

Mechanical Properties of Fiber-Reinforced Natural Rubbers Using Surface-Modified PET Fibers Under EB Irradiation

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ABSTRACT: Aiming to develop a high performance fiber-reinforced natural rubber (NR), a special technique using electron beam (EB) irradiation-induced graft-polymerization was applied to high-strength polyethylene terephthalate (PET) fibers. Although PET is chemically robust, allyl methacrylate (AMA) could be graft-polymerized onto the PET fiber surface with this special technique. The composite of NR and grafted-PET fibers indicated a linear increase in the initial modulus with the fiber content. At the fiber content of 10%, the initial modulus was

improved about five times with respect to that of the pure NR, whereas the breaking strength increased by ca. 35% and the breaking strain decreased by ca. 45%. The fiber-reinforced rubber with a good performance was obtained in the system of NR and grafted-PET fibers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2584–2590, 2009

Key words: natural rubber (NR); high-strength polyethylene terephthalate (PET) fiber; graft-polymerization; electron beam (EB) irradiation; composite

INTRODUCTION

It is well known that the adhesion between a rubber matrix and a fiber surface is quite important for the mechanical properties in a fiber-reinforced rubber composite material.^{1–3}

A tire is a typical one among fiber-reinforced rubbers, in which PET fibers have been much used as a tire-cord because of good physical characteristics except for the chemical robustness, which implies that an effective fiber-matrix adhesion cannot be expected. Therefore, as a matter of fact, lots of additives are required to enhance the adhesion between PET fibers and rubber (mainly natural rubber, NR).

Electron beam (EB) irradiation-induced graft polymerization is a new technique to provide a new function to a polymer by bonding various kinds of monomers to the main chain to form the side-grafted chains in the polymer. This method can be quite effective to a chemically robust polymer^{4–6} like PET or PE since EB irradiation with a high energy can generate active species such as radicals required for a chemical reaction even in such polymers. In addition, an attention has been paid to this method as a

clean process without using initiator of reactions.^{7–12} In our previous papers,^{13,14} it was found that the polar side chains of *N*-vinyl formamide (NVF) were successfully introduced on the surface of ultrahigh molecular weight polyethylene (UHMWPE) fibers by this method of graft polymerization, which showed the high interaction with the rubber matrix of SBR. In addition, the acrylate functional silane were found to be successfully graft-polymerized to the surface of PET fibers by the same method, and the composite of NR and the grafted-PET fibers provided a good result to some extent in the mechanical properties.¹⁵

In this study, the fiber-reinforced NR composites were prepared using PET fibers grafted with AMA and the effect of those fibers on the mechanical properties of the composites was discussed.

EXPERIMENTAL

Materials

PET fibers (1670 dtex, 500 F, crystallinity of 70%, high-modulus type for tire cord, Toyobo Co., Osaka, Japan) and natural rubber (SMR-L, Yokohama Rubber Co., Tokyo, Japan) were used. Allyl methacrylate (AMA) (reagent grade, Tokyo Chemical Industry Co., Tokyo, Japan) was used without further purification. Methacrylic acid and allyl alcohol (reagent

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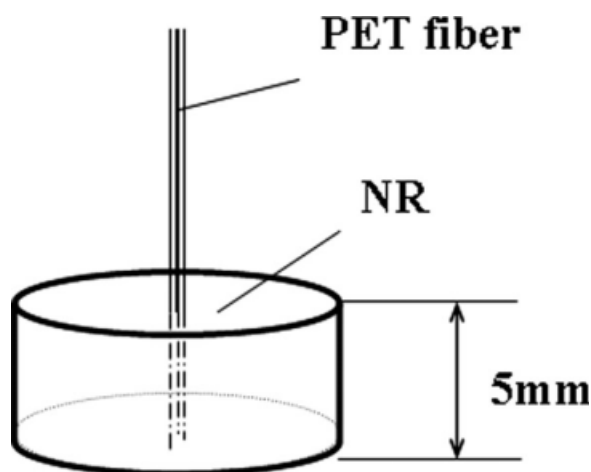


Figure 1 Illustration of test piece for the pulling test.

grade, Tokyo Chemical Industry Co.) were also used without further purification. Other chemical reagents (reagent grade) were used as purchased.

Graft-polymerization with EB irradiation to PET fibers

AMA was dissolved in ethanol to prepare a 4 mol/L solution (4.0M-AMA). PET fibers, which were rinsed with methanol to remove the adhesion of some stains on the fiber surfaces and immersed in the 4.0M-AMA solution at 85°C for 1 h before EB irradiation, were irradiated for a given time to be subjected to 50 to 500 kGy with an EC250/15/180L EB irradiation apparatus, Iwasaki Denki Co. They were graft-polymerized in the same way as described in the previous papers.¹³⁻¹⁵ Then, they were put in an oven at 60°C for 30 min so that subsequent polymerization would proceed further. Finally, the treated-PET fibers were washed with THF for 2 h, methanol for 1 min utilizing supersonic wave to eliminate nonreacted monomers and homopolymers of AMA which did not contribute to graft-polymerization and dried in the oven at 50°C for a few hours. In addition, the two compounds of methacrylic acid and allyl alcohol were examined for graft-polymerization instead of AMA. They were dissolved in a 75% ethanol-water mixture to prepare a 4 mol/L solution and graft-polymerized in the same way as the grafting of AMA except that the procedure of predipping was omitted and the postpolymerization was performed at room temperature instead of 60°C, because of the low-boiling point of allyl alcohol.

Preparation of PET fiber-reinforced NR composites

First, to obtain a vulcanizing mixture, sulfur (1.5 parts per hundred resin, phr), vulcanization promoter (NS-G, 1.0 phr), zinc white (3.0 phr), and

stearic acid (2.0 phr) were thoroughly mixed in an agate mortar with a pestle for a hundred resin of NR. Small bits of NR (ca. 2 mm square) were put on a mixing roller at 100°C, and then the powder of vulcanizing mixture was added to a softened and drawn sheet of NR on the roller. In addition, surface-modified PET fibers, which were cut into about 1 or 2 mm long, were added to it to make a prevulcanized rubber (green rubber) including vulcanizing reagents as well as short fibers of PET. In this way, we got the green rubber sheet with the thickness of about 0.2 mm. This sheet was cut into a lot of small pieces, and they were mixed again on the mixing roller at 100°C. This procedure was repeated five times to mix well the short fibers in the green rubber sheet. Subsequently, the green rubber sheet was cut into small pieces and a given amount of them was put in the metal dumbbell-shape mold and vulcanized at 160°C and 80 kgf/cm² for 20 min. The dumbbell-shape sample was obtained after cooling the mold in water.

Preparation of the sample test pieces for the pulling test

Two metal molding frames, each of which had a 20-mm-long ditch half-cylindrical in shape with a radius of 4 mm, were used. Both ditches were filled with a given amount of small pieces of NR including vulcanizing reagents, and the PET fibers with certain length and weight were aligned on one of them along the cylindrical centerline so that part of the fibers (ca. 10-mm long) was outside of the frame. Then, the other one was laid on it so as to fit the cylindrical line. This was then molded at 160°C and 20 kgf/cm² for 20 min to make a rod of NR with a diameter of 8 mm, including the fibers embedded in the rod along the centerline. Finally, to make the length of the rod constant (5 mm long), the rod was

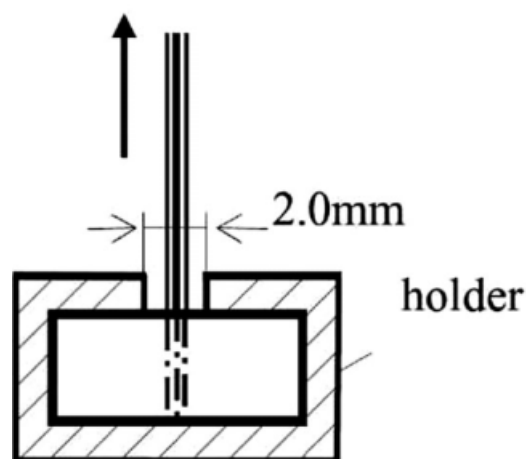


Figure 2 Schematic diagram of the pulling test.

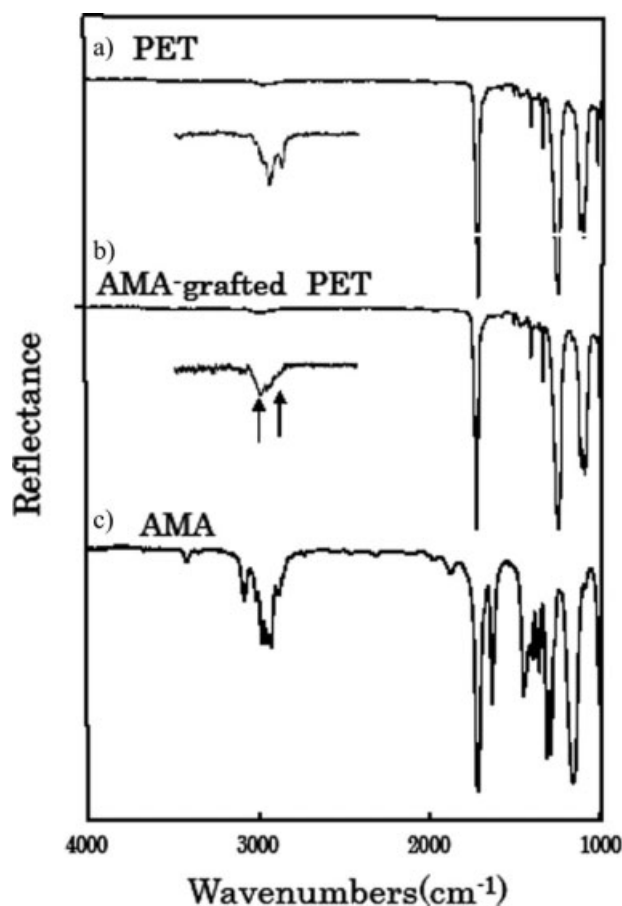


Figure 3 FTIR spectra of (a) untreated-PET fibers, (b) AMA-grafted-PET fibers, and (c) AMA homopolymer (AMA500H). (ATR method).

cut precisely to obtain a rod-like sample test piece, as shown in Figure 1, and this was set in the sample holder illustrated in Figure 2 before the pulling test.

Measurements

Fourier transform infrared (FTIR) spectra of the surface of the PET fibers were measured with the attenuated total reflection (ATR) method with an FTIR spectrophotometer (Nexus 870, Nicolet Instrument Corp.). This apparatus is equipped with a single-reflection ATR accessory with Ge crystal, which is suitable for the measurement to samples such as fine powders and fibers.

TABLE I
Model Compounds and Grafting

Model compound	Grafting (%)
Methacrylic acid $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	2.2
Allyl alcohol $\text{CH}_2=\text{CHCH}_2\text{OH}$	0.3

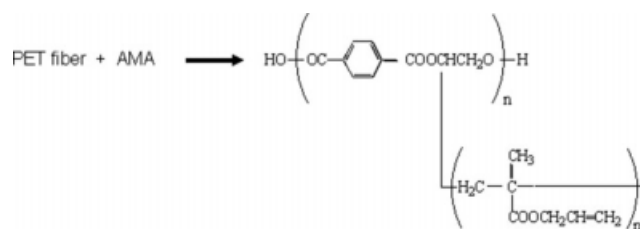


Figure 4 Proposed model for the reaction of grafting onto PET fibers.

The degree of AMA grafting was evaluated as follows with the weights of the PET fiber samples before and after the graft treatment:

$$\text{Grafting} = (w_2 - w_1)/w_1 \times 100 \quad (1)$$

where w_1 and w_2 are the weight of fibers before and after the treatment, respectively.

A pulling test was carried out at room temperature and at a pulling rate of 10 mm/min with a TENSILON UTM-111-100S tensile testing machine equipped with a holder, as illustrated in Figure 2. The relationship between the pulling load and displacement was recorded when the PET fibers were pulled out of the NR matrix.

To estimate the influence of short fibers on the mechanical properties of vulcanized NR composites, stress-strain curves of those composites including a given amount of short fibers of AMA-grafted-PET were measured with a TENSILON UTM-111-100S at an elongation rate of 20 mm/min. The composite sample was 25 mm long and 5 mm wide with the thickness of about 1 mm.

The fractured surfaces of the composites were observed by Scanning Electron Microscope (SEM, JEOL JSM-6390IH).

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectra of untreated and AMA-treated PET fibers together with AMA homopolymers are shown in Figure 3. It was found that the absorbance at 2920 cm^{-1} due to $-\text{CH}_2$ group decreased and that at 2970 cm^{-1} due to $-\text{CH}_3$ group increased by the graft treatment. Therefore, it was considered that the graft polymerization with AMA under EB-irradiation occurred on the surface of PET fibers, though the grafting amount seemed to be small even at the largest EB-dose of 500 kGy used here. Regarding the reaction of AMA to PET, there are two possibilities considered, because allyl methacrylate (AMA) possesses the two types of double bond; methacryl group and ally group. To evaluate the reactivity of them, the two model compounds of methacrylic acid and allyl alcohol were employed for graft-

TABLE II
Sample Preparation Condition and Obtained Grafting

Code	EB-dose (kGy)	Predipping condition	Grafting (%)
AMA100	100	–	–0.5
AMA300	300	–	–1.0
AMA50H	50	85°C for 1 h	–0.5
AMA100H	100	85°C for 1 h	0.3
AMA200H	200	85°C for 1 h	0.5
AMA300H	300	85°C for 1 h	0.6
AMA500H	500	85°C for 1 h	5.2

polymerization under EB-irradiation of 500 kGy. The results are shown in Table I. There was a significant difference in the amount of grafting between them. Methacrylic acid was grafted but allyl alcohol hardly. Taking account of this result, it might be suggested that methacryl group of AMA predominantly reacted to PET fibers upon grafting under EB-irradiation. From these considerations, the reaction scheme shown in Figure 4 was assumed.

Grafting amount

The AMA graft treatments to PET fibers were carried out at various EB-dose, with and without predipping in the monomer of AMA solution at 85°C for 1 h. The results are summarized in Table II. Without predipping, no reaction occurs. The negative value of grafting may be due to that traces of low-molecular-weight compounds, which remained in PET fibers, was degraded by EB-irradiation and removed away in the washing process. When the PET fibers were predipped in the monomer solution at 85°C, higher than the glass transition temperature of PET (about 80°C), the AMA monomer might possess higher mobility in the solution at such high temperature and thus it must be more apt to penetrate the surface of PET fibers in the rubbery state. In fact, the grafting amount increased slightly with EB-dose of 50 to 300 kGy in the predipped PET fibers but it was significantly small. The effective grafting amount of 5.2% was obtained by elevating EB-dose to 500 kGy, though the grafting was still not so large. The grafted-PET fibers (AMA500H) were provided in the following experiments.

Pulling load of PET fibers from the NR matrix

To estimate the effect of the AMA graft treatment on the interfacial adhesion between the treated-PET fibers and the NR matrix, the pulling test was carried out. The relationship between the pulling load and displacement during the pulling of the PET fibers is shown in Figure 5; sample fibers subjected to a 500-kGy dose (AMA500H) were used. In the pulling test, the elongation of the fibers could almost be neglected

because there was a significant difference in the strengths between the PET fibers and the NR matrix. Therefore, the behavior of the pulling-load/displacement of the fibers should reflect the interaction between them. If there is no interaction between them, the fibers are completely pulled out of the rubber at the displacement of 5 mm, because the initial length of the fiber embedded in the matrix rubber was 5 mm long. It was found that the load increased upto a maximum accompanied by the deformation of the NR matrix, whether the PET fiber surfaces were subjected to graft-polymerization or not. This may be due to the presence of the adhesion and/or friction in both cases. However, the maximum pulling load was observed to be higher in the surface-treated PET fibers than in the untreated one. It was improved by about 33% with AMA grafting, which implies that AMA grafting gives rise to a large improvement in the adhesion between PET fibers and the NR matrix.

Mechanical properties of vulcanized NR composites

The stress–strain curves of NR composites are shown in Figures 6 and 7, where the untreated-PET fibers and the grafted-PET ones (AMA500H) were used as the short fibers, respectively. In the composites of NR and untreated-PET, only a slight change was seen in the stress–strain curves compared with that of the pure NR without untreated-PET fibers, shown in Figure 6. A slight hardening occurred by containing PET short fibers. On the other hand, Figure 7 shows quite a different behavior in the stress–strain curves with increase of the fiber content of grafted-PET. Especially, the stress markedly increases in the strain region upto about 300% as the fiber content increases and the breaking stress also increases.

The initial modulus, E , which is evaluated from the stress–strain curves, is shown in Figure 8 as a function

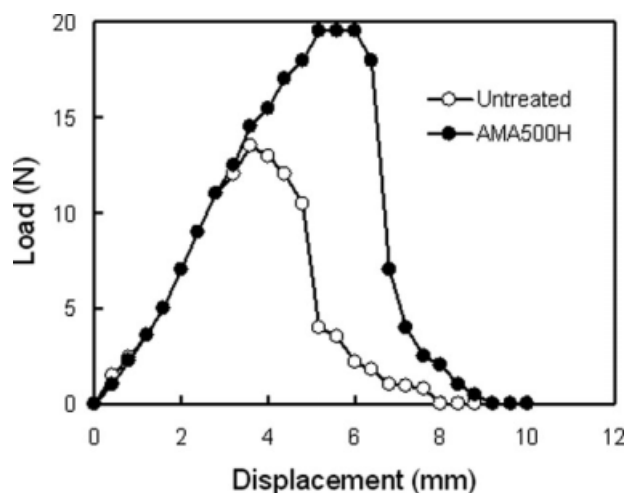


Figure 5 Pulling-load/displacement curve of PET fibers.

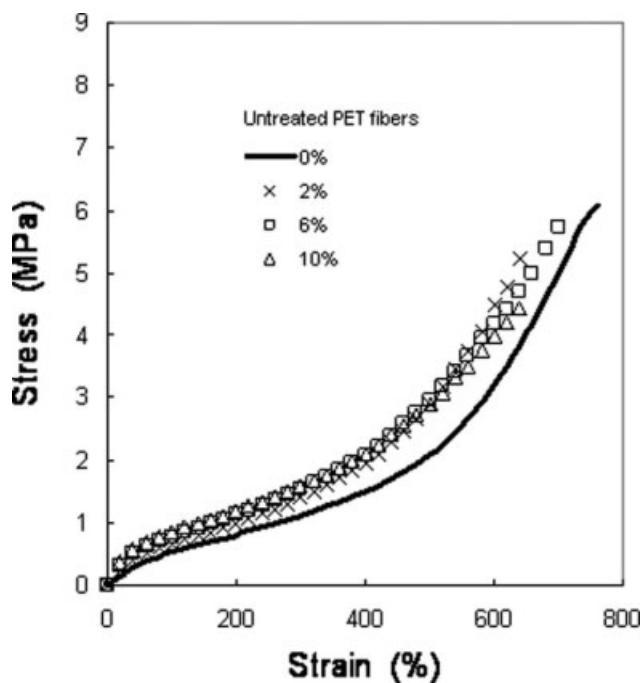


Figure 6 Stress-strain curves of NR composites with untreated-PET fibers.

of fiber content. In the composite of NR and untreated-PET fibers, the modulus slightly increases with the fiber content upto 10% and remains almost at the low values. This implies that untreated-PET fibers hardly have the interfacial adhesion to the rubber matrix of NR. The chemical robustness of PET enables us to easily understand this fact.

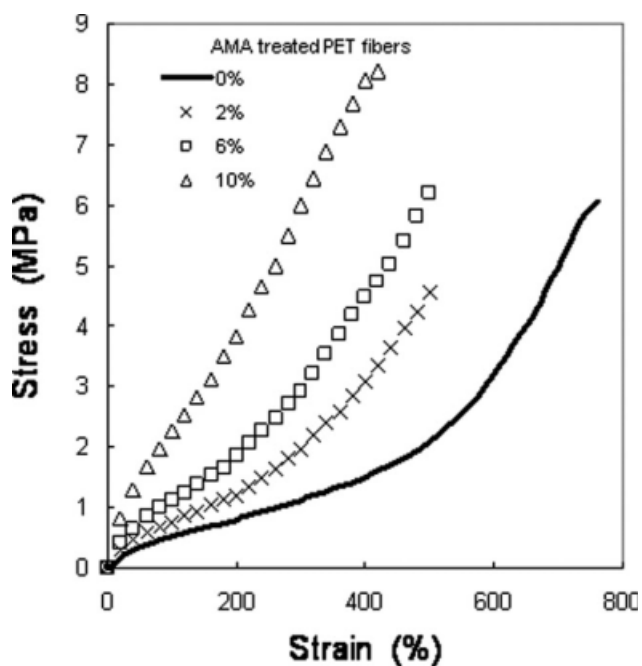


Figure 7 Stress-strain curves of NR composites with AMA-treated PET fibers.

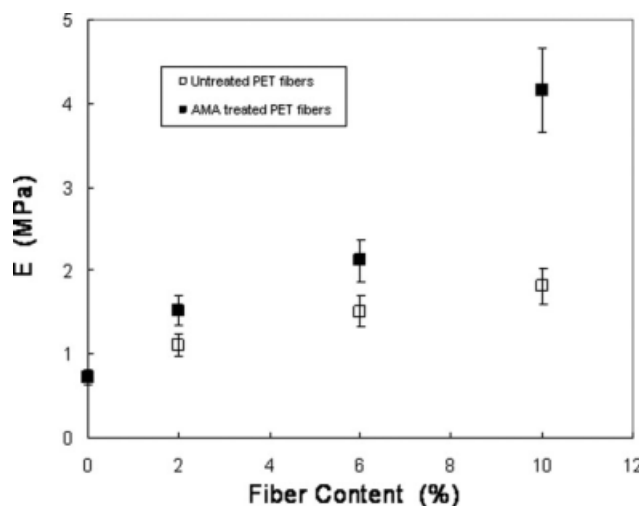


Figure 8 Effect of PET fiber content on the tensile modulus.

On the other hand, in the system of NR and grafted-PET fibers, we can see the tendency that the modulus increases linearly with the fiber content. Especially, it was noticed that the composite of NR with 10% AMA-treated PET fibers possessed the initial modulus five times as much as that of the pure NR. This must be due to the graft-polymerization of AMA onto the surfaces of PET fibers, though the grafting amount was quite low.

AMA-grafted-PET fibers have a lot of allyl groups in the grafted-side chains, which should behave as active sites to react with cross-linking atoms of sulfur in the process of vulcanization. As a result, PET fibers are assumed to be partially crosslinked with NR through AMA and sulfurs, as shown in the Figure 9. These results are supported by SEM observations for the fractured surfaces of vulcanized NR composites with untreated or grafted-PET fibers after stretching, shown in Figure 10. A crack that happened at break can be seen between the untreated-PET fiber and the NR matrix in Figure 10(a), which is typical to a poor adhesion in the interfacial region between them. On the contrary, the grafted-PET fiber was covered with matrix NR, as is seen in the fractured surface by stretching, shown in Figure 10(b). This implies a better adhesion between

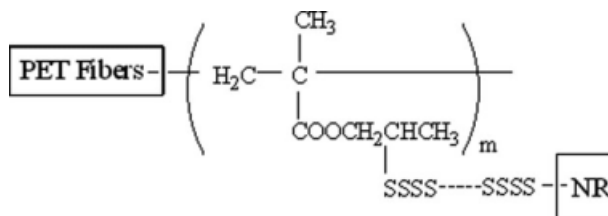
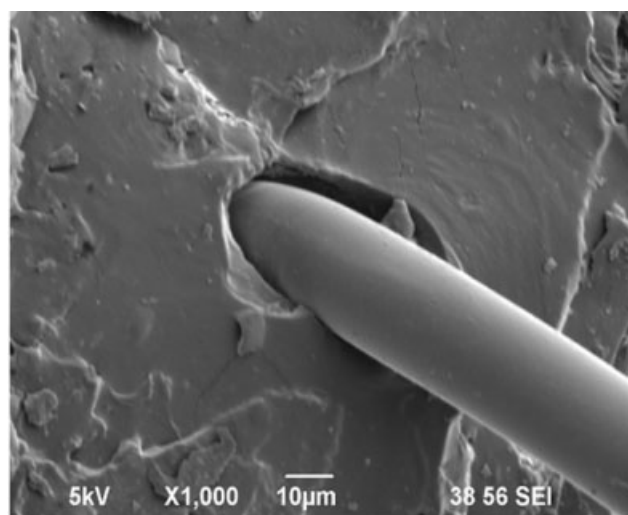
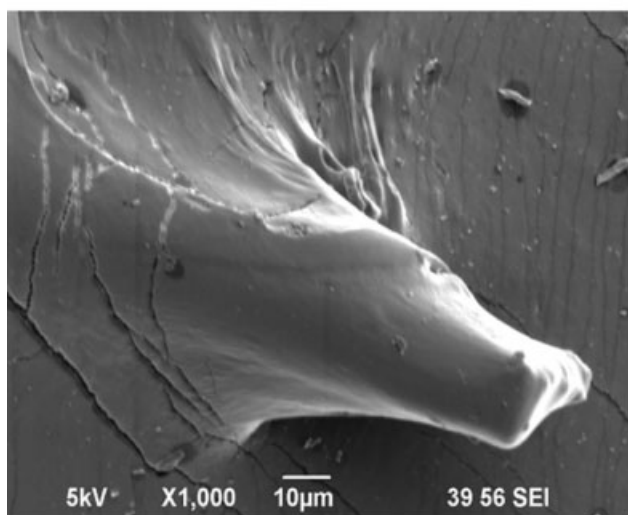


Figure 9 Proposed model for the reaction of AMA-grafted-PET fibers and NR.



(a) untreated PET fiber



(b) grafted PET fiber

Figure 10 SEM observations for fractured surfaces of vulcanized NR composites with (a) untreated-PET fibers and (b) grafted-PET fibers.

them and suggests the formation of partial crosslinkages between them.

The breaking strength and strain of the composites were evaluated from Figures 7 and 8, and shown in Figures 11 and 12, respectively. In the drawing process, the break may occur in the matrix rubber or the interfacial regions because it is hard to cut a short fiber of PET that has a small aspect ratio and a high strength compared with that of the NR matrix.

In the NR and untreated-PET fibers system, the strength inclines to slightly decrease with fiber content, though quite a small change was observed in the modulus.

The strain almost remains at about 700% a little less than that of the pure NR as shown in Figure 12.

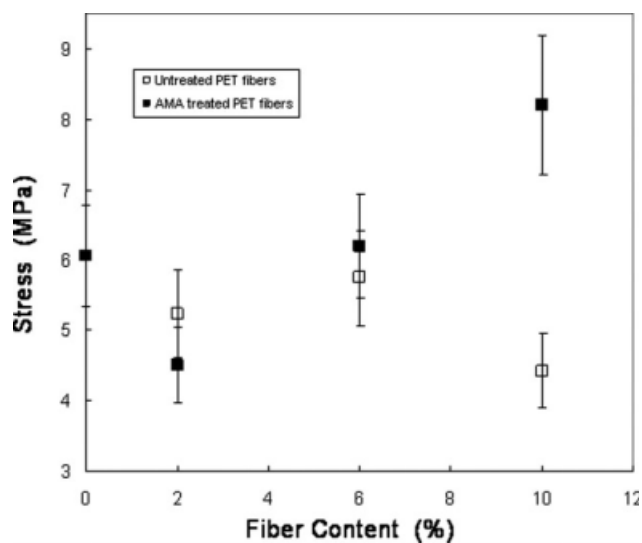


Figure 11 Effect of PET fiber content on the tensile strength at break.

These facts imply that the untreated-fibers contained in the NR matrix do not give much influence on the mechanical properties such as breaking strength, strain, and tensile modulus. It may be due to lack in interaction or quite weak interaction between the chemically robust PET fibers and the NR matrix. As a result, a slip should mainly occur in the interfacial region.

On the contrary, in the composite of NR and grafted-PET fibers, a large effect of the fibers on the strength could be obtained especially at the content of 10%, as is seen in Figure 11. At this moment, the fibers possessed the high adhesion to the matrix rubber, that is, the interfacial interaction was so strong

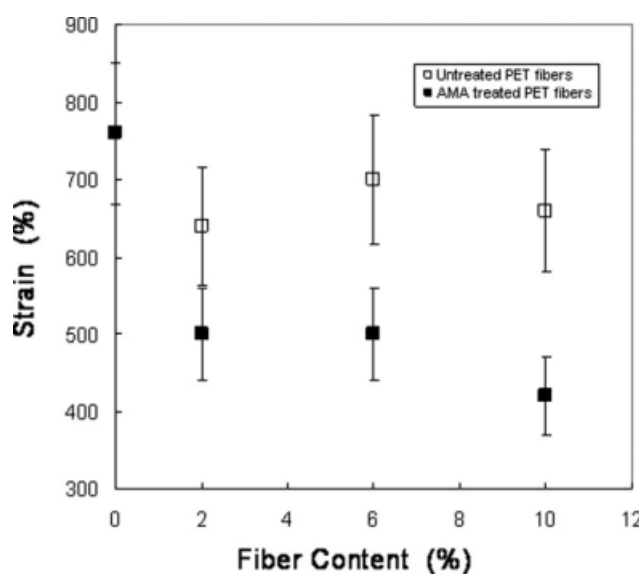


Figure 12 Effect of PET fiber content on the strain at break.

that the fibers seemed to be able to sufficiently bear a load applied. It may be caused by the formation of crosslinkage between PET fibers and NR matrix, mentioned earlier. In addition, the breaking strain is characterized to largely decrease with the fiber content, shown in Figure 12. These strains are much less than those of the NR composite with untreated-PET fibers. This fact also suggests the formation of crosslinkage in the process of vulcanization.

In general, the larger the strength becomes, the lower the strain does on the mechanical properties of polymers. The mechanical behavior of the NR composite with AMA-grafted-PET fibers is consistent with such general fashion.

Here, the modulus and strength are much improved and as a result, a so-called PET fiber-reinforced NR could be obtained. This must derive a good deal of effect from the high modulus of PET fibers. In addition, the effect of crosslinkage may be considered; the grafted-side chains of AMA, which have allyl groups to react with sulfur atoms to form crosslinkages with NR, may play an important role, as is expected.

CONCLUSIONS

To develop a fiber-reinforced rubber for natural rubber (NR) with high performance, polyethylene terephthalate (PET) fibers with high crystallinity, which possess high strength and high modulus but quite poor reactivity to other polymers, were used. To make the surface of chemically robust PET fibers reactive, AMA monomers were graft-polymerized with the aid of physical energy from electron beam (EB) irradiation with the dose of 500 kGy to result in the grafted-side chains with reactive allyl groups. The grafting amount of 5.2% was evaluated by weighing method, which was a small value but the existence of grafted-side chains could be recognized by FTIR measurements. The pulling load of PET fibers out of the NR matrix, which directly reflects the adhesion between them, largely increased when AMA-grafted-PET fibers were used instead of untreated-PET fibers.

The composite of NR and grafted-PET fibers provided almost a linear increase in the initial modulus with the fiber content and possessed the modulus five times as much as that of pure NR at the fiber content of 10%. At the same time, the strength became about 1.4 times and the strain about 0.6 times as much as those of pure NR without fibers, respectively. The adhesive states between PET fibers and NR matrix was observed by SEM, from which the results of mechanical properties of the composites were supported. These facts lead us to conclude that AMA monomers are grafted on the surface of PET fibers and then the allyl groups of grafted-side chains of AMA react with sulfur atoms to form the crosslinkages with NR through the sulfur crosslinking in the vulcanization process. The fiber-reinforced rubber with such a good performance was realized in the system of NR and PET fibers with grafted-side chains of AMA.

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