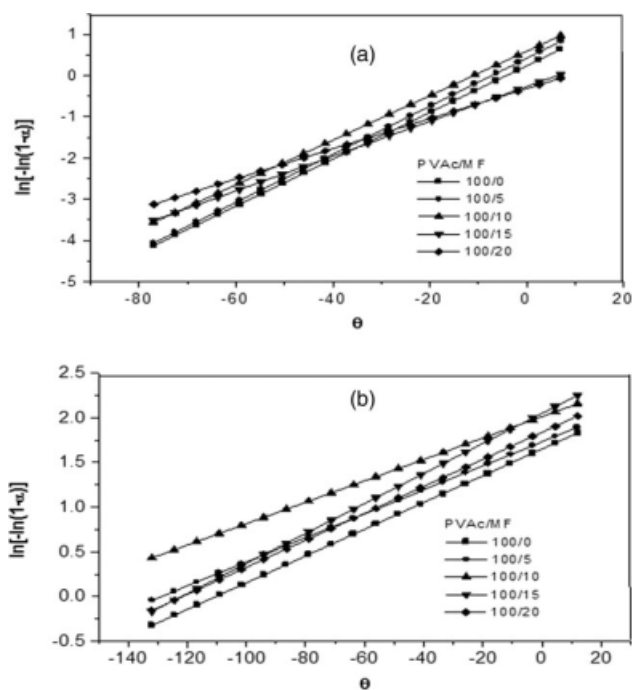

Figure 3 Typical Horowitz-Metzger (HM) plots for the determination of activation energies for; (a) first step and (b) second step weight loss for different amounts of MF-incorporated PVAc-polyester nonwoven fabric composites.

TABLE III
Activation Energies Calculated by Broido and Horowitz-Metzger Methods for
Different Amount of MF-loaded PVAc-Polyester Nonwoven Fabric Composites

PVAc/MF ratio (%, wt/wt)	Degradation step	Weight loss (%)	Activation energies ± (kJ/mol)			
			BR	R^2	HM	R^2
100/0	I	58	128	0.991	134	0.988
	II	35	70	0.982	73	0.993
100/5	I	58	135	0.988	139	0.985
	II	32	77	0.998	68	0.998
100/10	I	54	128	0.987	113	0.984
	II	35	71	0.987	50	0.982
100/15	I	46	111	0.983	114	0.988
	II	41	71	0.993	70	0.990
100/20	I	44	112	0.987	113	0.990
	II	43	64	0.984	63	0.980

thermogram over the entire temperature range of the TGA curves. From the Table II, it can be observed that the thermal stability of the MF-incorporated PVAc-polyester nonwoven fabric composites increased with increase in MF content. The IPDT values of composites containing MF were higher as compared to the composite without MF. Based on the OI values, it can be concluded that MF-incorporated PVAc-polyester nonwoven fabric composites exhibits flame retardant nature.

Kinetic parameters were evaluated from the TGA curves using the plots of Broido (BR) and Horowitz-Metzger (HM) methods. To know the activation energy of the PVAc-polyester nonwoven fabric composites containing different amounts of MF, the complete thermogram was divided into two distinct regions according to their degradation steps/processes. The plots of $\ln[-\ln(1-\alpha)]$ versus $1/T$ and $\ln[-\ln(1-\alpha)]$ versus θ for different thermal degradation processes for different amounts of MF-incorporated PVAc-polyester nonwoven fabric composites are given in Figures 2 and 3, for BR and HM methods, respectively. Regression analysis was 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 for each degradation steps. The R^2 values and calculated activation energy (E_a) are tabulated in Table III. The E_a values calculated by both BR and HM methods are almost identical. This result indicates that there is a good agreement between the E_a values calculated from both mathematical models. From Table III, it is clear that the first step degradation showed higher activation energy when compared with second step degradation. The percentage weight loss and the activation energy follow the same trend. A relationship between the percentage weight loss and activation energy at different degradation step for different amounts of MF-incorporated PVAc-

polyester nonwoven fabric composites are shown in Figure 4.

Morphological behavior

The SEM photomicrographs for the tensile fractured surface of different amounts of MF incorporated PVAc-polyester nonwoven fabric composites are shown in Figure 5(a–d). The number of fiber pull-outs is negligible and it is very minimal in 5 and 10 parts by weight MF-loaded composites [Fig. 5(a–b)]. The photomicrographs also indicate the minimal fiber breakage and this result confirm the good
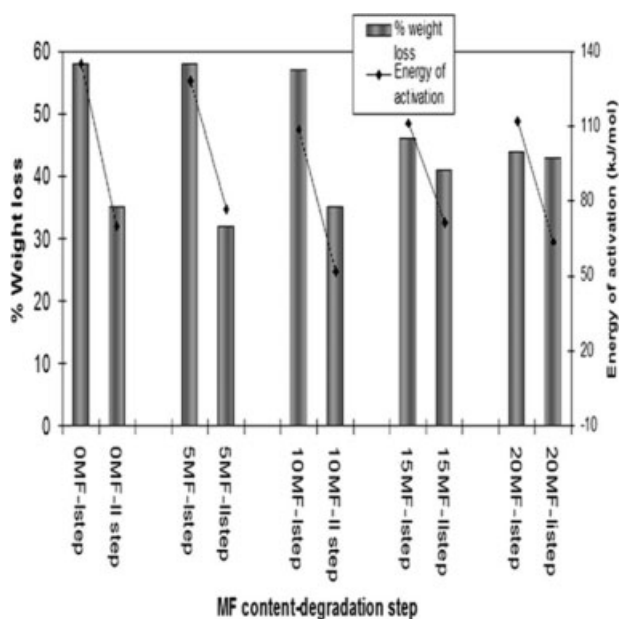

Figure 4 Relationship between the percentage weight loss and the activation energy of MF-incorporated PVAc-polyester nonwoven fabric composites at different degradation steps for Broido method.
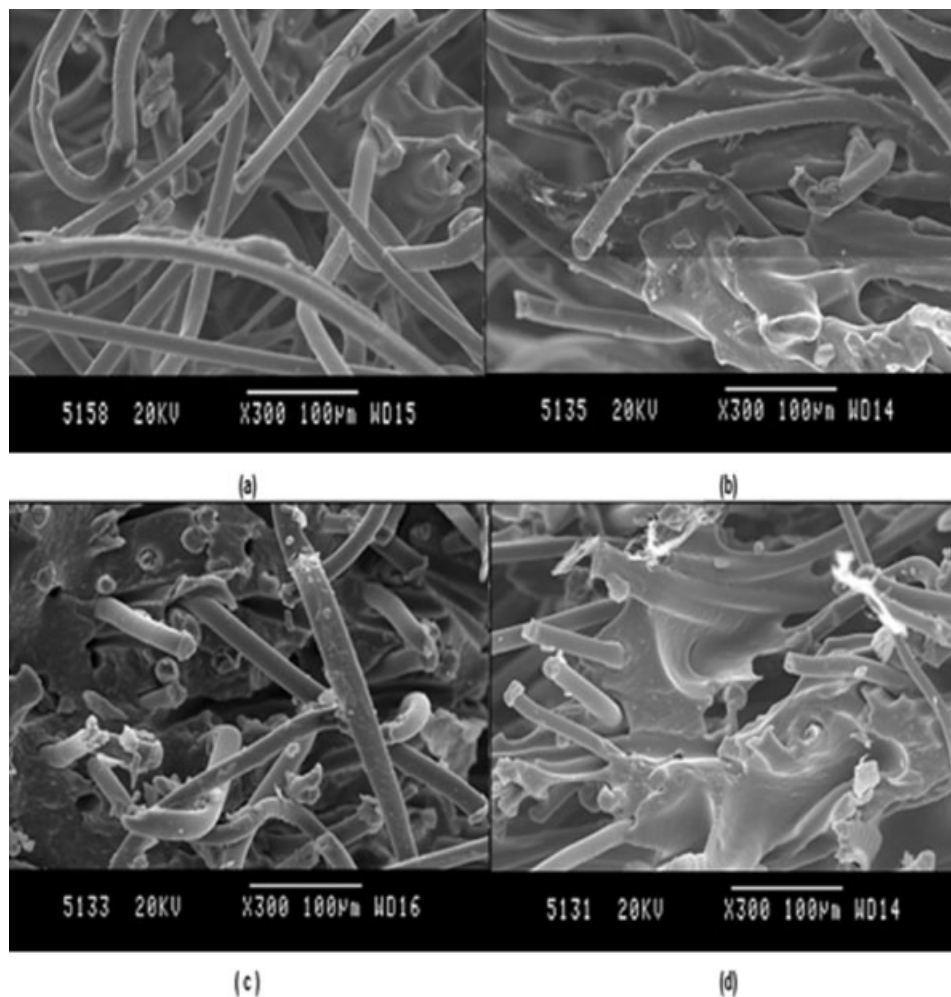
Figure 5 SEM photomicrograph of tensile fractured surface of PVAc-polyester nonwoven fabric composites containing different amounts of MF; (a) 5, (b) 10, (c) 15, and (d) 20 parts by weight.

interfacial adhesion between the fiber and the matrix. The matrix deformation and inhibition of the propagating fracture path by fiber-matrix adhesion can be noted generally.

CONCLUSIONS

The following conclusions can be drawn from the present study:

i. The thermal stability of PVAc-polyester nonwoven fabric composites enhanced after the incorporation of MF. It can be attributed to the increase in nitrogen content and formation of crosslinked polymer network in the composites.

ii. The percentage weight loss and activation energy follow the same trend for all composites.

iii. SEM images reveal the good interfacial adhesion between fiber and matrix.

References

1. Attwood, B. W.; White, D. G. Tappi 1979, 62, 39.
2. Villalobos, J. A. Tappi 1981, 64, 129.
3. Rigdahl, M.; Westerlind, B.; Hollmark, H.; De Ruvo A. J Appl Polym Sci 1983, 28, 1599.
4. Marriot, R. C. Tappi 1995, 75, 164.
5. Dever, M. Tappi 1993, 76, 191.
6. Lukic, S.; Jovanic, P. Mater Lett 2004, 58, 439.
7. Epstein, M.; Shishoo, R. L. J Appl Polym Sci 1993, 50, 863.
8. Verma, S. K.; Bisarya, S. C. J Appl Polym Sci 1986, 31, 2675.
9. Tuncer, D.; Salim, H. Build Environ 2004, 39, 1199.
10. Yalcin, O.; Musa, A.; Ayhan, O. J Appl Polym Sci 2000, 76, 1472.
11. Skietst, I. Hand Book of Adhesives; Van Nostrand Reinhold: New York, 1990; Chapter 21, p 390 and 404.
12. Daniels, W. E. Polyvinyl Acetate in Kirk-Othmer Encyclopedia of Chem Technology; Wiley: New York, 1983, p 839.

13. Hartley, F. D. J Appl Polym Sci 1959, 34, 397.
14. Kim, S.; Kim, H. J. Thermochim Acta 2006, 444, 134.
15. Lijun, Q. Q.; Allan, J. E.; Clive, J. B.; Philip, K. C.; Robert, A. F. Pigment Resin Technol 2000, 29, 152.
16. Kim, S.; Kim, H. J. J Adhes Sci Adhesives 2006, 25, 456.
17. Iwata, R.; Inagaki, N.; Kim, J. J Adhes Sci Technol 2006, 20, 663.
18. Satheesh Kumar, M. N.; Siddaramaiah, J Thermoplastic Comp 2007, 20, 305.
19. Satheesh Kumar, M. N.; Siddaramaiah, Polym Int 2007, 56, 409.
20. Doyle, C. D. Anal Chem 1961, 33, 77.
21. Broido, A. J Polym Sci 1969, A-2, 1761.
22. Horowitz, H. H.; Metzger, G. Anal Chem 1963, 35, 1465.
23. Lady, J. H.; Adam, R. C.; Kesse, I. J Appl Polym Sci 1960, 65, 3.
24. Yu, Y. H.; Lin, C. Y.; Yeh, J. M.; Lin, W. H. Polymer 2003, 44, 3553.