Characterization of Short Nylon-6 Fiber/Acrylonitrile Butadiene Rubber Composite by Thermogravimetry

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Abstract: The thermal degradation of short nylon-6 fiber reinforced acrylonitrile butadiene rubber (NBR) composites with and without epoxy-based bonding agent has been studied by thermogravimetric analysis (TGA). It was found that the onset of degradation shifted from 330.5 to 336.1°C in the presence of short nylon fiber, the optimum fiber loading being 20 phr. The maximum rate of degradation of the composites was lower than that of the unfilled rubber compound, and it decreased with increase in fiber concentration. The presence of epoxy resin-based bonding agent in the virgin elastomer and the composites improved the thermal stability. Results of kinetic studies showed that the degradation of NBR and the short nylon fiber reinforced composites followed first-order kinetics.

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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 such as 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] Corrêa et al. studied the influence of short fibers on the thermal resistance of the matrix and Tg and kinetic parameters of the degradation reaction of thermoplastic polyurethane and found that thermal resistance of aramid fiber-reinforced composite was greater than that of carbon fiber-reinforced composites.[13] The degradation characteristics of Kevlar fiber-reinforced thermoplastics were reported by Kutty et al.[14] Younan et al. studied the thermal stability of natural rubber polyester short fiber composites.[15] Suhara et al. studied thermal degradation of short polyester fiber-polyurethane elastomer composite and found that incorporation of the short fiber enhanced the thermal stability of the elastomer.[16] Rajeev et al. studied thermal degradation of short melamine fiber-reinforced EPDM, maleated EPDM, and nitrile rubber composite 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 the dry bonding system.[17] Shield et al. used thermogravimetric technique to study the blends of acrylonitrile butadiene rubber (NBR) and styrene butadiene rubber (SBR).[18] 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.'' Thermal studies on sulphur-, peroxide-, and radiation-cured NBR and SBR vulcanizates containing carbon black and silica fillers were carried out by Ahmed et al. and they found that radiation-cured vulcanizates had better thermal stability.[19] The cure and mechanical properties of short nylon-6 fiber-reinforced NBR were reported earlier by Sreeja and Kutty.[20] We have reported the cure and mechanical properties of short nylon-6 fiber-reinforced NBR containing epoxy resin as bonding agent.[21] Thermogravimetric studies of short nylon-6 fiber-reinforced NBR will provide an insight into the thermal stability and degradation pattern of these composites. The nylon fiber and other additives will influence the thermal stability of the NBR. No systematic study has been carried out on the thermal degradation of short nylon-6 fiber-NBR composites. In the present article we report the thermal degradation studies of short nylon-6 reinforced NBR rubber composites containing epoxy resin as bonding agent.

EXPERIMENTAL

Epoxy resin (LAPOX A31) and hardener (LAPOX K30) were procured from Cibatul Limited (Gujarat, India). Acrylonitrile butadiene rubber was supplied by Apar Polymers Ltd. (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 composites is given in Table I. The composites were prepared as per ASTM D 3182 (1989) on a two-roll laboratory size mixing mill. All the composites were vulcanized at 150°C in an electrically heated hydraulic press to their respective cure times, as obtained from a Goettfert Elastograph Model 67.85. Thermogravimetric analyses were carried out on a Universal V3 2B TA instrument with a heating rate of 10°C/minute under nitrogen atmosphere.

RESULTS AND DISCUSSION

The derivative TGA curves of composites A–D and neat fiber are shown in Figure 1. The temperature of onset of degradation (T_i), the temperature at which the rate of decomposition is maximum (T_{max}), the peak degradation rate, and the residue at 600°C are given in Table II. The NBR degrades in a single step. The degradation starts at a temperature of 330.5°C and the maximum rate of degradation is 9.1%/min. Neat nylon fiber also degrades in a single step with maximum rate of degradation 47.1%/min and the corresponding temperature is 455°C. The residue remaining at 600°C is 1.2% for fiber. It can be seen from Figure 1 that the composites show a degradation pattern similar to that of unfilled rubber. As fiber fraction increases, the temperature of onset of degradation is shifted to higher temperature up to 20 phr fiber loading

Table I. Formulation of composites

| Ingredients | Composites | | | | | | | | | | | |
	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[a]	0	0	0	0	3	3	3	3	5	5	5	5

[a]Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener (zinc oxide, 5 phr; stearic acid, 4 phr; sulphur, 0.7 phr; dibenzothiazyldisulfide (MBTS), 1 phr; tetramethyl thiuramdisulfide (TMTD), 1.8 phr are common to all mixes).
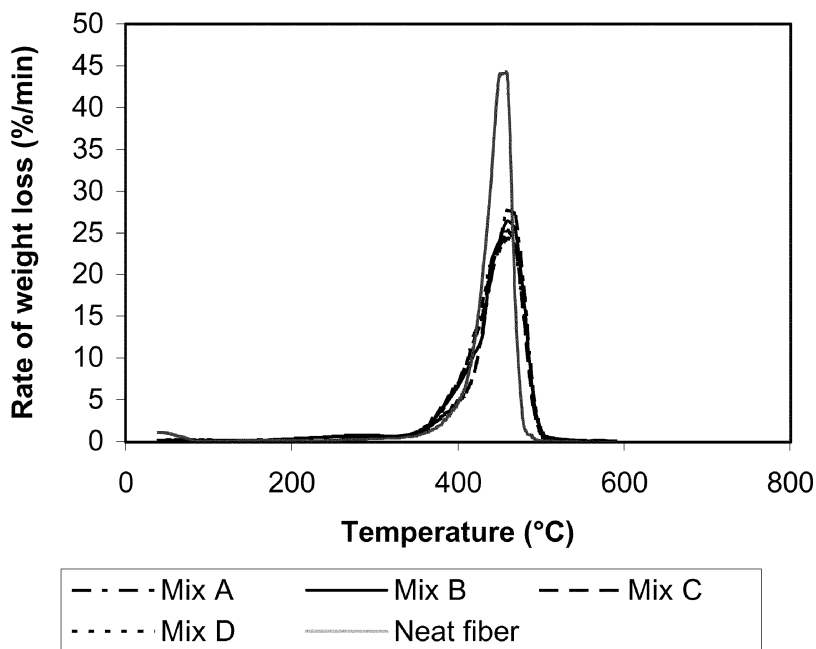
Figure 1. TGA traces of composites A–D.

(330.5 to 336.1°C), indicating improved thermal stability of the composites (Table II). Similar results have been reported earlier by Kutty et al.[14] Beyond 20 phr, fiber concentration T_i is not improved. T_{max} marginally decreases as fiber concentration increases. The maximum rate of degradation decreases with fiber concentration, and 30 phr fiber-loaded composite has the lowest maximum rate of degradation.

The residue remaining at 600°C is less for the composites than for the gum compound. Since the char yield of the neat fiber at 600°C is very low (1.2%), the composites show relatively lower residue weight at 600°C.

Table II. Degradation characteristics of composites A–D

Composite	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Maximum rate of decomposition (%/min)	Residue (%)
A	330.5	464.4	28.1	9.1
B	333.3	463.4	26.9	7.5
C	336.1	462.4	25.2	9.3
D	333.3	461.9	24.1	7.7
Neat nylon fiber	362.5	455.0	47.1	1.2

The order of degradation was calculated by the Freeman-Carroll method[22] using the equation

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

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 above 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 of the reaction and activation energies can be obtained from the intercept and gradient of the plot of the left side of Equation (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 in the case of short Kevlar fiber-reinforced thermoplastic polyurethane composites have been reported by Kutty et al.[14]

The degradation of virgin elastomer and composites containing epoxy resin as bonding agent was also studied. The temperature of
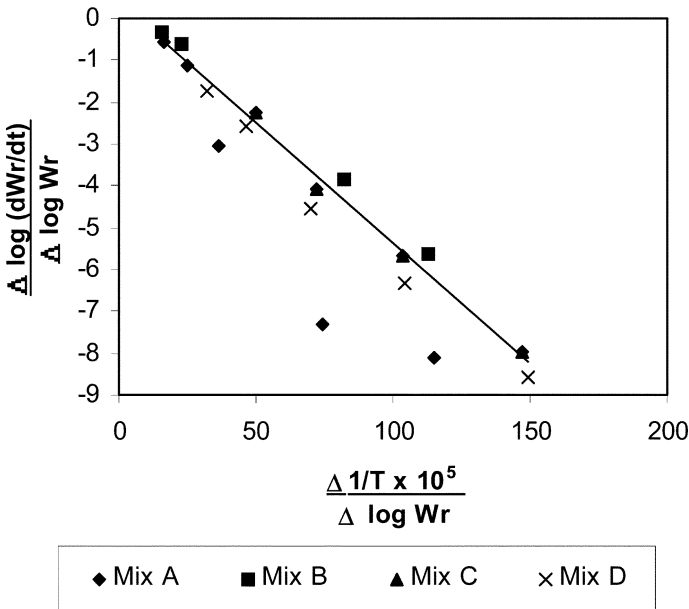

Figure 2. Freeman-Carroll plot of composites A–D.

Table III. Degradation characteristics of various composites

Composite	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Maximum rate of decomposition (%/min)	Residue at 600°C (%)
A	330.5	464.4	28.1	9.1
A3	336.1	463.7	27.2	8.9
A5	336.1	463.6	26.9	9.6
B	333.3	463.4	26.9	7.5
B3	341.6	458.3	26.9	9.4
B5	333.3	463.7	26.3	8.6
C	336.1	462.4	25.2	9.3
C3	336.1	461.4	26.0	9.0
C5	336.1	462.4	25.2	8.8
D	333.3	461.9	24.1	7.7
D3	333.3	458.7	23.7	12.5
D5	330.5	461.2	24.3	8.0

initiation of degradation, peak degradation temperature, maximum rate of decomposition, and residue remaining at 600°C of all the composites are given in Table III. The effect of resin on unfilled rubber is studied by varying resin concentration from 0 to 5 phr and it was found that the unfilled rubber containing bonding agent show a degradation pattern similar to that of virgin rubber. The T_i is shifted from 330.5 to 336.1°C in the presence of epoxy resin, indicating improved thermal stability of the unfilled rubber compound in the presence of bonding agent (Table III). Beyond 3 phr, T_i is not improved. Peak degradation temperature remains constant with resin concentration. The maximum rate of degradation decreases marginally with resin concentration. The residue at 600°C remains more or less constant with resin content. The Freeman-Carroll plot for the degradation of unfilled rubber with and without epoxy resin (A, A3, and A5) shows that all the mixtures follow first-order kinetics (Figure 3).

The effect of the resin on the composites is also studied by varying the resin concentration from 0 to 5 phr. At low fiber concentration (10 phr), the degradation starts at higher temperature in the presence of epoxy resin, indicating better thermal stability of the composite. In the case of higher fiber loaded composites, on introduction of resin, T_i is not much affected. However at 5 phr, there is a decrease in T_i. There is no significant change in T_{max} with resin content at all fiber loading. Maximum rate of degradation is not much affected by the presence of resin for all composites. The residue at 600°C remains almost independent of the resin loading.
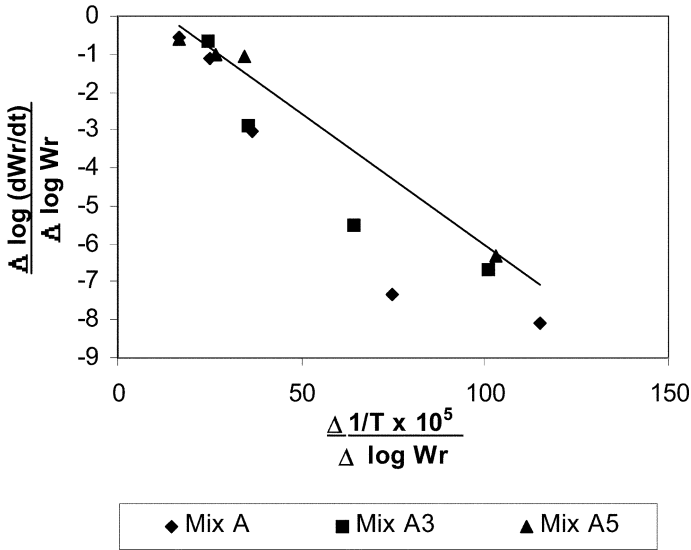
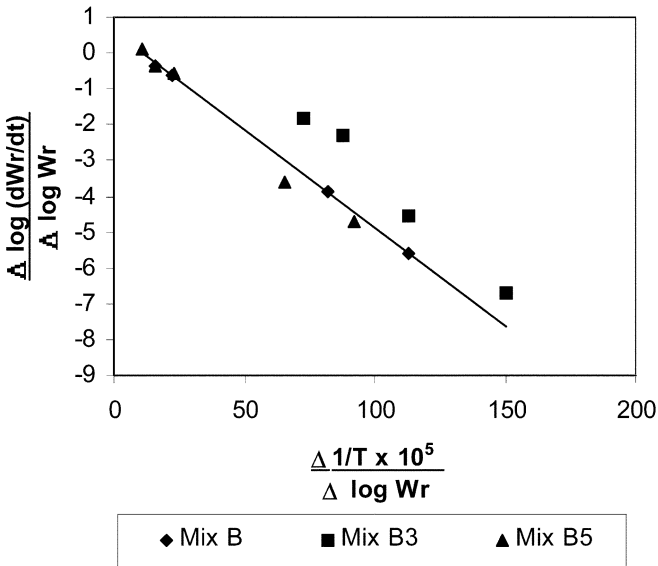**Figure 3.** Freeman-Carroll plot of unfilled rubber with various resin loadings.

Figure 4. Freeman-Carroll plot of composites B, B3, and B5.

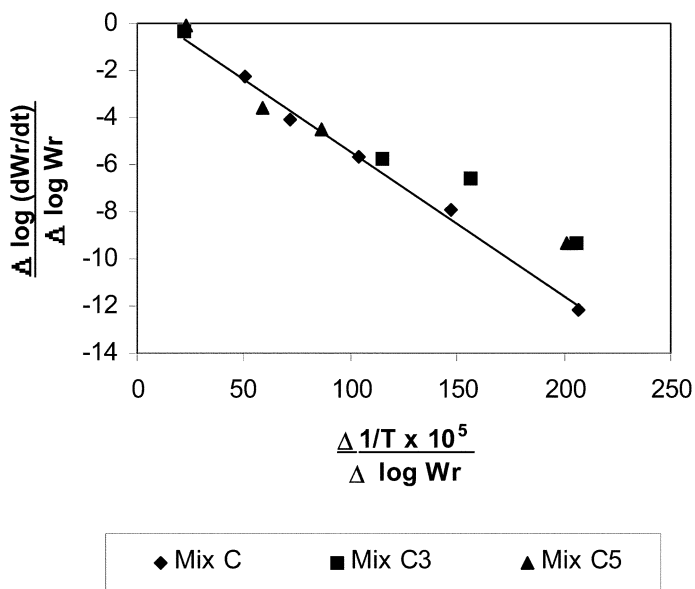A. Seema and S. K. N. Kutty

Figure 5. Freeman-Carroll plot of composites C, C3, and C5.
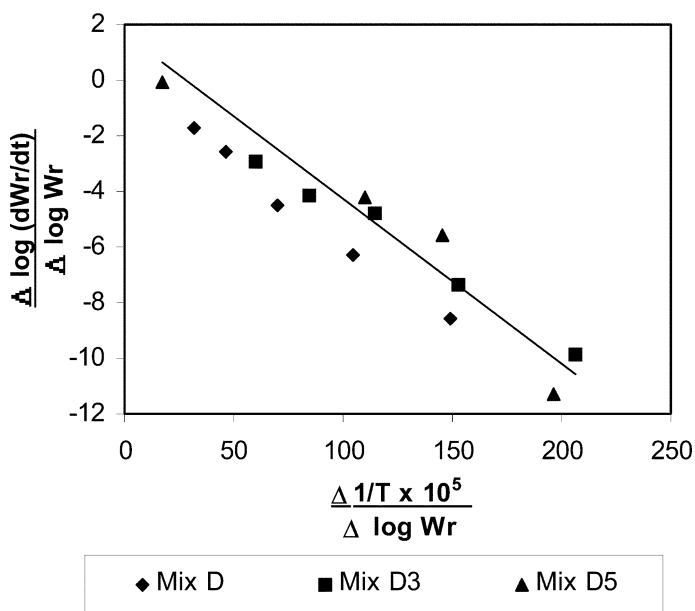

Figure 6. Freeman-Carroll plot of composites D, D3, and D5.

The Freeman-Carroll plots for the degradation of composites with and without bonding agent are shown in Figures 4–6. The presence of bonding agent does not alter the degradation kinetics and all the mixes follow first-order kinetics. Similar results have been reported by Suhara et al.[16] in the case of polyester fiber-polyurethane elastomer with bonding agents based on polypropylene glycol and glycerol with 4,4' diphenyl methane diisocyanate.

CONCLUSIONS

The following conclusions can be drawn from the present study.

The degradation of unfilled NBR and composites follows a single-step degradation pattern. Nylon-6 fibers increase the thermal stability of acrylonitrile butadiene rubber, the optimum being at 20 phr fiber loading. The presence of epoxy resin bonding agent improves the thermal stability of the virgin rubber and composites containing lower fiber loading. At higher fiber loading the resin does not effectively improve the thermal stability. The degradation of the virgin elastomer and the composites with and without bonding agents follow first-order kinetics.

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