

Surface Modification of Natural Rubber Film by UV-Induced Graft Copolymerization with Methyl Methacrylate

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ABSTRACT: Methyl methacrylate (MMA) was directly grafted on natural rubber (NR) or sulfur prevulcanized (SP) NR surface. The rubber sheet was primarily treated with argon plasma, followed by exposure to air for generating active functional groups. After immersing in a mixture of 30% hydrogen peroxide and MMA in ethanol and water (1 : 1), the MMA grafting took place after UV-irradiation for 30–120 min. Results from the contact angle measurement and attenuated total reflection–Fourier transform infrared (ATR-FTIR)

spectroscopy showed that the highest amount of MMA grafting was achieved when using 13 wt % of MMA and UV irradiation time of 60 min. The tensile strength and percentage elongation at break of the modified SPNR sheet, having similar MMA grafting to that of NR, were in acceptable range as indicated in the standard glove's test (ASTM D3577). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2270–2276, 2007

Key words: rubber; modification; graft copolymers

INTRODUCTION

Prevulcanized natural rubber (P-NR) latex has been widely used as a raw material in the fabrication of thin film products, including various types of gloves. Although P-NR glove's bulk property is excellent, problems with tack and high surface friction still persist and require attentions.¹ Powder talc or cornstarch was applied to reduce surface friction of rubber film.^{2,3} However, this caused serious contamination in electronic and biomedical applications.^{2,3} Furthermore, the powder-free glove developed by halogenation method is hard and brittle and assumed dark color quickly.^{4–7} It is therefore of great interest to coat a polymer having high glass transition temperature, e.g., poly(methyl methacrylate) (PMMA) on the rubber substrate to increase the film surface hardness and to decrease rubber's friction. Recently, polymerization of MMA on the NR film surface in the water-based system was carried out using a two-step process, i.e., immersing NR strip into an aqueous emulsion of MMA containing *tert*-butyl hydroperoxide, and then into an aqueous solution of ferrous ion to activate a redox initiation.⁸ Although the amount of MMA swollen on NR sheet could be adjusted by varying the immersion time, the maximum PMMA incorporation was only 4%. This low amount of

PMMA was, however, sufficient to significantly increase surface roughness and hardness and would potentially reduce the surface friction of the modified NR.

The deposition of PMMA latex particles on NR was an alternative method for generating PMMA on the rubber surface. Among various techniques, the simple and versatile Layer-by-Layer (LbL) technique is highly promising mainly because the alternating adsorption of this process is independent of the morphology and size of the substrate.^{9,10} LbL technique has found numerous applications,¹¹ including embedment of polystyrene (PS) latex particles into the assembled LbL film^{12,13} which resulted in an increase of the surface roughness. Recently, this technique has been used for deposition via electrostatic interaction of negatively charged PMMA latex particles onto NR film.¹⁴ The charge on NR substrate was generated by UV grafting of acrylamide (AAm) on the rubber surface pretreated with argon (Ar) plasma. The presence of PMMA particles on the grafted NR sheet was observed under scanning electron microscope (SEM), and the increase of surface roughness was examined by atomic force microscopy (AFM). The percent surface coverage of PMMA particles on the substrate was regulated by varying the latex concentration, immersion time, ionic strength, and pH of medium.

Although the previous studies for surface modification of NR film by producing PMMA at the outermost layer indicated enhancement of the surface roughness and hardness of NR, the processes involved multistep preparation. In this work, we omitted the steps of swelling MMA on the NR surface that might modify

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the bulk property and the grafting with AAm for generating charge on NR film. The MMA monomer dissolved in a mixture of ethanol and water was directly grafted, under UV, on rubber sheet pretreated with Ar plasma. To produce more free radicals at the NR sheet/aqueous medium interface where the polymerization loci were confined, a water soluble initiator hydrogen peroxide was added. Under UV, the hydroperoxide groups decomposed to hydroxy radicals which presumably initiated the grafting copolymerization on the NR surface. The optimum grafting conditions were examined by considering major factors, i.e., MMA concentration and UV irradiation time. The NR grafted with MMA (NR-g-PMMA) was then characterized by contact angle measurement, attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, and SEM. The tensile properties of the modified sulfur prevulcanized (SP) NR sheet were measured according to the standard glove's test (ASTM D 3577).

EXPERIMENTAL

Materials

A dried rubber sheet was casted from high ammonia (HA)-preserved NR (Rayong Bangkok Rubber Co., Rayong, Thailand) or SPNR (Dr.Boo Co., Chonburi, Thailand) latex on a glass plate at room temperature. The MMA monomer (Fluka, Purum) was purified by passing through a column packed with neutral and basic aluminum oxide (Fluka, Purum). The purified monomer was stored at 4°C until use. Other reagents, e.g., 30 wt % hydrogen peroxide (Carlo Erba, RPE), methanol (Fluka, AR), acetone (Fluka, Commercial), and ethanol (Fluka, AR) were used as received.

NR surface preparation

The rubber sample ($1.5 \times 4 \times 0.1 \text{ cm}^3$), adhered to a poly(ethylene terephthalate) (PET) film without using any adhesive, was cleaned by immersing in a beaker containing methanol and then Milli-Q water for 15 min in an ultrasonic bath (Sonorex RK 100 H, Bاندلین). The sample was allowed to dry at room temperature in open air.

UV-induced graft copolymerization with MMA

The dried rubber strip was treated with Ar plasma (Basic plasma kit BP-1, Samco) at 100 W, 13.56 MHz under 0.5 Torr for 10 s (NR) or 90 s (SPNR), and then exposed to air for 10 min to effect the surface peroxide formation.¹⁵ The pretreated rubber was subsequently immersed into a Pyrex[®] tube containing ethanol: water (1 : 1), 1–19 wt % MMA (40 mL), and 30 wt % hydrogen peroxide (1 mL). The grafting reac-

tion was performed by irradiation with UV (Mercury HPLN 1000 W, Phillips) from 30 to 120 min. The residual homopolymer was removed from the sample by washing with acetone at room temperature overnight. The nonirradiated or control sample was prepared according to the above procedure except for UV irradiation.

Surface characterization of modified rubber

The NR-g-PMMA sheet was characterized by measuring contact angle (G-1, Kruss) of a water droplet (~5 μL) on the sample surface. Each value reported was the average of 10 separate drops of water on a given surface. ATR-FTIR (EQUINOX 55, Bruker) spectra were collected from 32 scans at 4 cm^{-1} resolution by using a Ge crystal with single reflection mode. The average areas under peaks at 1730 and 1376 cm^{-1} , corresponding to C=O stretching of PMMA and CH₃ deformation of NR respectively, were calculated by using the OPUS program. Surface morphology of the sample, coated with gold by using a sputter coater (BAC-TEC, SCPO 50) for 80 s, was studied under SEM (SEM 2003s, Hitachi).

Tensile test

Tensile strength and elongation at break of the SPNR-g-PMMA were measured according to the ASTM D412-98a using a tensile tester (5569, Instron) at cross-head speed of 500 mm/min with the load cell of 1000 N. The dimension of test sample used was type IV according to ASTM D638-99. At least five specimens were used for one measurement.

RESULTS AND DISCUSSION

Ar plasma treatment

Ar plasma treatment was applied to produce carbon radicals at the rubber surface. When the activated rubber was exposed to air, surface oxidation took place, leading to the formation of peroxide and hydroperoxide species including other oxidized carbon species.¹⁵ The formation of these species increased in hydrophilicity and decreased the water contact angle of the modified rubber surface. The water contact angles of the rubber surface treated with Ar plasma at various treatment times are presented in Table I.

The values of water contact angle, shown in Table I, rapidly decreased with increasing plasma treatment times at the beginning and then approached constant. Results implied the presence of polar groups, possibly derived from various oxygen-based functionalities, and the peroxide and hydroperoxide groups¹⁵ as shown:

TABLE I
Water Contact Angles of NR and SPNR Sheets Treated with 100 W RF Power as a Function of Plasma Treatment Times

Plasma treatment time (s)	Contact angle (degree)	
	NR	SPNR
0	89.5 ± 1.1	89.7 ± 1.5
5	50.1 ± 2.2	78.5 ± 1.6
10	43.6 ± 1.7	61.9 ± 1.3
15	43.4 ± 1.6	55.4 ± 2.1
20	42.6 ± 1.4	53.2 ± 1.8
30	50.4 ± 1.3	50.2 ± 1.2
60	–	45.2 ± 1.5
90	–	39.9 ± 1.7
120	–	39.6 ± 0.9
180	–	38.4 ± 1.3



where P represents polymeric species.

The water contact angle of the treated NR surface was constant as reported previously^{14,15} indicating a complete coverage of these generated species on NR surface. The shorter plasma treatment time was required to attain the constant water contact angle of unvulcanized NR (10 s), when compared to that required in the case of SPNR (90 s), possibly due to the lower amount of double bond at the SPNR surface.

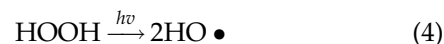
Surface characterization of NR-g-PMMA

Effect of MMA concentration

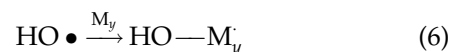
The presence of PMMA on the surface of NR sheet modified with various monomer concentrations was characterized by ATR-FTIR, a technique well suited for the study of surface chemical species.⁷ The spectra of the unmodified and modified samples are shown in Figure 1.

From ATR-FTIR spectrum of the unmodified NR, characteristic peaks at 2961, 2926, 2854 (C–H stretching), 1448 (C–H deformation of –CH₂–), 1376 (C–H deformation of –CH₃), and 836 cm⁻¹ (C–H deformation of *cis* C=C–H) were identified. After graft copolymerization, the characteristic absorption peak at 1730 cm⁻¹ corresponding to C=O stretching was clearly observed in all modified NR, indicating PMMA formation on the surface. Under UV irradiation, active radicals on the NR surface could be generated from hydroperoxide groups formed by plasma treatment and from the added initiator. The monomer was, therefore, grafted on the rubber by either transferring active radicals of growing PMMA chains to polyisoprene or generation of radicals on NR molecules as shown.¹⁶

Peroxide decomposition:



Chain initiation:



Termination:

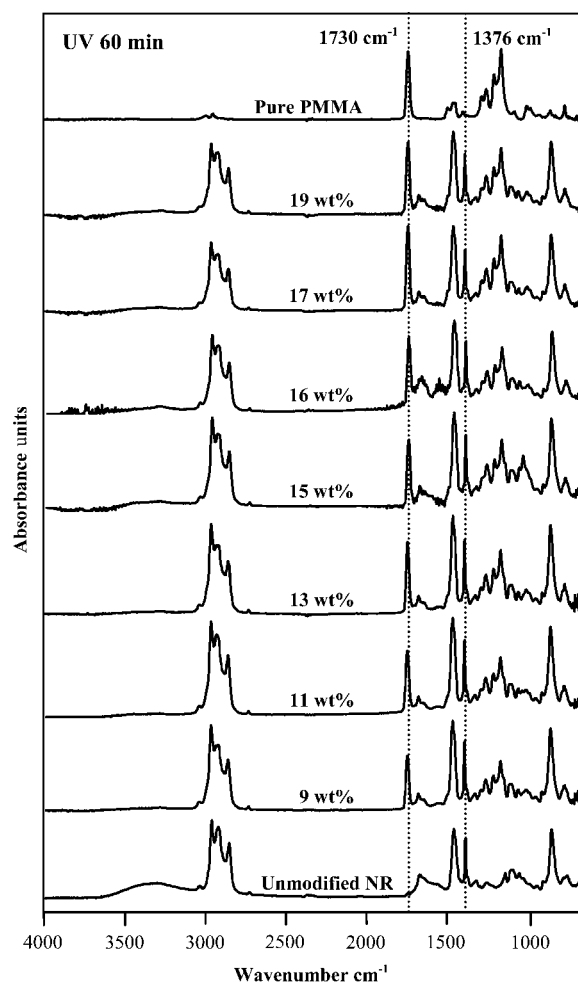
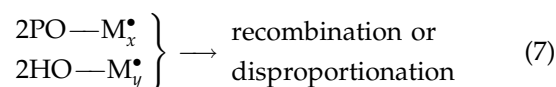


Figure 1 ATR-FTIR spectra of NR, pure PMMA, and NR-g-PMMA latex sheets prepared when using different MMA concentrations (9, 11, 13, 15, 16, 17, and 19 wt %) for UV-irradiation time of 60 min.

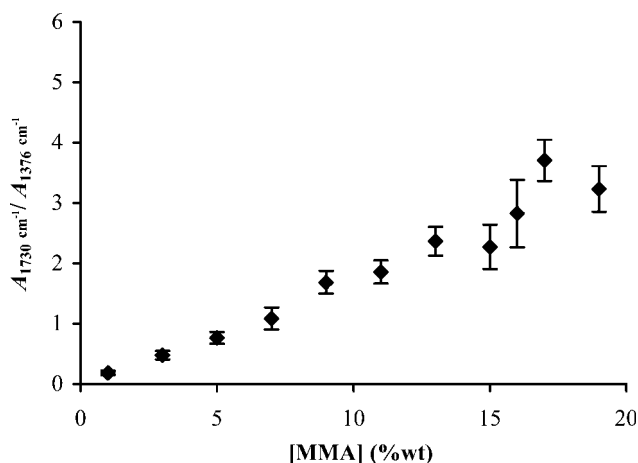
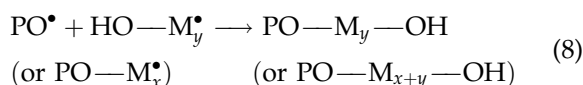


Figure 2 Effect of MMA concentrations on ratios of the area under peaks at 1730–1376 cm^{-1} (A_{1730}/A_{1376}) of the NR-g-PMMA sheets when using UV-irradiation time of 60 min.



where M represents a monomer.

To determine the amount of grafted MMA in all modified NR samples, the area under the peak at 1730 cm^{-1} of PMMA was compared to that corresponding to the bending vibration of the methyl group at 1376 cm^{-1} of NR. The ratios of area under both peaks (A_{1730}/A_{1376}) as a function of MMA concentrations are presented in Figure 2.

The linear relationship between the area ratio (A_{1730}/A_{1376}) and MMA concentration was observed. Results confirmed that the amount of MMA grafted on NR was directly proportional to the monomer content, which related to the increase in rate of radical

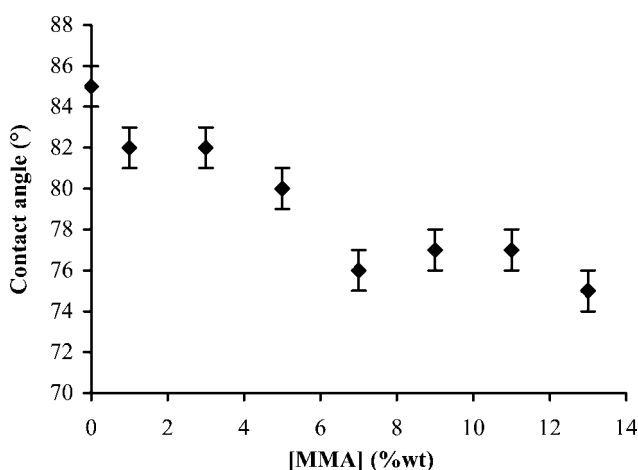


Figure 3 Water contact angles of the NR-g-PMMA sheet surfaces as a function of MMA concentrations.

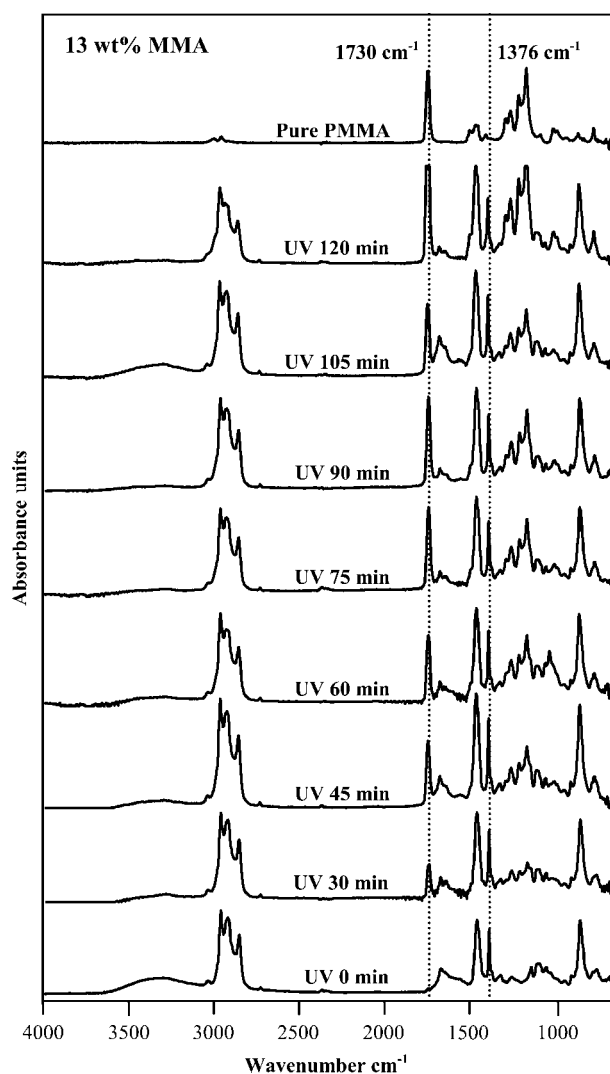


Figure 4 ATR-FTIR spectra of pure PMMA and NR-g-PMMA latex sheets prepared when using different UV irradiation time (0, 30, 45, 60, 75, 90, 105, and 120 min) and 13 wt % of MMA.

polymerization (R_p).¹⁷ However, the reproducibility of the area ratio decreased when increasing MMA concentration from 15 to 19 wt %. This might result from the formation of PMMA homopolymer, observable with naked eyes as white solid precipitating out in the reaction tube. The result agreed well with the previous work, which reported that homopolymerization in the solution was more pronounced at high monomer concentration.¹⁸ The high amount of homopolymer reduced UV intensity that could reach the outermost of rubber surface. Hence, the possible new active sites or grafting efficiency on the rubber molecule decreased. From the area ratio, we believed that the amount of PMMA grafted on NR was less than 4%, which was sufficient for modification of surface properties of the rubber.⁸

The formation of PMMA, relatively more hydrophilic than NR, lowered the hydrophobicity of the

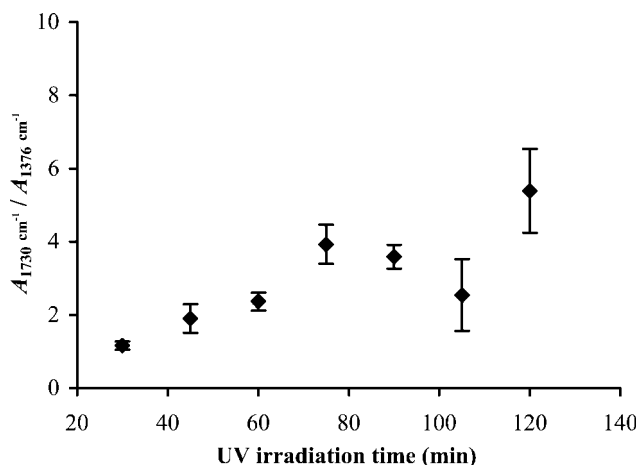


Figure 5 Effect of UV irradiation times on ratios of area under the peaks at 1730–1376 cm^{-1} (A_{1730}/A_{1376}) when using different UV-irradiation time (30, 45, 60, 75, 90, 105, and 120 min) and 13 wt % of MMA.

rubber. The water contact angle of NR-g-PMMA surface as a function of MMA contents was examined as displayed in Figure 3.

The water contact angle decreased from 85° to 76° with increasing MMA from 1 to 7 wt % and approached a constant. It was reported that the water contact angle for pristine PMMA was 67° .¹⁹ Therefore, PMMA was formed on the rubber surface, but the grafted yield was not high enough to completely cover the surface. In addition, the constant contact angle might be due to the limitation of the technique employed, i.e., the contact angle measurement is sensitive only for the outermost surface's analysis.²⁰ From the reproducibility and high grafted yield, the concentration at 13 wt % MMA was selected for further study.

Effect of UV irradiation time

The UV irradiation time used in the preparation of NR-g-PMMA was varied, while MMA concentration was held constant. The ATR-FTIR spectra of the NR grafted with MMA at various irradiation times are shown in Figure 4.

The spectrum of the nonirradiated specimen was similar to that of NR shown in Figure 1, implying that the MMA was not grafted on NR in the absence of UV irradiation. Besides UV irradiation, the added hydrogen peroxide was required to initiate the graft copolymerization, although hydroperoxide groups were previously generated by Ar plasma. The grafting sites on the *cis* positions of NR chains might sterically hinder the approaching monomer producing a high amount of initiator radicals.¹⁸ As expected, the peak at 1730 cm^{-1} of PMMA was detected in all spectra of the irradiated samples. The values of $A_{1730}/$

A_{1376} of the NR-g-PMMA, which were directly proportional to UV irradiation times, are presented in Figure 5.

The longer irradiation time caused more decomposition of hydroperoxide groups which consequently produced more grafted MMA.²⁰ During UV irradiation

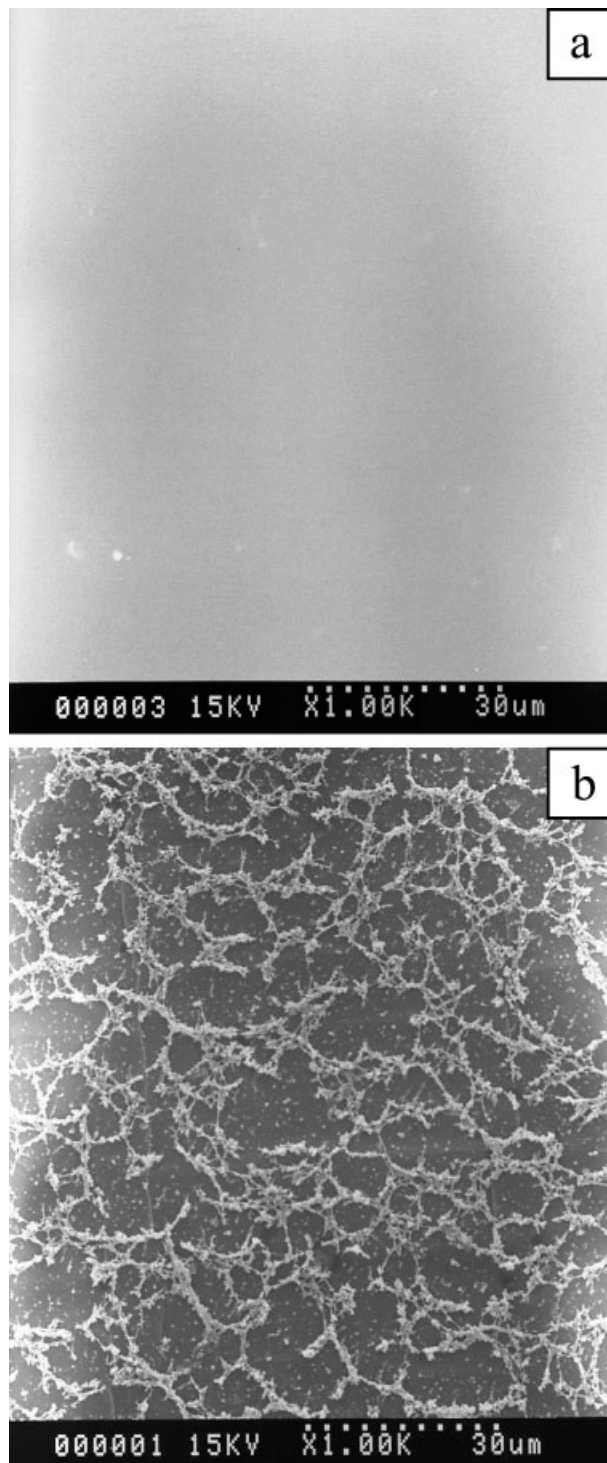


Figure 6 SEM micrographs of (a) unmodified NR and (b) NR-g-PMMA sheet when using 13 wt % of MMA and UV-irradiation of 60 min.

tion, the reaction temperature also increased, which had direct effect on the number of free radicals and the rate of polymerization. However, at high temperature, abundant radicals underwent either recombination or other side reactions.¹⁸ This should increase the amount of homopolymer shielding the intensity of UV source as previously mentioned. Consequently, the reproducibility of grafted yield decreased with increasing UV irradiation time from 75 to 120 min.

Surface morphology of NR-g-PMMA

SEM micrographs of the unmodified NR and NR-g-PMMA surfaces are shown in Figure 6(a,b), respectively.

Compared to the unmodified NR surface [Fig. 6(a)], the surface of NR-g-PMMA sheet [Fig. 6(b)] was not uniform showing the mesh-like structure. The grafted PMMA chain on NR surface might be responsible for this morphology. Due to the fact that the free radicals generated from the water-soluble initiator could not diffuse inside the substrate, the grafting reaction, therefore, took place largely on the NR surface. The low amount of grafted MMA was sufficient to increase the modified NR surface's roughness.⁸ It was expected that the presence of PMMA hardened and roughened the NR-g-PMMA surface and, hence, lowered the adhesive property against other substrate. Both factors potentially caused the reduction of the rubber's surface friction.

Tensile test

The commercial glove is generally prepared from SPNR latex, and this obliged to investigate the SPNR-g-PMMA. The effect of surface grafting on the tensile properties of SPNR was examined. The plots of elongation at break of SPNR-g-PMMA sheet when using different MMA concentrations (13, 15, and 17 wt %) and UV-irradiation time of 60 min.

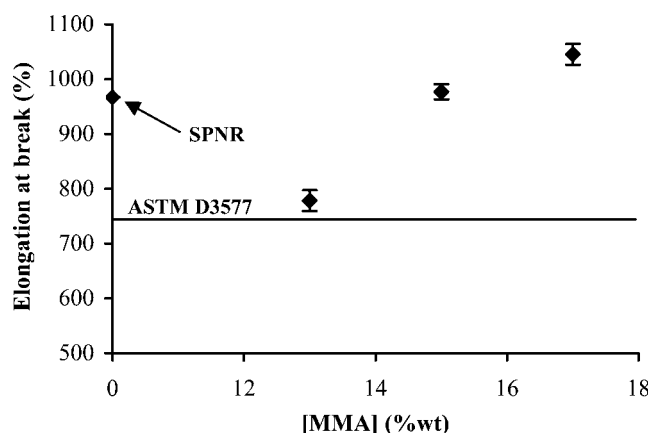


Figure 7 Effect of MMA concentration on elongation at break of SPNR-g-PMMA sheet when using different MMA concentrations (13, 15, and 17 wt %) and UV-irradiation time of 60 min.

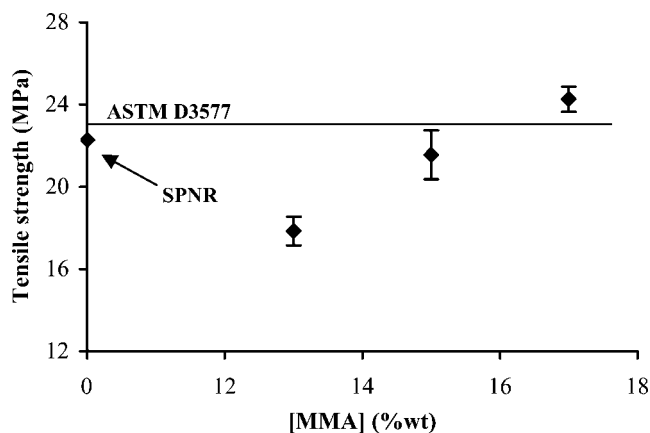


Figure 8 Effect of MMA concentrations on tensile strength of SPNR-g-PMMA sheets when using different MMA concentrations (13, 15, and 17 wt %) and UV-irradiation time of 60 min.

gation at break of the SPNR-g-PMMA sheets versus MMA contents are presented in Figure 7, whereas their tensile strength values are shown in Figure 8.

As anticipated, the tensile strength of SPNR was slightly lower than that of the standard because of the fact that the film formation of commercial SPNR latex, without adding any ingredient in this study, was carried out at room temperature. Although both elongation at break and tensile strength increased with increasing MMA concentration, only the tensile strength of the sample treated with 17 wt % MMA was in acceptable range as indicated in the standard glove's test (ASTM D3577). This might be due to the fact that the higher MMA should provide, under UV irradiation, the longer grafted PMMA chains. Even though PMMA is more hydrophilic than NR, some grafted PMMA chains could penetrate into a thin layer of SPNR surface, similar to the previous study concerning the surface modification of polytetrafluoroethylene film.²¹ The penetrated long PMMA chains could entangle well with rubber providing a good interlocking between PMMA and SPNR phases and, hence, good tensile strength and elongation at break.

CONCLUSIONS

MMA was directly grafted on NR and SPNR latex sheets using the Ar plasma pretreatment/UV-induced graft copolymerization technique. The higher MMA concentration and longer UV irradiation time significantly enhanced the grafted MMA yield. The nonuniform NR-g-PMMA surface, observed under SEM, potentially reduced the rubber's surface friction. Finally, mechanical properties of the SPNR-g-PMMA using 17 wt % of MMA and 60 min UV irradiation time were in acceptable range in the standard glove's test (ASTM D3577).

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