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Thermal Degradation of Short Nylon-6 Fiber–Reinforced Styrene Butadiene Rubber Composite

A. Seema

Centre for Materials for Electronics Technology, Thrissur, India

S. K. N. Kutty

Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, India

The thermal properties of short Nylon-6 fiber–reinforced Styrene butadiene rubber (SBR) composites were studied by Thermogravimetric Analysis (TGA). The effect of epoxy-based bonding agent on thermal degradation of the gum and the composites was also studied. The thermal stability of the SBR was enhanced in the presence of Nylon-6 fibers and the stability of the composites increased in the presence of bonding agent. The epoxy resin did not significantly change the thermal stability of SBR gum vulcanizate. Results of kinetic studies showed that the degradation of SBR and the short nylon fiber–reinforced composites with and without bonding agents followed first-order kinetics.

INTRODUCTION

Short fiber–rubber composites have the strength and stiffness of the fiber and the elastic behavior of the rubber matrix. Recently, short fiber–reinforced rubber has gained importance due to its advantages like design flexibility, anisotropy in technical properties, stiffness, damping, and processing economy [1–6]. Studies on the various properties of the short fiber composites have been done earlier [7–12]. The cure and mechanical properties of short Nylon-6–reinforced SBR were reported earlier by Sreeja and Kutty [13]. The rheological

characteristics of short Nylon-6–reinforced SBR with and without epoxy bonding agent were reported by the present authors [14–15]. Ronaldo et al. studied the influence of short fibers on the thermal resistance of the matrix, Tg, and kinetic parameters of the degradation reaction of thermoplastic polyurethane and found that the thermal resistance of aramid fiber–reinforced composite was greater than that of carbon fiber–reinforced composites [16]. The degradation characteristics of Kevlar fiber reinforced thermoplastic polyurethane were reported by Kutty et al. [17]. Younan et al. studied the thermal stability of natural rubber–polyester short fiber composites [18]. Suhara et al. studied thermal degradation of short polyester fiber–polyurethane elastomer composites and found that incorporation of short fiber enhanced the thermal stability of the elastomer [19]. Rajeev et al. studied the thermal degradation of short melamine fiber–reinforced EPDM, maleated EPDM, and nitrile rubber composites with and without bonding agent and found that the presence of melamine fiber in the vulcanizates reduced the rate of decomposition and the effect was pronounced in the presence of a dry bonding system [20]. Shield et al. used a thermogravimetric technique to study the blends of NBR and SBR [21]. The compositions of NBR/SBR blends were estimated by TGA from the linear correlation between the polymer composition and temperature required to pyrolyze a sample to a specific "% weight loss." Ahmed et al. reported thermal studies on sulphur, peroxide, and radiation cured NBR and SBR gum vulcanizates and also with fillers like carbon black and silica. It was found that radiation cured NBR and SBR vulcanizates had better thermal stability [22]. A study on the kinetics of the degradation of Styrene–Butadiene Rubber was done by S. C. Oh et al. [23]. The present article reports the thermal degradation of short Nylon-6 fiber–reinforced SBR rubber composites with and without epoxy resin as bonding agent.

EXPERIMENTAL

Materials

Epoxy resin (LAPOX, A31) and hardener (LAPOX K30) were procured from Cibatul Limited, Gujarat, India. Styrene butadiene rubber (Synaprene 1502) was supplied by Synthetics and chemicals Ltd. (Barielly, India) Nylon-6 fiber of 20 µm diameter obtained from SRF Ltd., Madras was chopped to approximately 6 mm length. All other ingredients were of commercial grade.

The formulation of the mixes is given in Table 1. The mixes were prepared as per ASTM 3182 (1989) on a two roll laboratory size mixing

TABLE 1 Formulation of Mixes

Ingredients	Mix no.											
	A	B	C	D	A3	B3	C3	D3	A5	B5	C5	D5
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

*Epoxy resin formed by 1:0.5 equivalent combination of Epoxy resin and amine type hardener (Zinc Oxide—5 phr; Stearic acid—1.5 phr; CBS—0.8 phr; Sulphur—2 phr; TMTD—0.2 phr are common to all mixes).

mill. All the mixes were vulcanized at 150°C in an electrically heated hydraulic press to their respective cure times as obtained from Goettfert Elastograph Model 67.85. Thermogravimetric analyses were carried out on Universal V3 2B TA Instrument with a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

The derivative TGA curves of mixes A–D and neat nylon fiber are shown in Figure 1. The temperature of initiation of degradation (T_i), the peak rate of degradation, and the corresponding temperature are given in Table 2. It is clear from the figure that the degradation of SBR occurs in a single step. The onset of degradation is at 325°C and peak degradation temperature (T_{max}) at 460.79°C for the gum compound. The neat nylon fiber degrades in single step with peak degradation rate of 47.13%/min and the corresponding temperature is 455.08°C. Residue remaining at 600°C is 1.255% for fiber. The fiber-containing mixes also show a similar pattern as that of gum vulcanizate. As the fiber concentration increases the onset of degradation is shifted to higher temperature, and degradation starts at 338.89°C for 30 phr fiber loaded sample. This indicates that the thermal stability of SBR is enhanced by the presence of nylon fibers. Similar results in the case of short Kevlar fiber–reinforced thermoplastic polyurethane composites have been reported by Kutty et al. [17].

Peak degradation temperature and peak rate of degradation remains more or less constant with fiber concentration. For 20-phr fiber filled sample the peak degradation temperature is 450°C. The percentage of residue remaining at 600°C decreased when fiber was
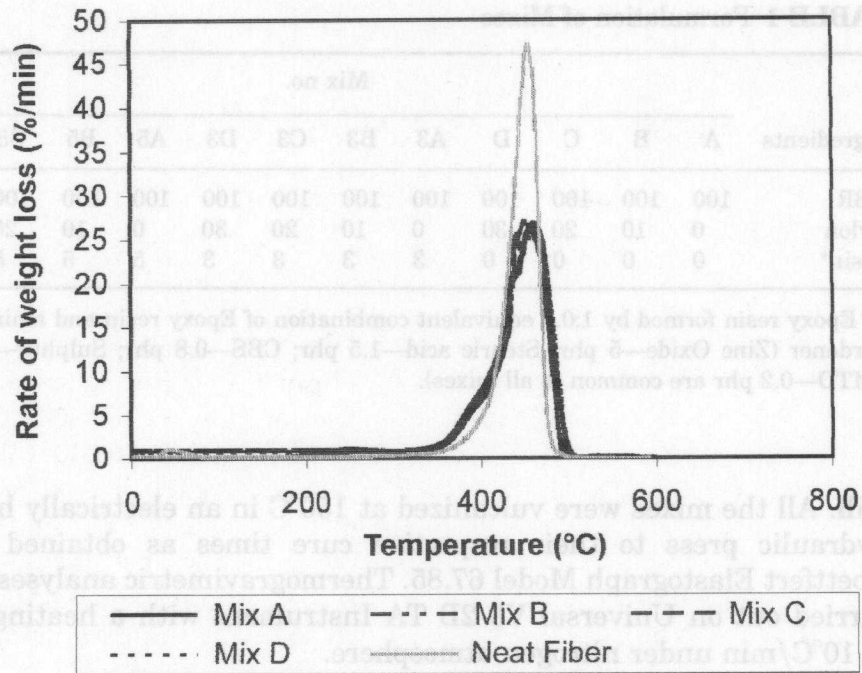
FIGURE 1 TGA traces of Mix A, Mix B, Mix C, and Mix D.

incorporated in the matrix. This is because neat nylon fiber has less residue at 600°C, hence the presence of fiber in the composite leads to lower residue. But further increase in fiber concentration decreases the residue remaining at 600°C only marginally.

The order of degradation was calculated from the Freeman–Carroll method [24] using the equation

$$\Delta \log(dW/dt) = n \cdot \Delta \log W_r - (\Delta E/2.3R)\Delta(1/T) \tag{1}$$

TABLE 2 Degradation Characteristics of Mixes A–D

Mix no.	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Peak rate of degradation (R_{max}) (%/min)	Residue at 600°C (%)
Mix A	325.00	460.79	27.00	5.822
Mix B	336.11	462.77	26.00	4.814
Mix C	356.22	449.84	27.00	4.556
Mix D	338.89	459.71	28.91	4.596
Neat nylon fiber	362.50	455.08	47.13	1.255

where dW/dt is the rate of reaction, n is the order of reaction, R is the gas constant, T is the absolute temperature, and W_r is proportional to the amount of reactant remaining.

The equation can be rearranged to

$$\frac{(\Delta \log dW/dt)}{\Delta \log W_r} = n - \frac{(\Delta E/2.3R)\Delta(1/T)}{\Delta \log W_r} \tag{2}$$

The order the reaction and activation energies, ΔE, can be obtained from the intercept and gradient of the plot of the left side of Eq. 2 versus $\Delta(1/T)/\Delta \log W_r$ and such plots are given in Figure 2. The intercepts show that the degradation of gum and composites follow first order kinetics. Similar results have been reported earlier [15,17].

The thermal degradation of the gum and the composites in the presence of epoxy resin–based bonding agent was also studied. Figures 3–6 show the derivative TGA curves of gum and the composites with bonding agent. It is observed that all the mixes containing bonding agent also show a single step degradation pattern. For the gum compound the onset of degradation remains constant with resin concentration and the maximum temperature of degradation does also not vary
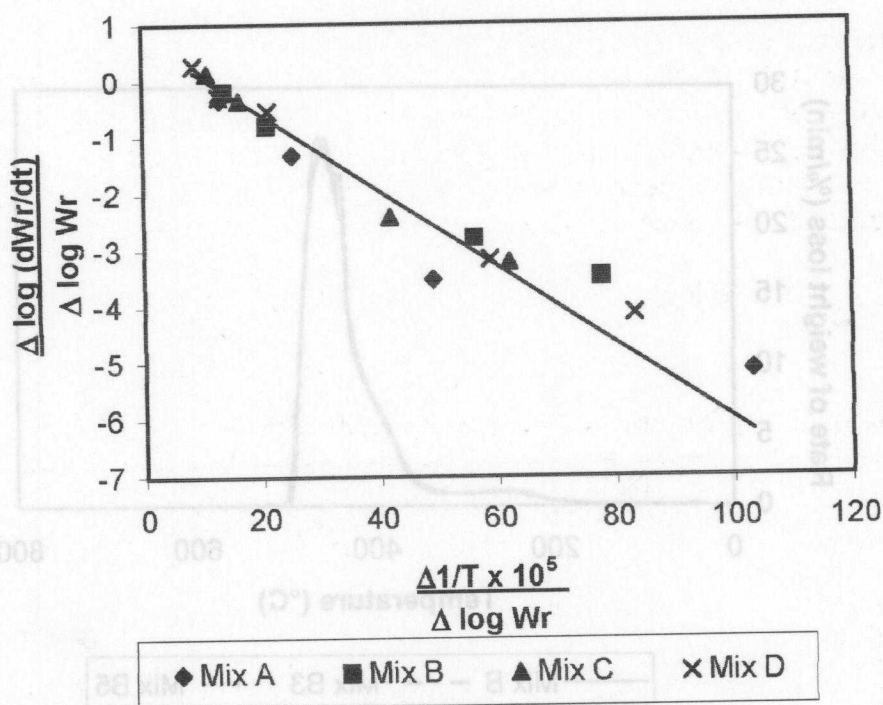

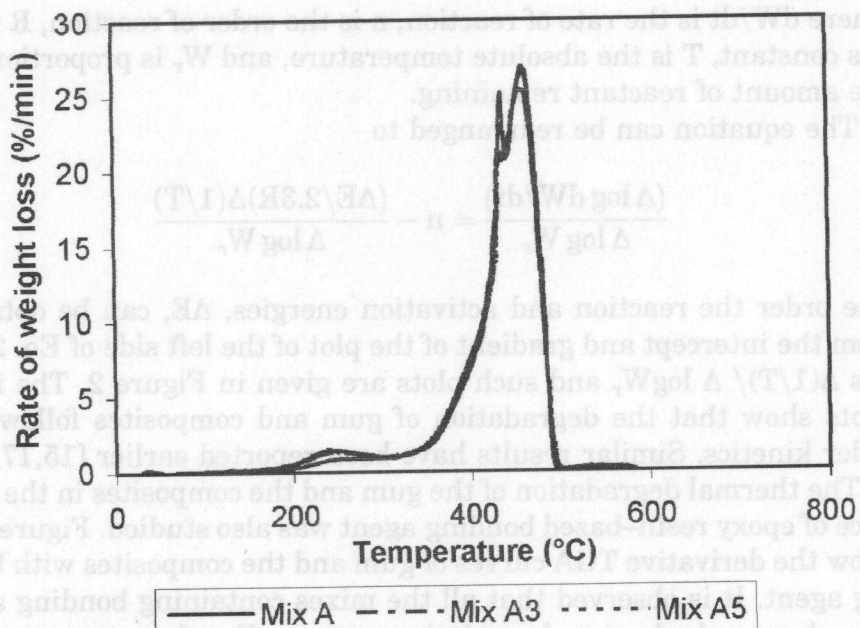**FIGURE 2** Freeman–Carroll Plot of Mix A, Mix B, Mix C, and Mix D.

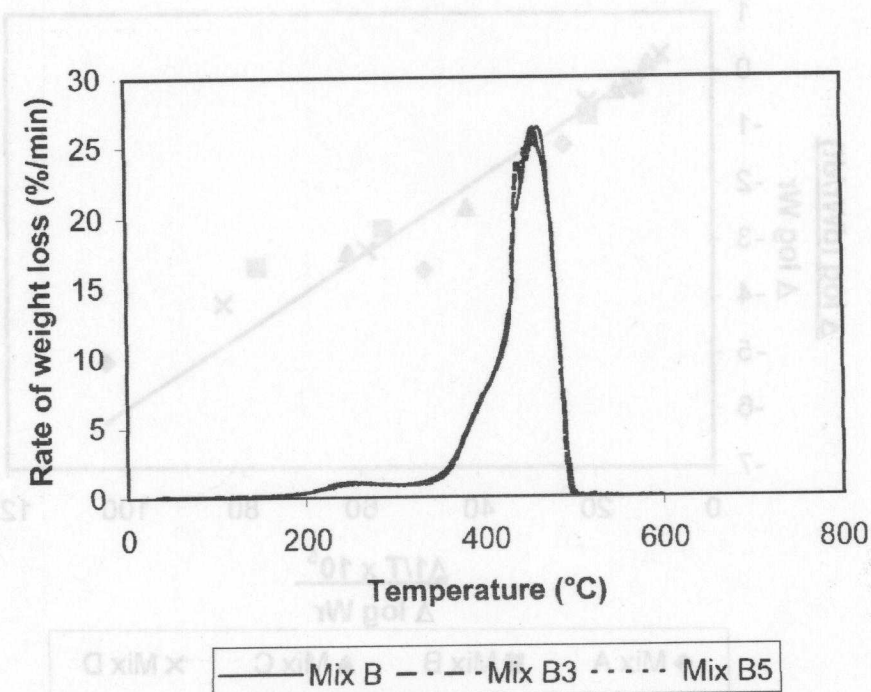**FIGURE 3** TGA traces of Mix A, Mix A3, and Mix A5.

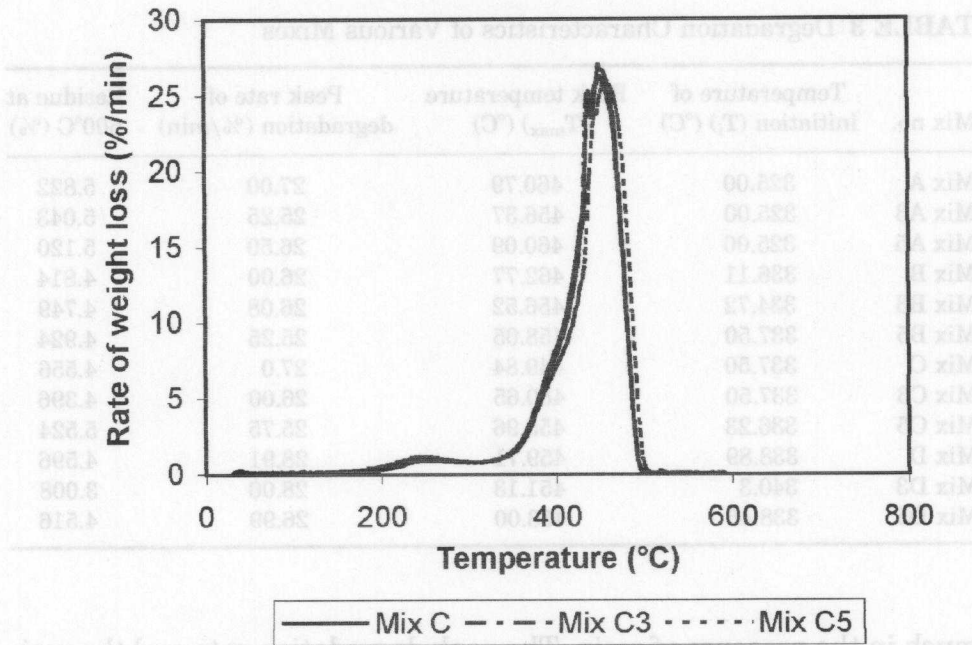**FIGURE 4** TGA traces of Mix B, Mix B3, and Mix B5.

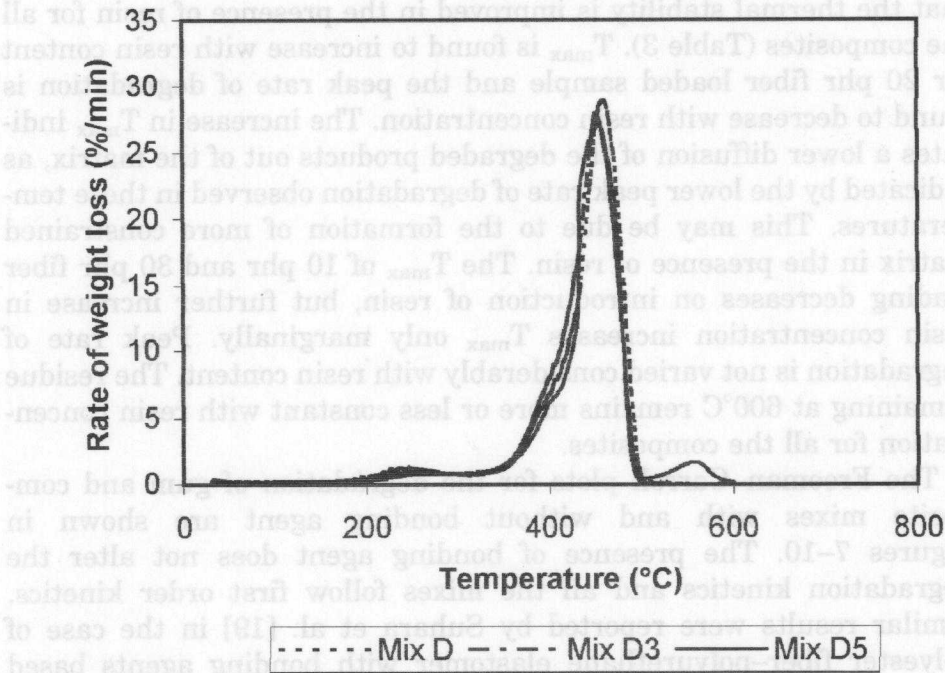**FIGURE 5** TGA traces of Mix C, Mix C3, and Mix C5.

much in the presence of resin. The peak degradation rate and the residue at 800°C only marginally increased with resin content in case of the SBR (Table 3).

In the case of composites the initiation of degradation (T_i) is shifted to higher temperature in the presence of bonding agent, indicating that the thermal stability is improved in the presence of resin for all the composites (Table 3). T_{max} is found to increase with resin content for 20 phr fiber loaded sample and the peak rate of degradation is found to decrease with resin concentration. The increase in T_{max} indicates a lower diffusion of the degraded products out of the matrix, as indicated by the lower peak rate of degradation observed in those temperatures. This may be due to the formation of more constrained matrix in the presence of resin. The T_{max} of 10 phr and 30 phr fiber loading decreases on introduction of resin, but further increase in resin concentration increases T_{max} only marginally. Peak rate of degradation is not varied considerably with resin content. The residue remaining at 800°C remains more or less constant with resin concentration for all the composites.

The derivative thermograms of the gum vulcanizates and composite mixes with and without bonding agent are shown in Figures 7–10. The presence of bonding agent does not alter the degradation kinetics and all the mixes follow first order kinetics. Similar results were reported by Sabaa et al. [19] in the case of polyester–polyurethane elastomers with bonding agents based on polypropylene glycol and glycerol with 4,4′-diphenyl methane diisocyanate.

FIGURE 6 TGA traces of Mix D, Mix D3, and Mix D5.

TABLE 3 Degradation Characteristics of Various Mixes

Mix no.	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Peak rate of degradation (%/min)	Residue at 600°C (%)
Mix A	325.00	460.79	27.00	5.822
Mix A3	325.00	456.37	25.25	5.043
Mix A5	325.00	460.09	26.50	5.120
Mix B	336.11	462.77	26.00	4.814
Mix B3	334.72	456.52	26.08	4.749
Mix B5	337.50	458.05	25.25	4.924
Mix C	337.50	449.84	27.0	4.556
Mix C3	337.50	450.65	26.00	4.396
Mix C5	336.23	455.96	25.75	5.524
Mix D	338.89	459.71	28.91	4.596
Mix D3	340.3	451.13	28.00	3.008
Mix D5	338.46	453.00	26.99	4.516

much in the presence of resin. The peak degradation rate and the residue at 600°C only marginally decrease when the resin is introduced to the SBR (Table 3).

In the case of composites the initiation of degradation (T_i) is shifted to higher temperature in the presence of bonding agent, indicating that the thermal stability is improved in the presence of resin for all the composites (Table 3). T_{max} is found to increase with resin content for 20 phr fiber loaded sample and the peak rate of degradation is found to decrease with resin concentration. The increase in T_{max} indicates a lower diffusion of the degraded products out of the matrix, as indicated by the lower peak rate of degradation observed in these temperatures. This may be due to the formation of more constrained matrix in the presence of resin. The T_{max} of 10 phr and 30 phr fiber loading decreases on introduction of resin, but further increase in resin concentration increases T_{max} only marginally. Peak rate of degradation is not varied considerably with resin content. The residue remaining at 600°C remains more or less constant with resin concentration for all the composites.

The Freeman–Carroll plots for the degradation of gum and composite mixes with and without bonding agent are shown in Figures 7–10. The presence of bonding agent does not alter the degradation kinetics and all the mixes follow first order kinetics. Similar results were reported by Suhara et al. [19] in the case of polyester fiber–polyurethane elastomer with bonding agents based on polypropylene glycol and glycerol with 4,4′-diphenyl methane diisocyanate.
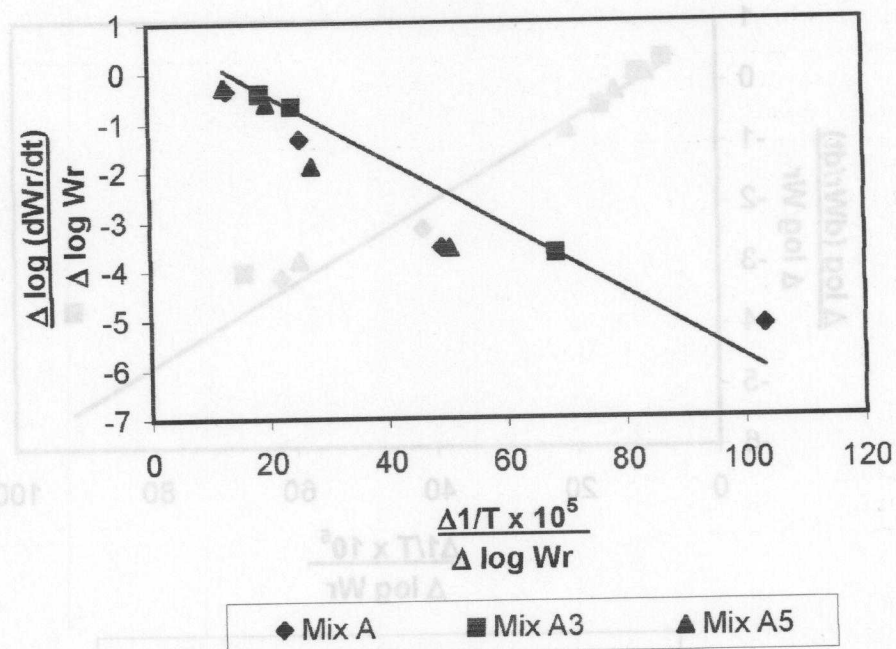
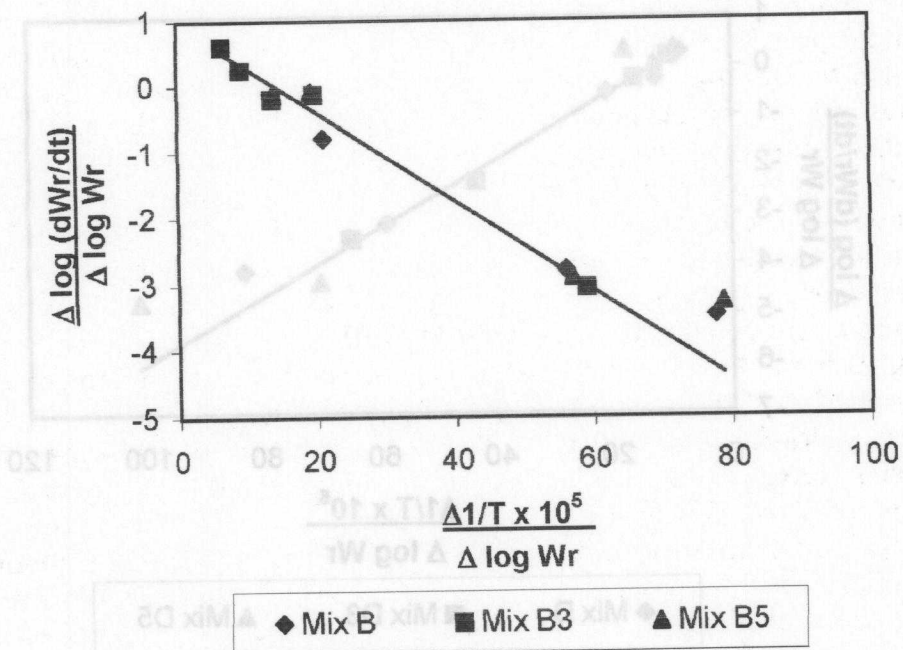FIGURE 7 Freeman–Carroll Plot of Mix A, Mix A3, and Mix A5.

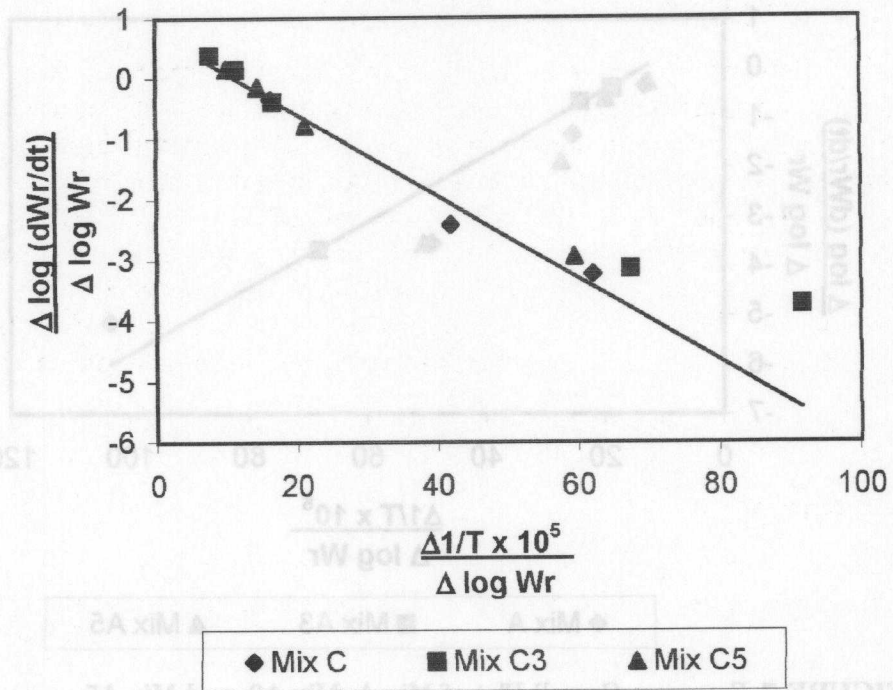FIGURE 8 Freeman–Carroll Plot of Mix B, Mix B3, and Mix B5.

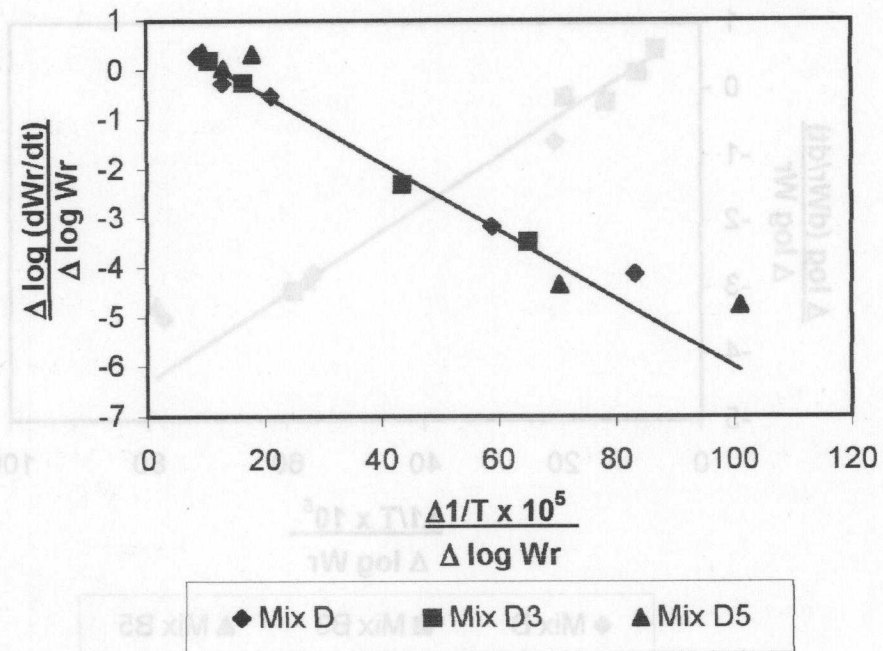FIGURE 9 Freeman–Carroll Plot of Mix C, Mix C3, and Mix C5.

FIGURE 10 Freeman–Carroll Plot of Mix D, Mix D3, and Mix D5.

CONCLUSIONS

The following conclusions can be drawn from the present study. The degradation of SBR gum compound and composites with and without epoxy bonding agent follows a single step degradation pattern. The thermal stability of the Styrene butadiene rubber increases in the presence of short nylon fiber. The thermal stability of SBR vulcanizate is not affected by the presence of bonding agent. Bonding agent improved the thermal stability of the composites and the effect is more pronounced at lower fiber concentrations. The degradation of the virgin elastomer and the composites with and without bonding agents follows first order kinetics.

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