Improvement of the Properties of Ground Tire Rubber (GTR)-Filled Nitrile Rubber Vulcanizates Through Plasma Surface Modification of GTR Powder

Xinxing Zhang, Xiaoqing Zhu, Mei Liang, Canhui Lu

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

ABSTRACT: The surface modification of ground tire rubber (GTR) powder to enhance its adhesion to nitrile rubber (NBR) vulcanizates was investigated. The hydrophobic surface of GTR powder has been transformed to a hydrophilic one through atmospheric pressure dielectric barrier discharge (DBD). The water contact angle dropped markedly from 116 to 0° after being treated for more than 10 s. Attenuated total reflectance Fourier transform infrared spectral (ATR-FTIR) studies revealed the increase in peak intensity at 3298 and 1640 cm^{-1} that correspond to O—H and C═C, respectively, on the surface of the GTR powder. The X-ray photoelectron spectroscopic (XPS) analysis further confirmed the presence of oxygen containing polar functional groups on the surface of the GTR powder after atmospheric plasma treatment. The improvement in tensile strength and tear strength was observed for the modified GTR-filled NBR vulcanizates, which is attributed to the enhanced interfacial interaction between modified GTR and NBR matrix. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1118–1125, 2009

Key words: rubber; recycling; cold plasma; modification; composites

INTRODUCTION

The reuse or recycling of rubber scraps has become an important topic and attracted many researchers' interests in recent years.[1–5] Nowadays, most waste tires have been subjected to incineration or landfilling, and only a small percentage of these scrap tires have gone into a variety of reuse/recycle options. However, incineration and landfilling produce severe environmental problems such as air pollution and soil contamination. A potentially attractive method is to grind waste rubber vulcanizates and use the resultant powder as a compounding ingredient or as a replacement of raw polymer. The reuse of ground tire rubber (GTR) not only protects the environment but also saves limited petroleum resource from which the raw material is originated. Unfortunately, the direct incorporation of GTR into polymer matrices significantly impairs the mechanical and viscoelastic properties of the resulting composites, even at low rubber contents, because of the poor matrix-filler adhesion and lack of reactive sites on the GTR surface.[6] Furthermore, the use of GTR in polar polymers such as nitrile rubber (NBR) is still a challenge in rubber industry. The hydrophobic surface of GTR restricts the wetting of GTR by hydrophilic matrices.

Surface modifications of GTR are widely used to enhance the compatibility with a polymer matrix. Colom et al.[7] modified rubber tire powder by a pretreatment with sulphuric acid to improve the compatibility between tire powder and HDPE matrix. Surface modification of rubber powder by using different concentrations of oxidizing agents such as nitric acid and 30% hydrogen peroxide solution was attempted.[8] It was found that the chemically modified rubber powder improves tensile strength and aging resistance of NR vulcanizates compared with untreated rubber powder. McInnis et al.[9] modified ground rubber powder by a gas-solid reaction with chlorine containing gas. However, these chemical modification approaches must use chemicals as modification agents which led to higher costs and environmental pollution.

Ultraviolet energy (UV) has been extensively applied to modify the surface properties of waste rubber powder using monomers and photosensitizer. The effects of thermal and UV-induced grafting of bismaleimide on mechanical performance of reclaimed rubber/natural rubber blends was studied by Du et al.[10]. Fuhrmann and Karger-Kocsis[11]

described the UV-initiated photografting of glycidyl methacrylate and methacrylic acid onto GTR. Photografting for surface modification of GTR powder using radiation in the presence of allylamine monomer and benzophenone as the photoinitiator was studied by Shanmugharaj et al.[12] However, photoinitiator and inert gases was indispensable in UV radiation procedure, which increased its processing cost.

The present investigation attempts to find a simple and cost-effective technique for surface modification of GTR powders through atmospheric pressure dielectric barrier discharge (DBD). DBD treatment has been widely used in modification of the surface of polymer films and plates.[13–15] In this study, the feasibility of the use of DBD treatment for modifying the surface of GTR powder has been investigated. To develop an easily industrialized technique, process gases and vacuum equipment were not used during the plasma discharge in this research. The modified GTR surface was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), contact angle measurements and scanning electron microscopy (SEM) to investigate the surface functionalization due to plasma treatment. The modified GTR powder was then incorporated into the NBR matrix, and its effect on the properties of the composites has been investigated.

EXPERIMENTAL

Materials

Acrylonitrile butadiene rubber (NBR) with 33 wt % of acrylonitrile content was purchased from Nitriflex S. A. Industria e Comercio (Cotia, Brazil). It had a Mooney viscosity [$ML_{(1+4)}$ at 100°C] of 46. The GTR powder used in this study was generated from passenger car and light truck tires, which was purchased from Sichuan Tianlimin Rubber Co. Ltd (China). The acetone extractable volatile content (8.6%) was obtained from Soxhlet extraction (acetone was used as a solvent). The average particle size of the raw GTR powder is $\sim$ 250 microns. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, and accelerator CBS (N-cyclohexyl-2-benzothiazole sulfenamide), DM (2,2-dibenzothiazole disulfide) were obtained commercially.

Plasma modification of GTR

The surface modification of GTR powder was carried out using a commercial parallel plate dielectric barrier discharge reactor (model CTP-2000K, Nanjing Suman Electronics Co., Ltd, China). Figure 1 is a digital camera picture of the equipment. It consisted of a reactor chamber for plasma treatment and a
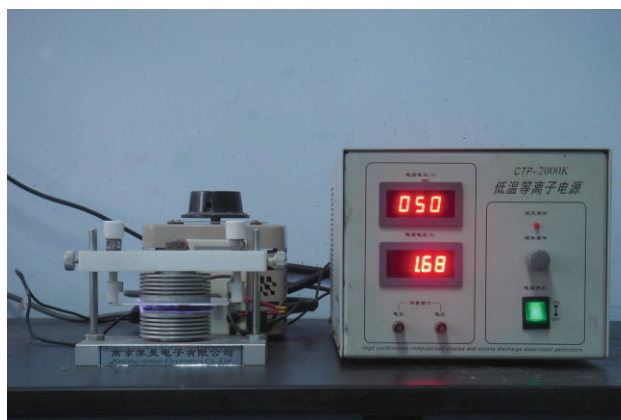
Figure 1 Digital photograph of the parallel plate dielectric barrier discharge reactor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

high voltage generator. The reactor chamber consisted of a pair of parallel disc electrodes with a diameter of 70 mm and a pair of quartz plates with a thickness of 2 mm. The upper electrode was connected to the high voltage generator. The generator fed the air dielectric barrier discharge in a power-controlled manner by variation of the frequency via an automatic impedance matching in the range between 3 kHz and 100 kHz. In this unsealed setup, ambient air at room temperature is blown freely. The GTR specimen is positioned between two insulated electrodes and placed onto the lower grounded electrode for plasma treatment and subsequently exposed to air for about 5 min for further oxidation.

Surface characterization

ATR-FTIR measurements

FTIR measurements were performed with s-polarized light in the ATR (attenuated total reflection) mode using a Nicolet 560 spectrometer (USA). The spectra were collected from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} over 20 scans. Prior to recording the spectra, GTR films about 0.1 mm thick were produced from the GTR powders by hot-pressing between two pieces of aluminum foil (180°C and 10 MPa). The presented spectra were averages over four single measurements at different measurement points on the coated foil to reduce statistic errors resulting from varying layer thickness. The procedure of FTIR, XPS, and water contact angle sample preparations is shown in Figure 2.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra were recorded on an XPS-spectrometer (XSAM800, KRATOS, England) with a monochromatized Al Kα X-ray source (1486.6 eV
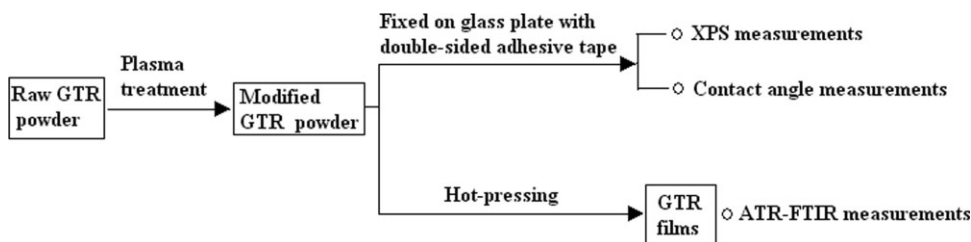
Figure 2 Schematic diagram of the procedure of FTIR, XPS and water contact angle sample preparations.

photons). The uncompacted powders which are fixed on a glass plate through the use of a double-sided adhesive tape may give more realistic values for the determination of contact angle of powders than the conventional approach that is using compacted plate.[16] The X-ray spot size was 1000 and 300 μm for the acquisition of the survey and narrow scan regions, respectively. Binding energies were corrected to the carbon 1s peak located at 285.0 eV.

Water contact angle

One method to appraise surface properties is the water contact angle measurement. When water is applied to the surface, the outmost surface layers interact with the water. A hydrophobic surface with low free energy gives a high contact angle with water, whereas a wet high-energy surface allows the drop to spread, that is, gives a low contact angle. The measurement of the contact angle of water was carried out with a JY-82 contact angle instrument at 25°C. As indicated by the schematic diagram of the sample preparation (Fig. 2), the GTR powder was fixed on glass plate with double-sided adhesive tape and then investigated by water contact angle measurement. The values for the contact angles were averaged over 5 different water drops. Our previous investigations demonstrated that a plasma treatment with air DBD reduces the water contact angle on fluoroelastomer surfaces.[17]

Preparation of rubber compounds

GTR after 120 s of plasma treatment (the discharge distance and discharge power were fixed at 2 mm and 60 W, respectively) were used in preparation of GTR/NBR composites in this study. The schematic diagram of whole experimental procedure of plasma modification and rubber vulcanizates preparation is shown in Figure 3. For the preparation of composites of GTR and virgin NBR, a two-roll mill was used. The compound recipes are listed in Table I. GTR powder was masticated with virgin NBR and then mixed with several compounding ingredients. The mixing time was 10 min. The vulcanization was carried out by using a compression-molding press at 150°C and by applying a pressure of 10 MPa for the optimum cure time (t90). Vulcanized sheets were obtained and used for mechanical testing.

Determination of mechanical properties

The stress–strain properties were measured according to ASTM D 412-80 specification using dumb-bell testing specimens by an Instron 5567 Universal Testing Machine at a crosshead speed of 500 mm/min. At least five measurements for each compound were made.

Morphology observation

A scanning electron microscope (SEM, JEOL JSM-5600, Japan) was used to observe the state of the adhesion performance between GTR and NBR matrix. The samples were cryogenically broken in liquid nitrogen, and the fractured ends of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Characterization by ATR-FTIR

To obtain information on structure and functional groups, ATR-FTIR spectrum studies was conducted.
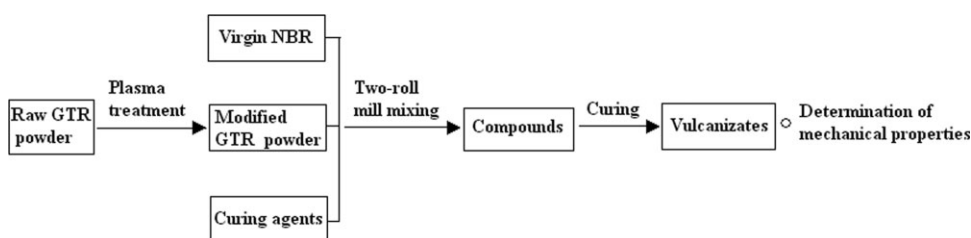
Figure 3 Schematic diagram of experimental procedure of plasma modification and rubber vulcanizates preparation.

TABLE I
Curing Recipes for GTR-Filled NBR Composites

Ingredients (phr)	Formulation code								
	1	2	3	4	5	6	7	8	9
NBR	100	100	100	100	100	100	100	100	100
Raw GTR	–	5	10	15	20	–	–	–	–
Plasma treated GTR	–	–	–	–	–	5	10	15	20
Zinc oxide	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DM	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Figure 4 compares the ATR-FTIR spectra of the GTR before and after the plasma treatment. The absorbance at 3298 cm^{-1} characterizes O—H stretching vibration. The O—H stretching vibration peak and C=C absorption (1634 cm^{-1}) in the ATR-FTIR spectra of the unmodified GTR may be ascribed to the degradation of the GTR during hot-pressing procedure for preparation of FTIR sample. After plasma treatment, the O—H stretching vibration peak intensity became stronger than that of unmodified GTR. The active species in the plasma, e.g., electron and ion, bombarded the surface macromolecular chains of GTR powder, and thus led to the breakage of C—H and C—C bond and generated a polymer radical there. These free radicals can react with oxygen in air and form peroxide bond on the GTR surface.

Significant difference in the ATR-FTIR spectra of the unmodified GTR and modified GTR was also observed in the region near 1634 cm^{-1}. The intensity of the peak at 1634 cm^{-1} corresponding to the carbon-carbon double bond (C=C) absorption shows a sharp increase after plasma treatment. C=C unsatu-

Figure 4 ATR-FTIR contrast spectrum of raw GTR and plasma treated GTR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rated double bond was formed by plasma's etching and hydrogen abstraction.[18]

XPS analysis

XPS analysis was further used to detect the variation of chemical composition of the GTR surface after plasma treatment. Surface compositions determined from XPS analysis of GTR powders before and after atmospheric plasma treatment are summarized in Table II. The results indicated that the oxygen content of the surface of the GTR powders increased after atmospheric plasma treatment.

The C1s core spectrum of unmodified GTR powders [Fig. 5(a)] reveals the peaks at 284.2 eV (C1), 284.8 eV (C2), and 285.5 eV (C3) corresponding to conjugated C=C, C_xH_y and C—S groups, respectively.[11] The C1s core spectrum of plasma modified GTR powders is shown in Figure 5(b). Compared with Figure 5(a), two new peaks with binding energies at 286.1 (C4) and 287.3 (C5) eV appeared after the atmospheric plasma treatment, which can be assigned to the C—O and C=O species. The two species arose from the surface oxidation of the atmospheric plasma treated GTR powder. The C—H bonds of GTR were disrupted by the active plasma species, resulting in the dehydrogenation and generation of free radicals. Because of their reactive nature, these radicals can react with oxygen and water in the atmosphere to form peroxide and hydroxyl peroxide species. The introduction of the oxygen containing polar functional groups onto the GTR surfaces corresponds to the increase in surface energy.
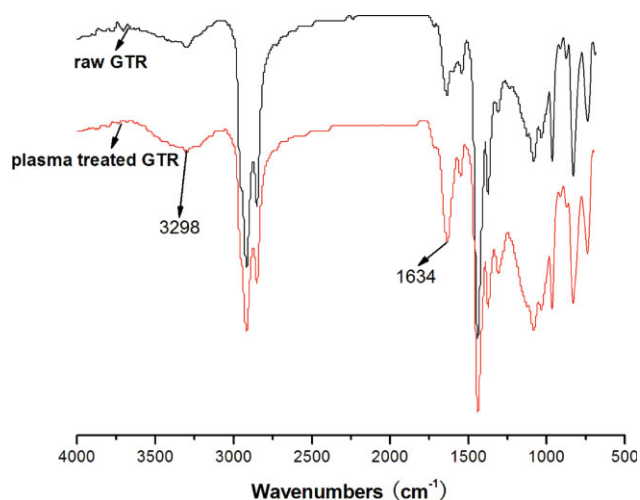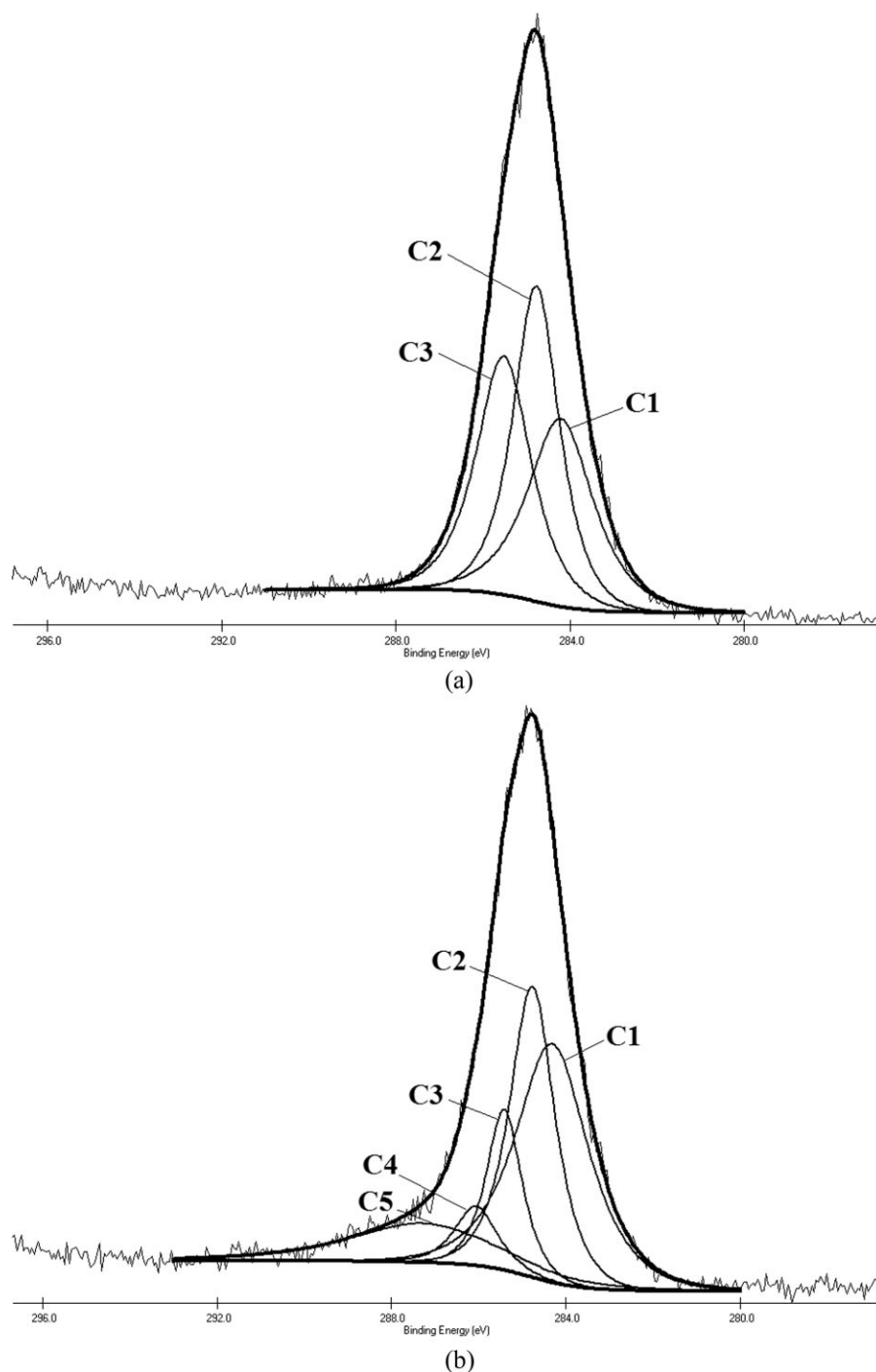
TABLE II
Relative Element Content of the GTR Powder before and after Plasma Treatement as Determined by XPS

Element	Raw GTR	Plasma-treated GTR
C (%)	91.26	86.25
O (%)	8.12	12.54
N (%)	0.63	1.20

Figure 5 C1s core spectrum of raw GTR (a) and plasma treated GTR (b), respectively.

Wettability of GTR powders

Water contact angle measurement was used to appraise the wettability of GTR powder before and after atmospheric plasma treatment. The variation of contact angle with plasma discharge power is given in Table III (the discharge distance and treatment time were fixed at 2 mm and 120 s, respectively). The water contact angle of the unmodified GTR powder was 124.7°, which revealed the hydrophobic

character of the unmodified GTR powders. With the discharge power of 30 w, the water contact angle of the GTR powders with plasma treated for 120 s

TABLE III
Variation of Contact Angle with
Plasma Discharge Power

Power (w)	0	30	40	50	60	70	80
Contact angle (°)	124.7	39.4	0	0	0	0	0

TABLE IV
Variation of Contact Angle with Plasma Treatment Time

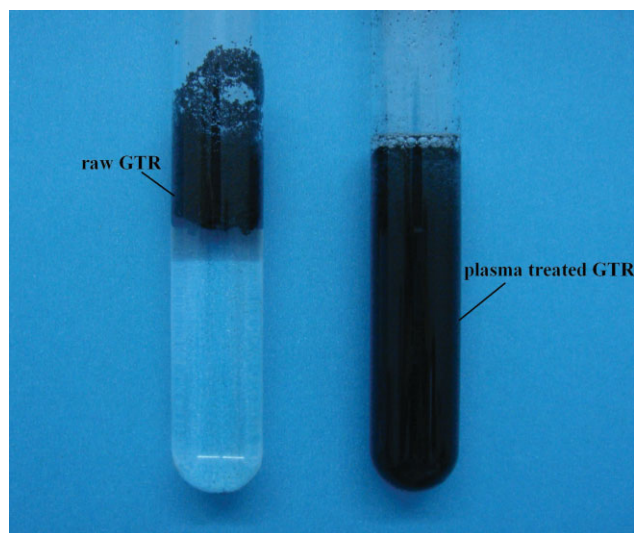| Time (s)	0	10	20	30	60
Contact angle (°)	124.7	0	0	0	0

decreased down to 39.4°, and became ∼ 0° when the discharge power was more than 40 w.

Table IV shows the variation of contact angle with plasma treatment time (the discharge distance and discharge power were fixed at 2 mm and 80 W, respectively). The results showed that the water contact angle dropped markedly to 0° after just 10 s treatment and remained constant with further increase of the treatment time. The increase in —OH groups on the GTR surface may responsible for the hydrophilic behavior of the modified GTR powder.
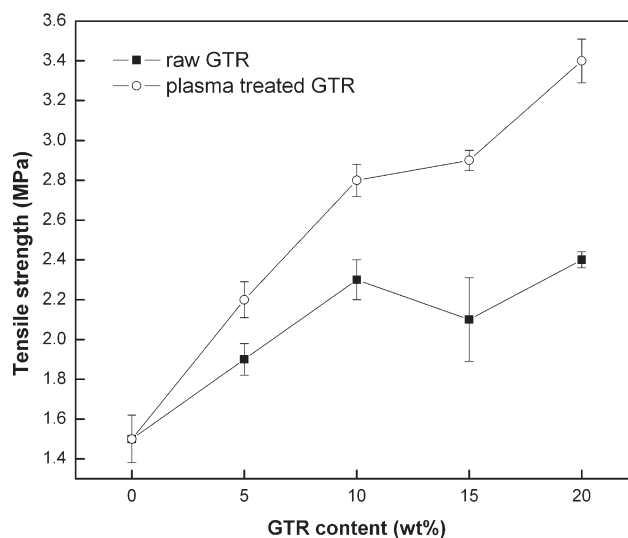
The dispersing stability of unmodified and plasma treated GTR (with the discharge distance of 2 mm, discharge power of 80 W and treatment time of 10 s) in water are shown in Figure 6. It is obvious that the unmodified GTR cannot be well dispersed in water due to its hydrophobic nature. However, the GTR powder with plasma treated for 10 s is well distributed in water, indicating its hydrophilic feature after surface modification.

Mechanical properties

Changes in the chemical structures of surface of GTR powder due to the atmospheric plasma treatment should also influence its adhesion ability to polar NBR matrix, and thus alter the mechanical properties of the GTR-filled NBR vulcanizates. The

Figure 7 Effect of GTR content and surface modification on tensile strength.

effects of the GTR content and surface modification of GTR powder on the tensile strength and tear strength of GTR filled-NBR vulcanizates are shown in Figures 7 and 8, respectively. It is obvious that the tensile strength and tear strength of the modified GTR-filled NBR vulcanizates are much better than those of the unmodified GTR-filled NBR vulcanizates, and this effect is more evident with the increasing in GTR content. At the GTR content of 20%, the tensile strength of the GTR-filled NBR vulcanizates was increased by 42%, and the tear strength increased by 21% through surface modification of GTR. The increase in tensile strength and tear strength are ascribed to the improved interfacial bonding between the modified GTR and the NBR matrix. The hydrophobic surface of unmodified GTR restricts the wetting of GTR by hydrophilic NBR
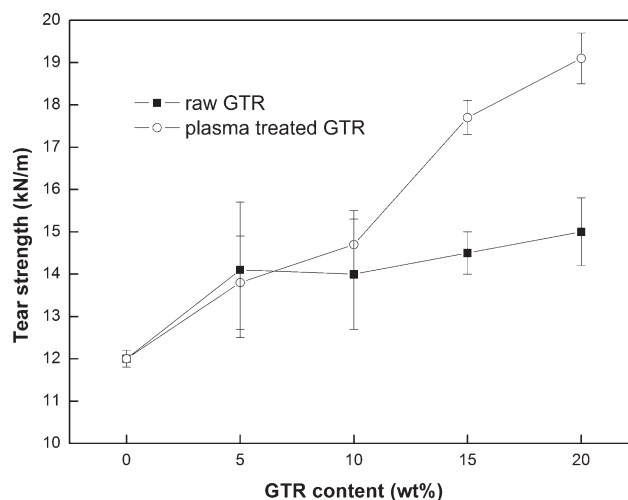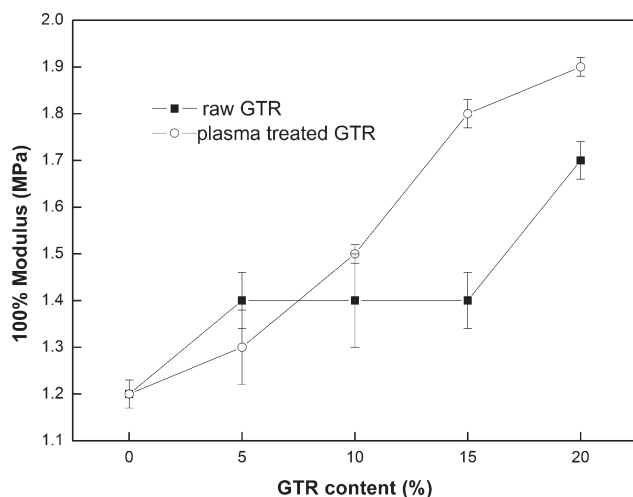
Figure 6 The dispensing stability of raw and plasma treated GTR (treated for 10 s) in water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
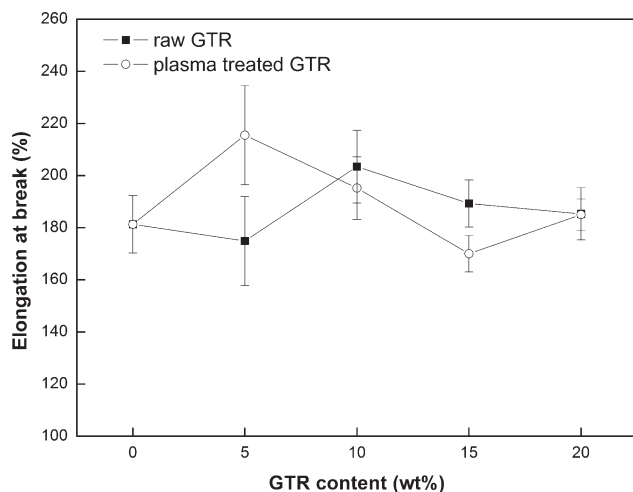
Figure 8 Effect of GTR content and surface modification on tear strength.

Figure 9 Effect of GTR content and surface modification on 100% modulus.

matrices. However, the oxygen containing polar functional groups were introduced onto the surface of the GTR powders after atmospheric plasma treatment. Thus, the interfacial bonding between the modified GTR and polar NBR matrix was improved. Furthermore, atmospheric plasma treatment created more carbon-carbon double bond (C=C) on the surface of modified GTR powders, as displayed in ATR-FTIR spectra. The unsaturated bond on the surface of modified GTR can interact with the unsaturated bond existing in the butadiene part of NBR matrix, leading to a better interfacial adhesion. There are two simultaneous processes such as vulcanization of the virgin rubber and revulcanization of partially devulcanized GTR (the reclaim rubbers with carbon-carbon double bond) and even the covulcanization of them during vulcanization of GTR/virgin rubber composites.[19]


**Figure 10** Effect of GTR content and surface modification on elongation at break.

Plasma modification of the GTR powder also enhance the tensile modulus at 100% elongation of the GTR-filled NBR vulcanizates (Fig. 9). The variation of elongation at break of the unmodified and modified GTR-filled NBR vulcanizates versus the GTR content is shown in Figure 10. The results indicated that the elongation at break of NBR vulcanizates was reserved even with the incorporation of 20 wt % modified GTR powder into NBR vulcanizates.

Morphological studies

Figure 11(a,b) shows the cryogenically fractured surface of the 20 wt % unmodified and plasma modified GTR-filled NBR vulcanizates, respectively. As displayed in SEM micrographs, the interfacial adhesion was considerably improved when the GTR powders were modified with air plasma treatment. The result can be ascribed to the introduction of polar functional groups on the surface of the GTR
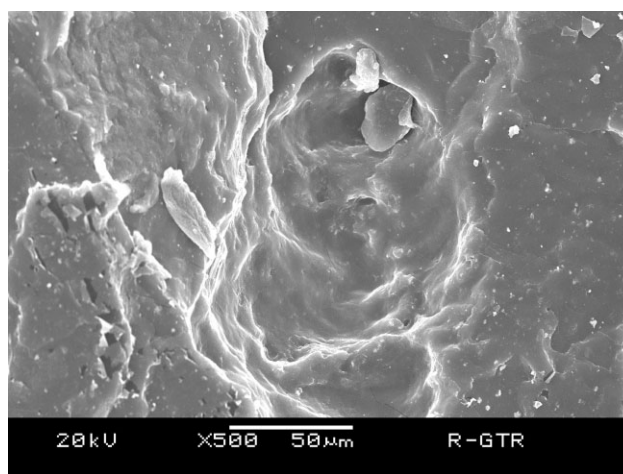
(a)
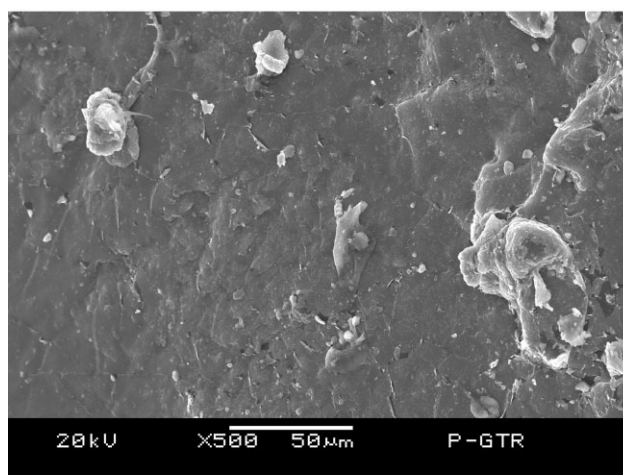
(b)

Figure 11 SEM fractographs of GTR/NBR 20/80 (wt/wt) blends (a) raw GTR; (b) plasma treated GTR at magnification of ×500.

powder, which were generated during atmospheric plasma treatment.

CONCLUSIONS

Surface functionalization of GTR powder was realized with plasma treatment at atmospheric pressure for improving interfacial adhesion. In comparison with other radiation methods, the modification procedure is simple and cost-effective. The increase in peak intensity at 3298 cm^{-1} indicates that —OH groups were introduced onto the GTR surface after atmospheric plasma treatment. The presence of carbon-carbon double bond (C=C) has been confirmed from the increase in peak intensity at 1634 cm^{-1}. The presence of oxygen containing polar functional groups on the surface of the GTR powder after atmospheric plasma treatment has also been confirmed from the XPS analysis. The water contact angle of the surface of GTR powder dropped markedly from 116 to 0° after being treated for more than 10 s, indicating the hydrophilic nature of the modified GTR powder. The improved mechanical properties are obtained for plasma modified GTR-filled NBR vulcanizates and that is attributed to the increased interfacial bonding between the plasma modified GTR and NBR matrix.

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