SYNTHESIS OF NATURAL RUBBER-g-MALEIC ANHYDRIDE AND ITS USE AS A COMPATIBILIZER IN NATURAL RUBBER/SHORT NYLON FIBER COMPOSITES*

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Abstract Natural rubber grafted maleic anhydride (NR-g-MAH) was synthesized by mixing maleic anhydride (MAH) and natural rubber (NR) in solid state in a torque rheometer using dicumyl peroxide (DCP) as initiator. Then the self-prepared NR-g-MAH was used as a compatibilizer in the natural rubber/short nylon fiber composites. Both the functionalization of NR with MAH and the reaction between the modified rubber and the nylon fiber were confirmed by Fourier transform infrared spectroscopy (FTIR). Composites with different nylon short fiber loadings (0, 5, 10, 15 and 20 phr) were compounded on a two-roll mill, and the effects of the NR-g-MAH on the tensile and thermal properties, fiber-rubber interaction, as well as the morphology of the natural rubber/short nylon fiber composites were investigated. At equal fiber loading, the NR-g-MAH compatibilized NR/short nylon fiber composites showed improved tensile properties, especially the tensile modulus at 100% strain which was about 1.5 times that of the corresponding un-compatibilized ones. The equilibrium swelling tests proved that the incorporation of NR-g-MAH increased the interaction between the nylon fibers and the NR matrix. The crosslink density measured with NMR techniques showed that the NR-g-MAH compatibilized composites had lower total crosslink density. The glass transition temperatures of the compatibilized composites were about 1 K higher than that of the corresponding un-compabilized ones. Morphology analysis of the NR/short nylon fiber composites confirmed NR-g-MAH improved interfacial bonding between the NR matrix and the nylon fibers. All these results signified that the NR-g-MAH could act as a good compatilizer of NR/short nylon fiber composites and had a potential for wide use considering its easy to be prepared and compounded with the composites.

Keywords: Natural rubber; Maleic anhydride; Graft; Natural rubber/short nylon fiber composite.

INTRODUCTION

Since 1990’s, short fiber reinforced rubber composites (SFRC) have gained considerable attention as a viable alternative of the long fiber reinforced and particle filled rubber composites[1-4]. Short fibers can be easily incorporated into the rubber compound along with other ingredients by normal rubber processing operations such as extrusion, calendaring, compression molding, injection molding et al[5]. The composites can exhibit the combined behavior of soft, elastic rubber matrix and stiff, strong fibrous fillers. The main drawback of SFRC is the incompatibility between hydrophilic fiber and hydrophobic rubber matrix, which causes weak interface and poor properties. Attempts have been made to overcome this drawback by using various coupling agents or bonding agent[6-8] and pre-treatment of the fibers with suitable chemicals[9-12].

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Maleic anhydride (MAH) is one of the most widely used vinyl monomers for the graft modification of various polymers. MAH modified polymers are widely used as chemical coupling agent, impact modifier and compatibilizer for polymer blends and filler reinforced composites\(^{[13-15]}\). Rzayev has summarized the main advances published over the last 15 years outlining the different methods of grafting, including reactive extruder systems, surface modification, grafting and graft copolymerization of synthetic and natural polymers with maleic anhydride and its isostructural analogues such as maleimides and maleates, and anhydrides, esters and imides of citraconic and itaconic acids, derivatives of fumaric acid, etc. The structural phenomena, unique properties and application areas of these copolymers and their various modifications and composites as high performance engineering materials have been also described\(^{[16]}\).

The grafting of maleic anhydride (MAH) to natural rubber (NR) was one of the earliest tries for the chemical modification of NR. Early in 1940s, Bacon\(^ {\cite{17}}\) and Farmer\(^ {\cite{17, 18}}\) reported that MAH could be fixed to rubber hydrocarbon in the presence of benzyl peroxide in solution and suggested two structures of the graft copolymer related to intra and intermolecular reactions respectively. Pinazzi \textit{et al.}\(^ {\cite{19}}\) did a series of research on the reaction between MAH and rubber at high temperatures without catalyst or oxygen. The modified rubber was cross-linked by metallic oxides such as MgO and ZnO and the physical properties of the new material were studied. But their work still mainly focused on the reaction mechanism between rubber and MAH. After that, few works about the maleic anhydride grafted natural rubber were reported. However, in the past ten years, reports on preparation and application of maleic anhydride grafted natural rubber appeared in succession. Nakason \textit{et al.}\(^ {\cite{20}}\) reported their work on synthesis of graft copolymers of natural rubber and maleic anhydride or maleated natural rubber (MNR) in toluene with benzoyl peroxide (BPO) as initiator. Styrene was used by Saelao \textit{et al.}\(^ {\cite{21}}\) to assist the grafting of maleic anhydride onto natural rubber in toluene. Influence of monomer and initiator BPO concentrations together with effect of the reaction temperature and reaction time were investigated. Riyajan \textit{et al.}\(^ {\cite{22}}\) prepared maleated sulfur-prevulcanized natural rubber (M-SPNR) from grafting maleic anhydride onto vulcanized SPNR latex particle by using BPO as an initiator. They found the swelling ratios of M-SPNR latex film decreased with increasing MA contents. The tensile strength, modulus, hardness and elongation at break of SPNR latex film dramatically increased after grafting with MA. Due to the reduction of double bonds, the thermal stability of M-SPNR films was better than that of SPNR ones. Hesham \textit{et al.}\(^ {\cite{23}}\) synthesized NR-g-MA in a solution state by using ultraviolet radiation and added the NR-g-MA to a 50/50 blend of NR/NBR as a compatibilizer. Elastic constant, Poisson's ratio, cross-link density and microhardness were tested in different percentages of the blend components. They found that the addition of NR-g-MA to the blend showed improvement of compatibility in certain concentration ranges and deterioration of compatibility in other ranges. Zeng\(^ {\cite{24}}\) prepared maleated natural rubber (MNR) by blending NR and maleic anhydride in an internal mixer through mechanochemistry and used as a coupling agent of natural rubber/cotton fiber composites. The composites with MNR showed higher modulus and tensile strength than those without MNR. Phrommedetch \textit{et al.}\(^ {\cite{25}}\) compared the reinforcing effects of rice husk ashes in natural rubber and maleated natural rubber (MNR) to those of conventional reinforcing fillers, such as silica and carbon black. They found that the tensile strengths and moduli of MNR composites filled with bagasse ashes were improved, together with lower degree of swelling. Cao \textit{et al.}\(^ {\cite{26}}\) tried to use maleic anhydride grafted natural rubber (MANR) to enhance the recycled high density polyethylene (rHDPE)/natural rubber (NR) composites performance and found the addition of MANR as a coupling agent could improve the tensile properties of rHDPE/NR/KP biocomposites and reduce their water absorption.

The rubber-filler interaction is essential due to its influence on numerous properties of rubber compounds and vulcanizates. In this paper, maleic anhydride grafted natural rubber (NR-g-MAH) was prepared by mixing MAH and NR in solid state in a torque rheometer using dicumyl peroxide (DCP) as initiator. The self-prepared NR-g-MAH was then used as a compatibilizer for the natural rubber/short nylon fiber composites considering that the anhydride groups could react with the amine groups of nylon fiber to enhance the interfacial interaction between fiber and NR matrix. Fourier transform infrared spectroscopy (FTIR) was used to analyze the molecular characterization of the NR-g-MAH and the reaction between NR-g-MAH and nylon fiber. The influence of
NR-g-MAH on the tensile and thermal properties as well as the interaction between the fibers and rubber matrix of the composites was investigated in detail.

**EXPERIMENTAL**

**Materials and Sample Preparation**

SCR10 grade natural rubber was purchased from the Zhanjiang State Farm Bureau, China. Polyamide 6 short fibers (PA6) with diameter of 10−16 μm and length of 2−3 mm were supplied by Fujin Pretreated Short Fibers Company, Heilongjiang, China. Maleic anhydride (MAH), purchased from China Medicine Group Shanghai Chemical Reagent Corporation, Shanghai, China, was an analysis pure reagent. Dicumyl peroxide (DCP) produced by Taicang chemical factory, Jiangsu, China, was a chemical pure reagent. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, 2,2′-dibenzothiazyl disulfide (accelerator DM) and tetramethyl thiuram disulfide (accelerator TMTD) were all commercially available and were used as received.

NR-g-MAH was prepared in a torque rheometer (XSS-300). On the basis of our earlier work[27], 100 phr NR, 5 phr of MAH and 0.75 phr DCP were mechanically blended in the mixer at about 130 °C and a rotor speed of 50 rpm. The mixing was continued for 3−5 min. The obtained products were used without further treatment.

The NR-g-MAH compatibilized NR/short nylon fiber composites were prepared by the incorporation of different loadings (0, 5, 10, 15 and 20 phr) short PA6 fibers into NR matrix. Compounding was carried out on a laboratory-sized two roll mill (XK-160) according to ASTM standard D 3184-80. NR was masticated on the mill for 2 min followed by addition of the ingredients. The basic formulation used is shown in Table 1. The nip gap and roll speed ratio were kept the same for all compounding. PA6 fiber was added at the end of the mixing process. The flow direction of the compounds was carefully maintained so that the majority of fiber followed the direction of the flow. The samples were conditioned at ambient temperature for 24 h before vulcanization. Each sample was compression moulded at 150 °C for optimum cure time \( t_{90} \), which was determined by a rubber curometer (P3555B2).

**Table 1.** Formulation of NR/short nylon fiber composite (phr*).

| Sample number | A0   | A5   | A10  | A15  | A20  | B0   | B5   | B10  | B15  | B20  |
|---------------|------|------|------|------|------|------|------|------|------|------|
| NR            | 100  | 100  | 100  | 100  | 100  | 90   | 90   | 90   | 90   | 90   |
| NR-g-MAH      | 0    | 0    | 0    | 0    | 0    | 10   | 10   | 10   | 10   | 10   |
| PA6 short fiber | 0   | 5    | 10   | 15   | 20   | 0    | 5    | 10   | 15   | 20   |

Other ingredients in every composite are constants and the dosages are as following: zinc oxide 5.0 phr, stearic acid 1.0 phr, accelerator DM 1.2 phr, accelerator TMTD 0.3 phr, sulfur 2.5 phr;

* Parts per hundred rubber

**Sample Characterization**

**Fourier transform infrared spectroscopy**

Fourier transform infrared spectroscopy (FTIR) of NR, NR-g-MAH, NR/short nylon fiber composite and NR-g-MAH compatibilized NR/short nylon fiber composite were recorded in the wavenumber range of 400−4000 cm\(^{-1}\) with a Niconol 6700 instrument.

The NR and NR-g-MAH samples were subjected to Soxhlet extraction with acetone to eliminate the residual MAH and then dried under vacuum before analysis. The dried rubber samples were dissolved in chloroform and then cast into a thin film on a KBr disk.

To explore the interaction between the NR-g-MAH and PA6 fiber, only NR, PA6 fiber and purified NR-g-MAH were compounded together to prepare samples for FTIR test. Samples were cold cut from the composites, washed with acetone and also dried under vacuum before analysis.

**Stress-strain test**

Tensile stress-strain properties were measured with a CMT4204 Universal Testing Machine at room temperature with a crosshead speed of 500 mm/min according to ASTM D 412-98a (2002). The cured NR/short nylon fiber composites were tested after at least 24 h storage at room temperature.
Optical microscope and scanning electron microscope
The morphologies of NR/short nylon fiber composites were recorded with an Olympus SZ61 stereomicroscope. For the morphology observation, the composites were compressed and vulcanized into films thin enough to allow light transmission. Scanning electron microscope (SEM) studies were performed with an S-3400N scanning electron microscope (Hitachi Company, Japan) at an accelerating voltage of 15 kV. The specimens were gold coated before observation.

Equilibrium swelling experiment
The rubber-fiber interaction was determined through the swelling of the NR/short nylon fiber composites in toluene according to ISO 1817. Samples with dimensions of 10 mm × 10 mm × 2 mm were weighed and then immersed in toluene at 25 °C in a dark environment for 72 h until equilibrium swelling was achieved. After the conditioned period, the samples were wiped free of surface liquid softly with tissue and weighed again. And finally, the samples were dried in a vacuum oven at 40 °C until constant weights were reached, and the weights were recorded.

Crosslink density measurement
Crosslink density (XLD) measurements were carried out using an IIC XLDS-15 crosslink density spectrometer. Samples about 2 mm in thickness, 10 mm in length and 3 mm in diameter were cut from uncured and cured NR/short nylon fiber composites especially. The samples were measured at a temperature of (60 ± 0.1)°C. Each signal decay covered 1024 data points at an acquisition time of 10 ms and 64 measurements at different tau values (T2, XLD) were carried out. Data analysis was performed with the IIC Analysis Software package, using a non-linear Marquardt-Levenberg algorithm.

Differential scanning calorimetry
Differential scanning calorimetry analysis was conducted using a Perkin-Elmer DSC-2 instrument (Perkin Elmer Corp, Waltham, MA, USA) under nitrogen atmosphere. Each sample was cooled down to −100 °C using liquid nitrogen and then heated up to 20 °C at a rate of 10 K/min.

RESULTS AND DISCUSSION

Synthesis of NR-g-MAH
To increase the interfacial bonding between NR and short nylon fiber, NR-g-MAH is first synthesized via solid graft polymerization of MAH onto NR in a torque rheometer. The product is purified and tested with FTIR, which is one of the most widely used techniques for the identification of grafted polymers. Figure 1 shows the FTIR spectra of purified NR and NR-g-MAH samples. As illustrated in Fig. 1, the FTIR spectrum features of

![Fig. 1 FTIR spectra of the NR and NR-g-MAH](image-url)
NR-g-MAH show no significant difference to those of NR. The absorptions at 2960, 2911 and 2850 cm\(^{-1}\) are attributed to the stretching vibrations of the methyl and methane in NR. The absorptions at 1443 and 1375 cm\(^{-1}\) belong to the bending vibrations of methane and the vibrations of methyl in NR. The absorption at 841 cm\(^{-1}\) is caused by bending vibrations of C—H bond in the double bond. In the case of NR-g-MAH, the only new absorption signals occur at 1708 and 1629 cm\(^{-1}\), which can be assigned to asymmetric and symmetric C=O stretching vibration modes of five-membered cyclic anhydride, respectively. Similar results are reported for grafting of MAH onto other polymers\(^{[10-14]}\). Since MAH is difficult to homopolymerize because of its structural symmetry and deficiency of electron density around the double bond, normally only one monomer unit is grafted on each generated radical active site. This evidence can therefore be used to confirm that the MAH had grafted onto the NR backbone in the form of a succinic anhydride unit.

Mechanism of a radical-induced MAH grafting onto a polyolefin backbone has been well established\(^{[10, 14-18]}\). The reaction starts with hydrogen abstraction on the polymer backbone by radical species generated from the decomposition of a radical-type initiator. The formed macroradical subsequently reacts with MAH. In this work, DCP is used as a radical initiator for grafting MAH onto NR. The high cis-1,4-polyisoprenic structure of NR possesses labile allylic protons in every repeating unit. These protons are prone to hydrogen abstraction by radical active species generated from DCP decomposition. The reaction mechanism of MAH grafting onto NR is therefore proposed in Scheme 1.

**Scheme 1** The reaction mechanism of the grafting of MAH onto NR

First, DCP is decomposed into active radicals under heating. The generated radical then abstracts a proton on the NR backbone, preferably at an allylic position. The formed rubber radical will subsequently react with MAH. Radical termination may then be achieved by radical chain transfer reaction onto another rubber chain, resulting in a so-called maleic anhydride grafted natural rubber (NR-g-MAH).

**Compatibilization of NR/nylon Fiber Composites by NR-g-MAH**

In theory, the maleic anhydride groups of NR-g-MAH can react with the amine groups of PA6 fibers to form graft copolymers in the interfacial regions, which will reduce interfacial tension and retard fiber coalescence during mixing. At the same time, the long NR segments of NR-g-MAH can form strong entanglement with the NR matrix. The proposed interactions among NR-g-MAH, PA6 fibers and NR matrix are shown in Scheme 2.

FTIR technique is also used here to further confirm the proposed compatibilization mechanism of NR-g-MAH to the NR/short nylon fiber composites. As illustrated in Fig. 2, the features of FTIR spectra of NR/short nylon fiber composite compatibilized by NR-g-MAH are quite similar to those of the uncompatibilized one. The absorption at 2960 cm\(^{-1}\) is attributed to the asymmetric stretching vibrations of CH\(_3\) in NR. The absorptions at 2917 and 2852 cm\(^{-1}\) are attributed to the asymmetric and symmetric stretching vibrations of CH\(_2\) in NR and PA6 fiber. The absorptions at 1430 and 1375 cm\(^{-1}\) are the angular deformations of CH\(_2\) and CH\(_3\). The absorption at 835 cm\(^{-1}\) is belong to angular deformation of C—H bond in the double bond in NR. The absorption at 1662 cm\(^{-1}\)
could be assigned to asymmetric and symmetric stretching vibration of $C=O$ in PA6 and the absorption at 1540 cm$^{-1}$ is belong to the stretching vibrations of $N-H$. In the case of NR-g-MAH compatibilized NR/short nylon fiber composite, the absorption signal at 1540 cm$^{-1}$ obviously weakens which means the $N-H$ groups become less. This evidence confirms that the maleic anhydride group of NR-g-MAH has reacted with the amine group of PA6 fiber, just as proposed before.

Scheme 2 The interactions among NR, PA6 fiber and NR-g-MAH

Fig. 2 FTIR spectra of the NR-g-MAH compatibilized NR/short nylon fiber composite and un-compatibilized composite (b is the partially enlarged FTIR spectra.)

**Tensile Properties of NR/Nylon Fiber Composites**

In general, the aim of incorporation of fibers to the rubber is for better mechanical performance. So the tensile properties of the NR/nylon fiber composites in the longitudinal direction are studied since it is proved to be superior to those in the transverse direction\[2, 3\]. Figure 3 are the stress-strain curves of the NR/nylon fiber composites with different fiber loadings. As can be seen in Fig. 3, the tensile strength of the NR/nylon fiber composites steadily decreased with the increasing of fiber loadings. Since the NR matrix and the fibers experience different tensile strains due to their different modulus, the longitudinal strain in the matrix will be higher than that in the adjacent fibers due to lower modulus. If the fiber-matrix interface is weak, the debonding of the fibers will happen during the extension. When the fiber loading is increased, the dispersion and orientation of the hydrophilic nylon fiber in the hydrophobic NR matrix became more difficult and more weak interfacial regions formed. So the deterioration of tensile strength may be attributed to the increasing agglomeration of
fibers and the dewetting of NR matrix at the interface which generate weak structure by creating stress concentration points. But with the same fiber loading, the NR-g-MAH compatibilized NR/nylon fiber composites exhibit higher tensile properties. The incorporation of NR-g-MAH is helpful to the dispersion of PA6 fibers and increase the fiber-matrix interfacial adhesion which leads to the improvement of tensile properties.

Comparison of tensile modulus at 100% strain (M100) of the NR-g-MAH compatibilized and un-compatibilized NR/short nylon fiber composites is shown in Fig. 4. The M100 of both the two types contrast composites increase with the increase of the fiber content. Since the modulus of the nylon fiber is much higher than that of the rubber, the tensile strain of the fiber will be much smaller than that of the rubber matrix when a pulling force is applied to the composite. So the movements of the rubber chains may be hindered by the fibers at the initial extension. The content of the fiber is higher, the hindrance is greater and the composite shows higher initial tensile modulus. The M100 of the NR-g-MAH compatibilized composites is about 1.5 times that of the un-compatibilized ones with the same fiber content. The enhancement of M100 again can be attributed to the improvement in the interfacial adhesion of the PA6 fibers to the NR matrix in the presence of NR-g-MAH. For the NR-g-MAH compatibilized NR/short nylon fiber composites, the restriction of the fiber to the rubber is stronger and the composites are more rigid and tough. Similar results are also reported in other graft compatibilized composites\[21, 22\].

**Morphology of NR/Nylon Fiber Composites**

Since the dispersion of fibers and the interactions between fibers and rubber matrix can affect the tensile strength of the composites greatly, film samples of the NR/short nylon fiber composites are first examined with a stereomicroscope to find out the orientation and dispersion of the short nylon fiber in the NR matrix. Figure 5 are the photos of the NR/short nylon fiber composites with different fiber contents and the arrows show the orientation directions of the fibers. For the composites, it can be seen that the orientation and dispersion of the fibers turned worse with the increase of fiber content. This may help to explain why the tensile properties of the composites decrease with the increasing of the fiber loadings. In the NR-g-MAH compatibilized composites, the fibers distribute more homogenously which is benefit for the mechanical properties of the composites.

To gain further insight into the interfacial adhesion between the nylon fibers and the NR matrix, the fracture surfaces of tensile specimens are investigated with scanning electron micrographs (SEM), as shown in Fig. 6. Comparing with the stereomicroscope observations, the contents of the fibers for the same composites in the SEM photos seem less due to the fiber orientation direction is perpendicular to the fracture surface. From the SEM photos, several debonding fibers and some holes can be seen. The appearance of the holes is attributed to the pulling out of the fibers from the matrix during the tensile property testing. For the uncompatibilized
NR/short nylon fiber composite with 5 phr short nylon fibers (A5), the clearly visible voids and the clean surface of the fiber indicate poor interfacial bonding between the nylon fibers and the NR matrix. However, for the compatibilized composite with 5phr short nylon fibers (B5), the fracture surface is rough and some pull-out fibers are cover with rubber. This observation highlights the fact that the interfacial bonding between the fibers and the NR matrix is significantly improved by the NR-g-MAH. As we know, when a load was applied to the NR/short nylon fiber composites, it spread smoothly through the NR matrix until reaching the rubber-fiber interface. If the interface is weak, the fibers may debond from the matrix and lead to the fracture of the composites. But if the interface is well bonded, the stress can be transferred from the matrix to the fibers and then spread throughout the fibers. The fibers then act as the main carrier of the stress and the composites show high tensile strength. Thus the good dispersion and interfacial adhesion of the nylon fibers to the NR matrix lead to effective and uniform stress distribution and consequently result in better tensile properties of the compatibilized NR/short nylon fiber composites.

**Fig. 5** Optical morphology photos of the NR/short nylon fiber composites under stereomicroscope

**Fig. 6** SEM morphology of tensile fracture surface of the NR/short nylon fiber composites filled with 5 phr of nylon fiber
Rubber-Fiber Interaction Analysis

As we discussed before, the fiber-matrix interfacial adhesion is very important in determining the mechanical properties of the composites. The Kraus theory and Kraus equation\(^{(28)}\) have been successfully used by some researchers to assess the interfacial interaction in fiber-reinforced rubber composites\(^{(9-11)}\). The Kraus equation is expressed as follow:

\[
\frac{V_{r0}}{V_{rf}} = 1 - m\left(\frac{f}{1 - f}\right)
\]  

where \(V_{r0}\) and \(V_{rf}\) are the volume fractions of rubber in the gum vulcanizate and in the fiber filled swollen sample, respectively, \(f\) is the volume fraction of fiber, \(m\) is the rubber-fiber interaction parameter. The ratio of \(V_{r0}/V_{rf}\) represents the degree of restriction of the swelling of the rubber matrix due to the presence of filler. The volume fraction of rubber in the fiber filled swollen sample \(V_{rf}\) can be calculated according to the Eq. (2):

\[
V_{rf} = \frac{(m_1 - fm_0)\rho_r^{-1}}{(m_1 - fm_0)\rho_r^{-1} + (m_s - m_1)\rho_s^{-1}}
\]

where \(m_0\) is the initial weight of the sample, \(m_1\) is the weight of the sample at equilibrium swelling, \(m_s\) is the weight after being dried, \(\rho_r\) and \(\rho_s\) are the densities of the polymer and the solvent (NR, \(\rho_r = 0.973\) g/cm\(^3\), toluene, \(\rho_s = 0.867\) g/cm\(^3\)), \(f\) is volume fraction of filler.

Samples of both the NR-g-MAH compatibilized NR/short nylon fiber composites and the un-compatibilized ones are swollen in toluene. The results of \(V_{r0}\) and \(V_{rf}\) calculated according to Eq. (2) are listed in Table 2 and the \(V_{r0}/V_{rf}\) to \(f/(1-f)\) relation curves fitted by origin software are shown in Figs. 7(a) and 7(b). From the results in Table 2, it is observed that for both the two types of contrast composites, the equilibrium solvent uptake of the samples decreased as fiber loading increased, which caused an increase in \(V_{rf}\). So the ratio \(V_{r0}/V_{rf}\) decreases since \(V_{r0}\) is a constant. This is obviously due to the increased hindrance exerted by the fibers at higher loadings. The diffusion mechanism in the composite is essentially connected with the ability of the rubber to provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with fiber loading, the solvent uptake also decreases. A highly bonded system will exhibit high resistance to swelling compared to the un bonded systems. The ratio, \(V_{r0}/V_{rf}\), represents the degree of restriction of the swelling of the rubber matrix due to the presence of fibers. According to the Kraus theory and Kraus equation, the compatibilized composites have a negative high slope as shown in Fig. 7(a). Further reduced \(V_{r0}/V_{rf}\) values are associated with the enhanced fiber-rubber adhesion. On comparing the solvent uptake of composites compatibilized by NR-g-MAH with that of un-compatibilized ones, it can be seen that the former composites are better than the latter in resisting the uptake of toluene. Equilibrium swelling measurement proves that for the NR-g-MAH compatibilized NR/short nylon fiber composites, a strong interface between the fibers and the rubber matrix is developed which restricts the entry of the solvent.

| Table 2. \(V_{rf}\) and \(V_{r0}/V_{rf}\) of NR/short nylon fiber composites in toluene |
|---------------------------------------------------------------|
| Samples | \(V_{rf}\) | \(V_{r0}/V_{rf}\) |
| A0      | 0.1915     | –                  |
| A5      | 0.1972     | 0.9706             |
| A10     | 0.1970     | 0.9718             |
| A15     | 0.2021     | 0.9475             |
| A20     | 0.2053     | 0.9330             |
| B0      | 0.1915     | –                  |
| B5      | 0.2013     | 0.9513             |
| B10     | 0.2037     | 0.9397             |
| B15     | 0.2067     | 0.9264             |
| B20     | 0.2080     | 0.9205             |
The properties of rubber composites are not only dependent upon fillers, but also affected by many other factors such as the crosslinking density. Because properties of materials are always related to molecular mobility, further knowledge of network structure is essential for desired properties. \(^1\)H-NMR relaxation measurements are used as a new method for characterizing the network structure of NR vulcanizates\(^{[29-31]}\). In contrast to the Mooney Rivlin and equilibrium swelling tests, NMR techniques can also measure the physical crosslink density in the uncured compound, which is understood as the long hydrocarbon chain entanglements. The total crosslink density and chemical crosslink density can be measured on the basis of cured rubber.

Uncured and cured NR/short nylon fiber composites with different fiber loadings are characterized by \(^1\)H-NMR and the results of physical crosslink density (XLD), chemical XLD, total XLD, and average molecular weight of chains between two adjacent crosslinks (\(M_c\)) are listed in Table 3. The results showed that the composites have more or less the same physical crosslink densities, due to the controlled, similar compounding condition, but different total crosslink densities. The NR-g-MAH compatibilized composites have lower total XLD and chemical XLD than the corresponding un-compatibilized ones. The reduction of chemical XLD for the NR-g-MAH compatibilized composites may be caused by the maleic anhydride group on NR-g-MAH and the residual MAH in the NR-g-MAH (as the NR-g-MAH is used without further purification) since acidic agents have an adverse effect on the vulcanization of the rubber. So the addition content of NR-g-MAH as a compatibilizer in the rubber composite should be controlled carefully.

Table 3. XLD and \(M_c\) of NR/short nylon fiber composites measured by NMR

| Samples | Total XLD \(\times 10^5\) (mol/cm\(^3\)) | Chemical XLD \(\times 10^5\) (mol/cm\(^3\)) | Physical XLD \(\times 10^{-5}\) (mol/cm\(^3\)) | \(M_c\) (kg/mol) |
|---------|---------------------------------|---------------------------------|---------------------------------|----------------|
| A0      | 13.93                           | 12.88                           | 5.32                            | 6.96           |
| A5      | 14.95                           | 13.81                           | 5.73                            | 6.55           |
| A10     | 13.93                           | 12.61                           | 5.91                            | 7.11           |
| A15     | 13.22                           | 11.96                           | 5.62                            | 7.57           |
| A20     | 12.76                           | 11.63                           | 5.26                            | 7.76           |
| B0      | 13.34                           | 12.21                           | 5.36                            | 7.42           |
| B5      | 14.43                           | 13.27                           | 5.65                            | 6.79           |
| B10     | 13.56                           | 12.38                           | 5.53                            | 7.30           |
| B15     | 13.04                           | 11.91                           | 5.97                            | 7.59           |
| B20     | 11.40                           | 9.77                            | 5.88                            | 8.68           |
Differential Scanning Calorimeter Analysis of NR/Nylon Fiber Composites

Figure 8 gives the DSC curves of NR-g-MAH compatibilized NR/short nylon fiber composites and un-compatibilized ones. The glass transition temperature ($T_g$) of the composites with different fiber loadings is also shown along with every single curve in Fig. 8. The $T_g$ values of the composites with different fiber loadings are quite close. This suggests that the fiber content has little effect on the flexibility of NR chain segments, which may arise from the relative weak interfacial bonding in the composite. While the $T_g$ of the NR/short nylon fiber composites compatibilized by NR-g-MAH was about 1 K higher than that of the un-compatibilized composites with same fiber content. This may be attributed to chemical bonds formed between NR-g-MAH and PA6 fibers as discussed previously, which restricted the mobility and flexibility of NR chains.

![Fig. 8 DSC curves of the NR-g-MAH compatibilized NR/short nylon fiber composites and un-compatibilized composites](image)

CONCLUSIONS

Improvement in rubber-filler interaction is desirable for rubber technologists due to its influence on numerous properties of rubber compounds and vulcanizates. To improve the interfacial adhesion between the hydrophilic nylon fiber and hydrophobic NR matrix, NR-g-MAH was synthesized by mixing NR and MAH in a torque rheometer with DCP as initiator. The successful grafting of MAH on to NR backbone and the reaction between the maleic anhydride group of NR-g-MAH and the amine group of PA6 fiber were both confirmed by FTIR. At equal fiber loading, the NR-g-MAH compatibilized NR/short nylon fiber composites showed improved tensile properties, especially tensile modulus at 100% strain which was about 1.5 times that of the corresponding un-compatibilized ones. And the glass transition temperature of the compatibilized composites also increased by about 1 K. The adhesion between the rubber and short nylon fibers was evaluated by the equilibrium swelling method. NR-g-MAH compatibilized composites showed enhanced restriction to swelling, due to the strong interfacial adhesion. NMR technique was used to measure the crosslink density of the un-cured and cured composites and the results showed that the NR-g-MAH compatibilized composites had lower total crosslink density and chemical crosslink density than the corresponding un-compatibilized ones. The microscope pictures revealed better dispersion of fibers in the NR matrix and increased fiber-matrix interfacial adhesion for the NR/short nylon fiber composites compatibilized by the NR-g-MAH, which were the main reasons for the improved tensile properties and higher $T_g$ of the composites.

REFERENCES

1. Wada, N. and Uchiyama, Y., Wear, 1993, 162-164(2): 930
2. Zhang, L.Q. and Zhou, Y.H., China Rubber Industry (in Chinese), 1994, 41(3): 132
