

Thermal Degradation of Epoxy Resin Reinforced with Polypropylene Fibers

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ABSTRACT: The influence of polypropylene fibers on the thermal degradation of epoxy composites was investigated with thermogravimetric analysis. Three composites with 5, 10, or 15 wt % polypropylene fibers were prepared with epoxy as a matrix material. The polypropylene fibers, used as reinforcing materials, retarded the thermal decomposition, and increasing the weight percentage of the fiber material increased the thermal stability to a certain extent. Of the three composites, the 10 wt % polypropylene fiber/epoxy resin composite showed very good thermal stability, which was indicated by the increase in the resin decomposition

temperature from 280°C for the 5 wt % polypropylene fiber/epoxy resin composite to 375°C for the 10 wt % polypropylene fiber/epoxy resin composite. The Horowitz–Metzger method was used to calculate the activation energies, and the results were tabulated. A morphological analysis was carried out with scanning electron microscopy to evaluate the dispersion of the fibers in the epoxy matrix. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 500–503, 2007

Key words: activation energy; composites; fibers; matrix; poly(propylene) (PP); thermogravimetric analysis (TGA)

INTRODUCTION

Polypropylene (PP) fibers are attractive candidates as reinforcing components for low-cost composite materials because of their low cost, relatively high fiber strength, and low density.¹ Because of these properties, PP and its composites have been used in many applications, such as automobiles, electrical and electronic applications, furniture, construction and architecture, interiors, and insulation.² Most of the polymers are generally subjected to a degradation of the mechanical and physical properties with an increase in the temperature. Fundamental information regarding the thermal stability of the composite materials to be processed is obtained from thermogravimetric analysis (TGA) and differential scanning calorimetry.³ It has been reported that the chemical composition, heating rate, temperature, and inorganic substances are the major factors that affect the thermal behavior of composites.⁴ The kinetics of exothermic reactions is important in assessing the potential of both the materials and systems for thermal exposition. The determination of detailed kinetic parameters such as the activation energy from TGA is carried out to analyze a composite's thermal degradation behavior.⁴ PP fibers have been used to

enhance the properties of both fresh and hardened concretes, and PP-fiber reinforcement retards the corrosion of reinforcing steel in concrete.⁵ Even though voluminous literature is available on composite materials with PP^{6–8} and modified PP⁹ as matrix materials, much less attention has been paid to the use of PP fibers as filler materials. A literature survey has revealed that the incorporation of thermoplastic fibers into thermosets has not been reported. These types of composites are unique materials involving the combination of thermosets and thermoplastics. Therefore, in this study, the thermal behavior of composites with PP fibers as filler materials and an epoxy resin as a matrix were evaluated with TGA.

EXPERIMENTAL

Materials

The matrix system consisted of a medium-viscosity diglycidyl ether of bisphenol A epoxy resin (Lapoxl-12) and a room-temperature-curing hardener with a tetraamine functional group (K-6), which were supplied by Atul India, Ltd. (Bombay, India). The density of the cured neat resin was 1120 kg/m³. The short PP fibers were obtained from Reliance Polymers, Ltd. (Bombay, India). These PP fibers were cut into short fibers with an average length of 3 mm.

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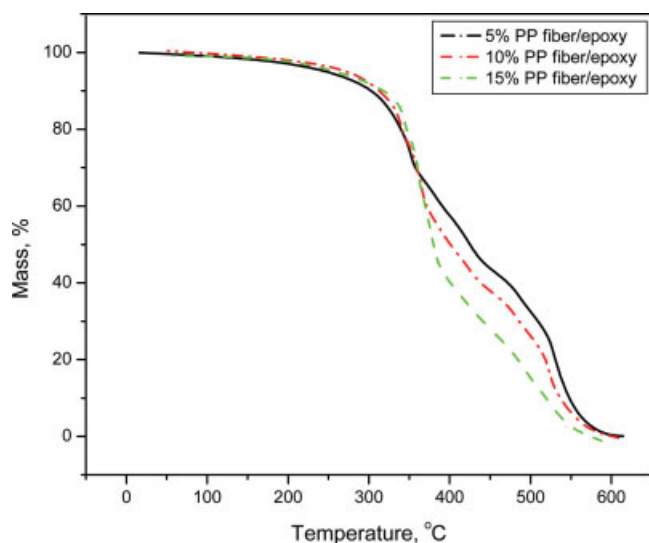


Figure 1 Thermograms of composites of PP fiber and epoxy resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparation of the composites

A measured quantity of the epoxy resin was mixed with a preweighed amount of the PP fibers, and the hardener was added to this with gentle stirring to minimize the formation of air bubbles. The mold for the specimen preparation was 320 mm \times 170 mm \times 3 mm and was completely covered on all sides with a Teflon sheet with a coating of a silicone releasing agent for the easy removal of the cast specimen. The mixture was then slowly decanted to the mold. The mixture was left to cure at room temperature for about 24–26 h. The cured rigid-plate sample was withdrawn from the mold, and the edges were trimmed. In this way, epoxy-based systems with various concentrations of short PP fibers (5, 10, and 15 wt %) were cast.

TGA and morphological analysis

TGA measurements were carried out with 10 mg of PP fiber/epoxy resin composite samples at a heating rate of 10°C/min in a nitrogen atmosphere with a thermogravimetric analyzer (SDTQ 600, TA Instruments). The thermal decomposition of each sample occurred in a programmed temperature range between room temperature and 600°C. The continuous records of the weight loss and temperature were determined and analyzed to determine the nature of the thermal degradation, initial degradation temperature, and complete degradation temperature. The morphology of the prepared composites was examined with a Hitachi S-4700 scanning electron microscope (Hitachi Technologies America, Inc.).

RESULTS AND DISCUSSION

The weight loss of the prepared composites as a function of temperature was determined by a TGA technique and was an irreversible process due to thermal degradation. Thermograms of 5, 10, and 15 wt % PP fiber/epoxy resin composites are shown in Figure 1. The thermograms of these materials show a two-stage weight loss. The small initial weight loss of all three PP fiber/epoxy resin composites can be attributed to the evaporation of moisture and removal of air bubbles present.

The 5 wt % PP fiber/epoxy resin composite system (Fig. 1) shows an earlier onset of thermal degradation between 275 and 375°C, seemingly because of resin decomposition. This can be clearly confirmed by the derivative weight-loss curve exhibiting a peak at 280°C. However, the filler material retards the main weight loss of the polymer. In the derivative weight-loss curve, the major decomposition rate of the polymer appears at 520°C, and complete decomposition occurs around 600°C.

The 10 wt % PP fiber/epoxy resin composite system (Fig. 1) shows an earlier onset of thermal degradation between 250 and 380°C because of resin decomposition. This is confirmed by the derivative weight-loss curve exhibiting a distinct peak at 375°C. The main weight loss in this case occurs at 530°C. The complete decomposition occurs around 600°C.

The 15 wt % PP fiber/epoxy resin composite system (Fig. 1) shows interesting thermal degradation that looks like major decomposition between 265 and 380°C; this is confirmed by the derivative weight-loss curve exhibiting a distinct peak at 380°C.

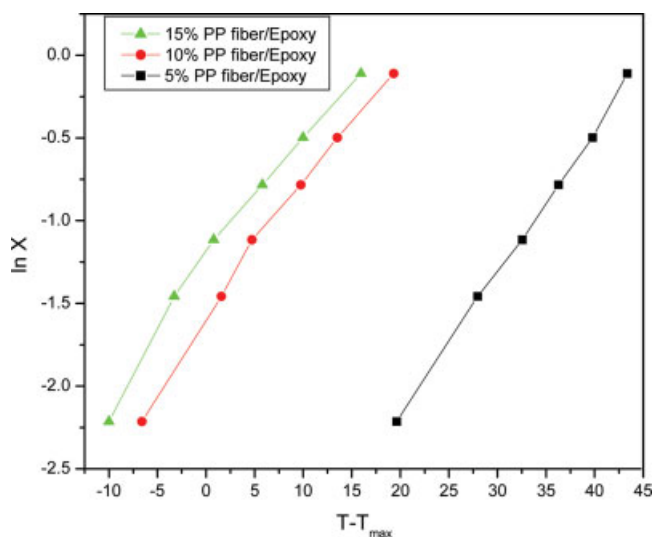


Figure 2 Plots of $\ln X$ versus $T - T_{\max}$ for calculating the activation energies of stage I of the decomposition for all samples by the Horowitz–Metzger method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

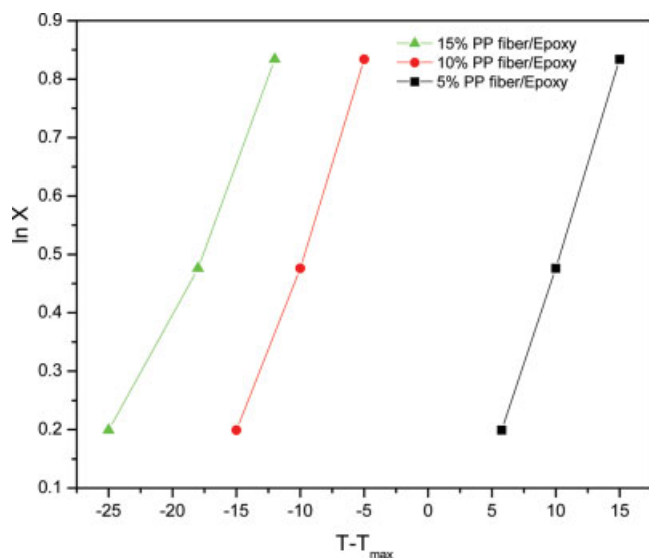


Figure 3 Plots of $\ln X$ versus $T - T_{max}$ for calculating the activation energies of stage II of the decomposition for all samples by the Horowitz–Metzger method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This can be attributed to the fact that the optimum resin fraction is reduced because of an increase in the fiber fraction. However, the fiber retards complete degradation until the temperature reaches approximately 600°C, with second-stage decomposition occurring at 530°C.

The results show that PP fibers used as reinforcing materials retard the thermal decomposition, and this can be attributed to the binding of the fiber material to the resin. An increase in the weight percentage of the fiber material increases the thermal stability to a certain extent. This may be due to the increased binding of fibers to the resin. Of the three composites, the 10 wt % PP fiber/epoxy resin composite shows very good thermal stability, which has been shown by the increase in the resin decomposition (first-stage decomposition) temperature from 280°C for the 5 wt % PP fiber/epoxy resin composite to 375°C for the 10 wt % PP fiber/epoxy resin composite. However, there is a marginal increase in the resin decomposition temperature of 380°C for the 15 wt % PP fiber/epoxy resin composite. Because increasing the volume fraction beyond a certain limit reduces the per-

formance of the composite, as a minimum amount of the matrix is necessary for the system,¹⁰ an increase in the weight percentage of the PP fiber may not contribute much to increasing the resin decomposition temperature for the 15 wt % PP fiber/epoxy resin composite. For all three composites, the major decomposition occurs between 520 and 530°C, and complete decomposition takes place around 600°C.

The Horowitz–Metzger integral kinetic method¹¹ was applied to calculate the kinetic parameters. This method can determine the decomposition activation energy with only one heating rate. In this study, the TGA curves at a heating rate of 10°C/min were used to calculate the degradation kinetics for all samples with the following equation:

$$\ln X = E\theta/RT_{max}^2$$

where X is equal to $\ln[\ln(1 - \alpha)^{-1}]$, E is the activation energy, θ is the difference between the temperature (T) and maximum temperature (T_{max}), R is universal gas constant and α is the heating rate. The activation energy can be determined from a linear fit to the plot of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ . The plot for stages I and II of the decomposition for all samples by the Horowitz–Metzger method is shown in Figures 2 and 3, respectively. The calculated activation energies and maximum decomposition rates are reported in Table I. The obtained results show that the activation energy increases with increasing fiber content in both stages. This is attributed to the fact that the addition of fibers influences the degradation behavior of the epoxy resin by self-decomposition at relatively low temperatures and then forms protective layers and releases noncombustible gases at higher temperatures to increase the thermal stability. To compare the degradation behaviors, Table I lists the maximum weight-loss rates for both stages of degradation of the samples.

Scanning electron microscopy pictures of the fractured surfaces of the prepared composites are shown in Figure 4. Figure 4(a) highlights the brittle fracture of the neat resin, and the remaining figures are of composites. An increase in the fiber loading results in more ductile tearing of the matrix resin. However, most of the fibers are intact without any damage. This further reveals the possibility of matrix-dominated

TABLE I
Calculated Values of the Activation Energy (E) and Maximum Weight-Loss Rate (R_{max}) for Stages I and II of All Samples by the Horowitz–Metzger Method

Sample	Stage I		Stage II	
	E (kJ/mol)	R_{max} (wt %/min)	E (kJ/mol)	R_{max} (wt %/min)
5% PP fiber/epoxy	95.6	0.97	120.78	4.66
10% PP fiber/epoxy	101.84	5.12	127.83	4.96
15% PP fiber/epoxy	103.33	5.82	165.7	4.37

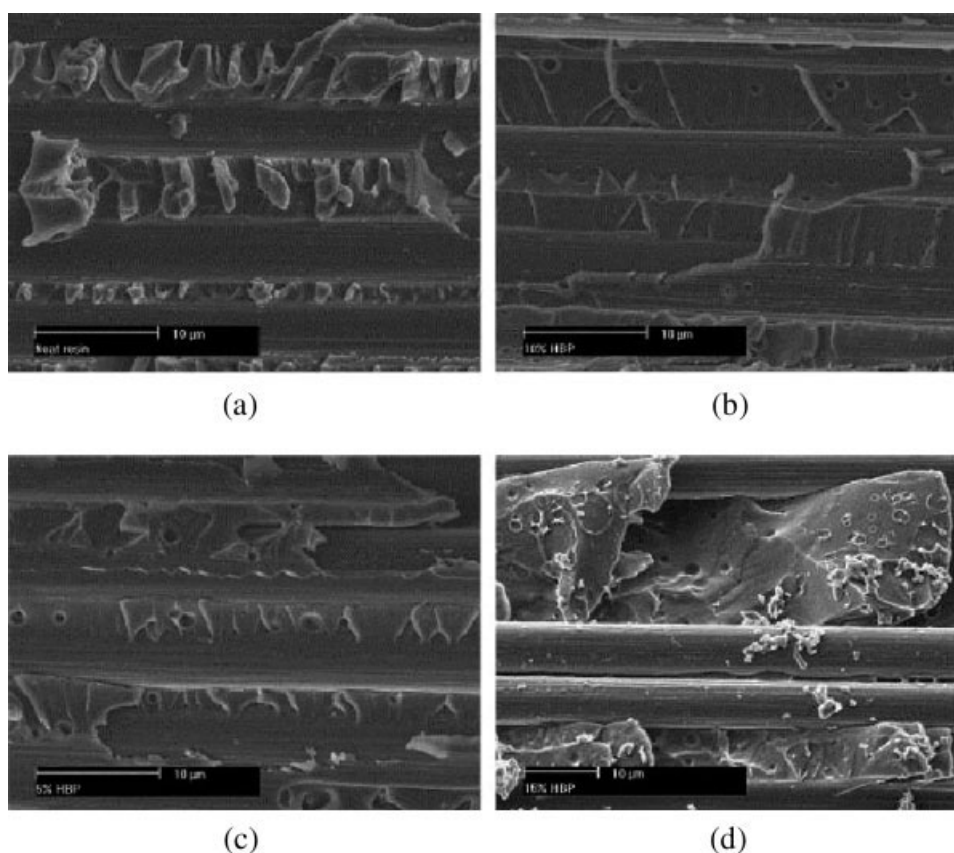


Figure 4 Scanning electron microscopy pictures of fractured surfaces of (a) neat epoxy, (b) epoxy loaded with 10% PP fibers, (c) epoxy loaded with 5% PP fibers, and (d) epoxy loaded with 15% PP fibers.

failure in such materials. The scanning electron microscopy pictures undoubtedly indicate a uniform distribution of the fibers in the matrix.

CONCLUSIONS

An increase in the fiber content increases the thermal stability of composites to a certain extent. Fibers can be added until the optimum fraction to get thermally stable composites. The 10 wt % PP fiber/epoxy resin composite gives better thermal stability because the 15 wt % PP fiber/epoxy resin composite's thermal stability is marginally increased with an increase in the weight percentage of the reinforcing material. The activation energy in both degradation stages increases with an increase in the fiber content. This is attributed to the fact that the addition of fibers influences the degradation behavior of the epoxy resin by self-decomposition at relatively low temperatures and then forms protective layers and releases noncombustible gases at higher temperatures. Scanning electron microscopy analysis has indicated the good dispersion of the fibers in the matrix.

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