Glycidyl Methacrylate Grafted Natural Rubber: Synthesis, Characterization, and Mechanical Property

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ABSTRACT: Glycidyl methacrylate (GMA) was grafted onto natural rubber (NR) using emulsion polymerization method. The structures of copolymers were characterized by ^{1}H nuclear magnetic resonance (^{1}H-NMR), solid state ^{13}C-NMR spectroscopy, and Fourier transform infrared spectrometer (FTIR). The %grafting obtained from the gravimetric method and the absorbance ratio were compared. Effects of reaction temperature, GMA content, and reaction time on %grafting, grafting efficiency, and %conversion of GMA monomer were determined. Effect of %grafting on mechanical properties of the graft copolymer was studied. Experimental result showed that the appropriate reaction time was 8 h at a reaction temperature of 30°C. Moreover, tensile strength and modulus of the graft copolymer increased with increasing %grafting. However, elongation at break of the graft copolymer decreased with increasing %grafting. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3152–3159, 2011

Key words: compatibilization; rubber; graft copolymers; NMR; FT-IR

INTRODUCTION

Natural rubber (NR) is an unsaturated elastomer obtained from renewable resource. Its good properties, such as high resilience, high elongation at break, and fatigue resistance makes it become an interesting biomaterial [1]. However, NR is very sensitive to heat, oxidation reaction and solvent, mainly due to the double bond in its chain and its non polar character.[2] Moreover, it has low tensile modulus and tensile strength which causes limitation in variety of applications. To overcome these drawbacks, chemical modification of NR has been widely studied. Various methods have been used to improve properties of NR such as maleated natural rubbers,[3] epoxidized natural rubber,[4] and graft copolymer of NR. To graft NR, various types of monomers such as styrene,[5] dimethylaminoethyl methacrylate (DMAEMA),[6] methacrylic acid,[7] and methyl methacrylate (MMA)[8] have been widely used. Oliveira et al. found that tensile strength of NR was improved by grafting DMAEMA onto NR.[6] George et al. studied mechanical properties of NR grafted MMA.[9] They found that modulus of the films was increased with increasing MMA content. Glycidyl methacrylate (GMA) is one of interesting acrylate monomers because of its relatively low toxicity, polarity and lower price compared with others acrylate monomers.[10] Furthermore, it has an epoxy group in its chemical structure which exhibits a large number of chemical reactions by opening of their oxirane ring. Copolymers of GMA have been used for various industrial applications such as nonlinear optics,[11] polymer membranes,[12] bioactive bone cement,[13] paper strength additives,[14] and leather adhesives[15,16] Moreover, GMA grafted polymers such as styrene/acrylonitrile/glycidyl methacrylate copolymer (SAN-GMA),[17] poly (ethylene-glycidyl methacrylate) (EGMA),[18] and glycidyl methacrylate grafted poly (ethylene octane) (GMA-*g*-POE)[19] can be employed as compatibilizer for promoting the interaction between immiscible phases in the polymer blends. These studies demonstrated an improvement in the mechanical characteristics of polymer by its reactive blending with graft copolymer of GMA.

According to the status of NR from the natural source which is in latex form, the emulsion polymerization is a suitable method for modifying NR. Moreover, low viscosity, good heat transfer and

faster rate of polymerization can be obtained from this method. Thus graft copolymerization of NR using emulsion polymerization has attracted great attention from many researchers.[20–22] To initiate polymerization reaction, various methods were used including high energy reaction technique,[23,24] photochemical technique,[25] and redox polymerization.[26] Redox polymerization is among the most popular techniques for grafting reaction especially for NR. This initiation system was very effective for emulsion polymerization in the NR latex, because it worked well with the present of ammonia and was not sensitive to oxygen.[27]

In this work, graft copolymer of GMA onto NR was synthesized by emulsion polymerization. Cumene hydroperoxide (CHP) and tetraethylenepentamine (TEPA) were used as initiators. It was expected that mechanical properties of NR can be improved by grafting GMA onto NR. Moreover, glycidyl methacrylate grafted natural rubber (NR-g-GMA) may be used for many applications such as a compatibilizer. From our study,[28] NR-g-GMA was shown to be an effective compatibilizer for PLA composites. Our results showed that the toughness of PLA composites was improved by adding NR-g-GMA as a compatibilizer.

EXPERIMENTAL

Materials

NR latex containing 61.05% dried rubber was purchased from Thaihua Latex Co., Ltd. Glycidyl methacrylate (GMA) and tetraethylene-pentamine (TEPA) were obtained from Aldrich. GMA was purified to remove inhibitor by basic alumina pack column (Aldrich) before used. Sodium dodecyl sulfate (SDS) and cumene hydroperoxide (CHP, 80%) were purchased from Fluka.

Synthesis of NR-g-GMA

The graft reactions were carried out in a three neck round bottom flask reactor of 250 mL with agitation of 100 rpm under nitrogen atmosphere, using distilled water as continuous phase. In each reaction, NR latex was added first. The distilled water, surfactant and GMA were then added, respectively. After that CHP was added and then 5×10^{-4} g/mL solution of TEPA was added at a rate of 0.08 mL/min for 6 h. Hydroquinone was added to stop the reaction and then the emulsion samples were poured on petidish and dried in an oven at 70°C for 48 h to remove water and unreacted monomers. After that, the film samples were obtained. Then they were cleaned with excess of 20% methanol in water and then extracted with acetone in a soxhlet setup for 24 h. Acetone was expected to extract unreacted GMA and polyglycidyl methacrylate (PGMA). This technique was used to extract PGMA from samples by several researchers.[29,30] This extraction is known to be sufficient for removing almost all homopolymer in the film. To confirm the effectiveness of soxhlet extraction, NR were melt blended with PGMA at the ratio of 83.3/16.7% (w/w) by using an internal mixer (Hakke Rheomix, 3000p) at the temperature of 170°C with a rotor speed of 60 rpm for 10 min. NR/PGMA blend before and after soxhlet extraction were characterized by FTIR spectrophotometer. The FTIR spectra of NR/PGMA blend before and after soxhlet extraction are shown in Figure 1. Polyglycidyl methacrylate (PGMA) showed a strong peak at 1716 cm^{-1}, which corresponded to carbonyl group (C = O). This characteristic peak did not exist in FTIR spectrum of NR. For NR/PGMA blend sample, C = O stretching (1729 cm^{-1}) of PGMA can be observed. After soxhlet extraction of NR/PGMA, this characteristic peak (C = O) disappeared indicating that PGMA can be extracted from sample.

After extraction the undissolved part of sample was dried in an oven at 70°C for 24 h to a constant weight and characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. Weight of GMA grafted was obtained from the difference between weight of extracted sample and weight of NR. Weight of GMA homopolymer was obtained from the difference between weight of initial sample and extracted sample. Grafting efficiency, %grafting and %conversion of GMA monomer are defined and calculated as follows:[31]

$$\text{Grafting efficiency} = \left(\frac{\text{Weight of GMA grafted}}{\text{Weight of GMA grafted } + \text{ Weight of GMA homopolymer}} \right) \times 100$$

$$\% \text{ grafting} = \left(\frac{\text{Weight of GMA grafted}}{\text{Weight of NR}} \right) \times 100$$

$$\% \text{conversion} = \left(\frac{\text{Weight of GMA grafted} + \text{Weight of GMA homopolymer}}{\text{Weight of GMA monomer}} \right) \times 100$$
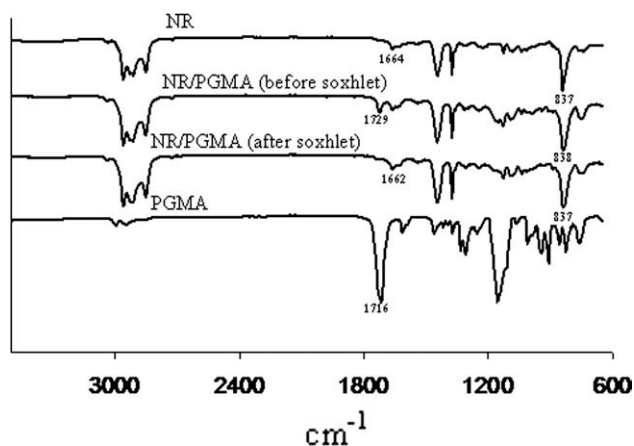
Figure 1 The FTIR spectra of NR and NR/PGMA blend before and after soxhlet extraction.

FTIR

The structural characterization of NR, PGMA, and NR-*g*-GMA was conducted by using a Spectrum one FTIR spectrophotometer. Spectra were obtained at 4 cm^{-1} resolution in the wave number range from 650 to 4000 cm^{-1}. All samples had been dried in an oven at 70°C for 24 h before testing.

NMR

^{1}H-NMR spectra of polymer samples including NR and NR-*g*-GMA were run on a Varian model Inova 300 NMR spectrophotometer at 30°C and 300 MHz using CDCl$_3$ as a solvent and TMS as an internal standard. Solid state ^{13}C-NMR measurements were performed at room temperature on a Bruker Biospin DPX-300 at 75 MHz.

Tensile tests

Rubber compounds were prepared by two-roll mill at room temperature. During compounding NR was added first. Zinc oxide, stearic acid, benzothiazyl disulfide (MBTS), and sulfur were added accordingly. To prepare glycidyl methacrylate grafted natural rubber (NR-*g*-GMA) compound, the same compounding method was applied. The compositions of the rubber compounds are shown in Table I. Vulcanizing conditions (temperature and time) were previ-

TABLE I
Composition of the Rubber Compounds

Ingredients	Content (phr)
NR or NR-*g*-GMA	100
Zinc oxide	5
Stearic acid	1
Benzothiazyl disulfide (MBTS)	1
Sulfur	2.5
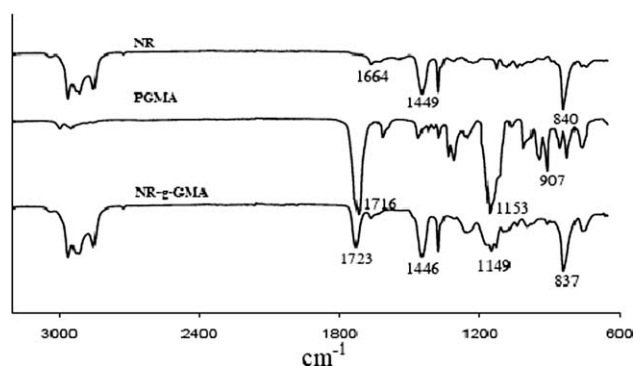
Figure 2 FTIR spectra of NR, PGMA, and NR-*g*-GMA.

ously determined by a Monsanto Moving Die Rheometer (MDR GT2000E). Rubber compounds were vulcanized at 150°C in a compression molding machine. Tensile properties were obtained according to ASTM D638 using an Instron universal testing machine (UTM, model 5565) with a load cell of 5 kN at a rate of 500 mm/min.

RESULTS AND DISCUSSION

Characterization of polymers

The FTIR spectra of NR, polyglycidyl methacrylate (PGMA), and glycidyl methacrylate grafted natural rubber (NR-*g*-GMA) are shown in Figure 2. The FTIR spectrum of NR showed absorption bands at 840, 1449, and 1664 cm^{-1} which were corresponded to the characteristic vibrations of =C-H stretching, CH$_2$ stretching and C = C stretching, respectively. Polyglycidyl methacrylate (PGMA) showed peak at 907 cm^{-1} which was the characteristic vibration of epoxy groups.[32] A strong peak at 1716 cm^{-1} was corresponded to carbonyl group (C = O) and a strong peak at 1153 cm^{-1} was attributed to C-O stretching of the ester group.[33] For NR-*g*-GMA sample, C = O stretching (1723 cm^{-1}) and C-O stretching (1149 cm^{-1}) of GMA can be observed. Moreover, C-H stretching (837 cm^{-1}), CH$_2$ stretching (1446 cm^{-1}), and C = C stretching (1664 cm^{-1}) of NR were also appeared in the FTIR spectra. These indicated the occurrence of grafting reaction in NR-*g*-GMA sample. In addition, it is well known that free radical initiators may promote grafting in two different ways including abstraction allylic hydrogen (C = C-C-H) and addition to allylic double bond (H$_2$C = CH-CH$_2$). The allylic double bond is an electron withdrawing group and it will withdraw electron from allylic hydrogen which results in the decrease of electron density of allylic hydrogen. Therefore allylic hydrogen is more acidic than hydrogen atom at other sites resulting in the easily abstraction. Moreover, Oliveira et al. reported that the CHP in the presence of the base TEPA can form radicals by the
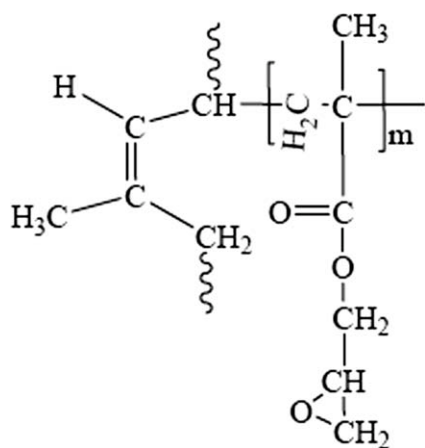
Figure 3   The probable structure of NR-*g*-GMA.

abstraction reaction over the addition to allylic double bonds.[8] Figure 3 shows the probable structure of NR-*g*-GMA obtained from this grafting method.

The structure of NR and NR-*g*-GMA and their ^{1}H-NMR spectrum are shown in Figure 4. The protons peaks of NR were denoted by a, b, c and the proton peaks of grafted GMA were denoted by 1 to 5. The ^{1}H-NMR spectrum of unmodified NR is shown in Figure 4(A). The unsaturated methyne proton (a, 1H of $=$CH) showed a signal at 5.1 ppm. The signal at 2.1 ppm might be attributed to the methylene protons (b, 4H of $(CH_2)_2$) and signal at 1.7 ppm was corresponded to the singlet resonance of the methyl proton (c, 3H of CH_3). The ^{1}H-NMR spectrum of NR-*g*-GMA is shown in Figure 4(B). The methyl protons of GMA (1, 3H of CH_3) showed signals at 0.93 and methylene protons of GMA (2, 2H of CH_2) showed signals at 1.29 ppm. The methylenoxy protons in GMA unit (3, 2H of $-CH_2-O-$) showed signal at 3.8 ppm. The methoxy protons resonance of GMA (4, 5, 3H of epoxy group) appeared at about 2.9 ppm.[34] These indicated that GMA can be grafted onto natural rubber. Nevertheless, some signals in ^{1}H-NMR spectrum showed low intensity and was not clear, which might be attributed to the fact that NR-*g*-GMA only swell in CDCl$_3$ solvent. So ^{13}C-NMR spectroscopy was used to confirm the structure of NR-*g*-GMA.

The solid state ^{13}C-NMR spectrum of NR sample is shown in Figure 5(A). The ^{13}C peaks of NR were denoted by a, b, c, d, and e. The signal at 135, 126, 33, 27, and 24 ppm were assigned to olefinic carbons (a, b, C $=$ C), methylene carbons (c, d, CH$_2$) and methyl carbon (e, CH$_3$) of NR, respectively.

Figure 5(B) shows the solid state ^{13}C-NMR spectrum of the NR-*g*-GMA. The ^{13}C peaks of the grafted GMA were denoted by 1 to 7. The peaks at 19, 55, 50, and 180 ppm were assigned to methyl carbon (1, CH$_3$), methylene carbons (2, CH$_2$), backbone quaternary carbon (3, $-\overset{|}{\underset{|}{C}}-$), and carbonyl carbon (4, C $=$ O)
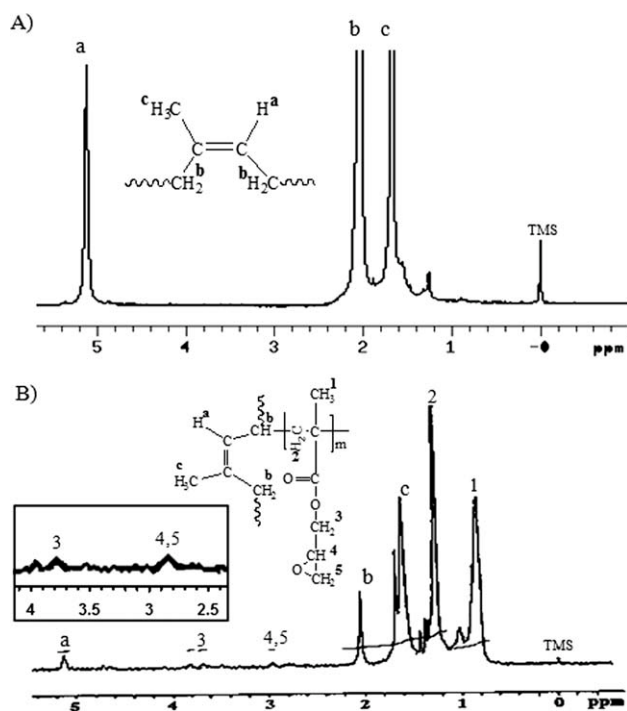

Figure 4   ^{1}H-NMR spectrum of unmodified NR (A) and NR-*g*-GMA (B).

of GMA, respectively. The methylenoxy carbon (5, $-CH_2-O-$) in GMA unit showed signal at 68 ppm. The methyne (6, CH) and methylene (7, CH$_2$) carbons of the epoxy group showed signals at about 45 ppm. These confirmed that GMA can be grafted onto natural rubber. Furthermore, the
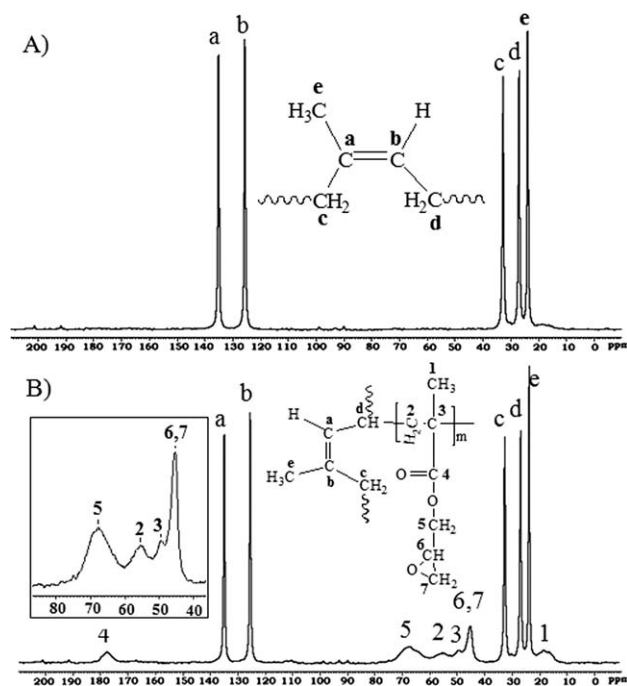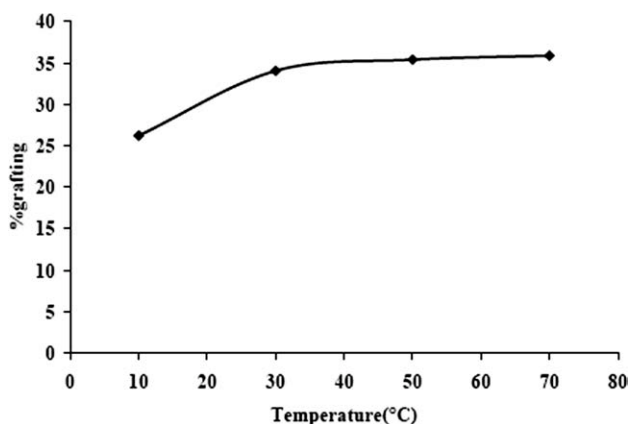

Figure 5   ^{13}C-NMR spectrum of unmodified NR (A) and NR-*g*-GMA (B).

Figure 6 %Grafting at various reaction temperatures with reaction time of 8 h.

intensity of signals at 126 and 135 of olefinic carbons of NR before and after grafting with GMA were quite similar. This indicated that the initiator seems to be appropriate to create sites of grafting by the abstraction reaction over the addition to allylic double bonds.

Effect of reaction temperature on grafting efficiency, %grafting, and %conversion

To study the effect of reaction temperature on grafting efficiency, %grafting, and %conversion, the graft copolymerization was carried out at 10, 30, 50, and 70°C using GMA content at 40 phr and the reaction time for 8 h. The effect of reaction temperature on %grafting is shown in Figure 6. %Grafting increased from 26 to 34% with increasing temperature from 10 to 30°C and it remained constant at 34% above this temperature. Figure 7 shows the effect of reaction temperature on grafting efficiency and %conversion. The result showed that at 10°C %conversion was 73% and increased to 99% at the temperature of 30°C. The %conversion remained constant above this temperature. The increasing %conversion at higher temperature might be attributed to an increase in
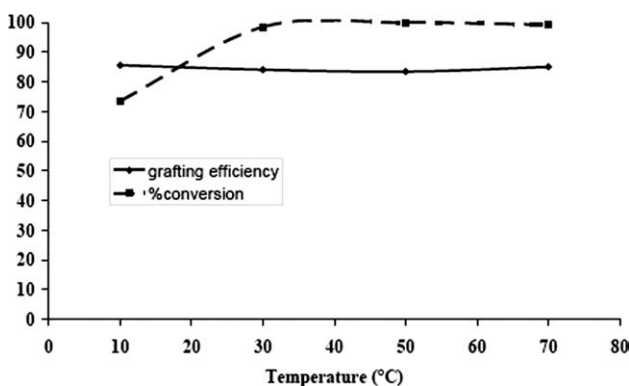
Figure 7 Grafting efficiency and %conversion of GMA at various reaction temperatures with reaction time of 8 h.
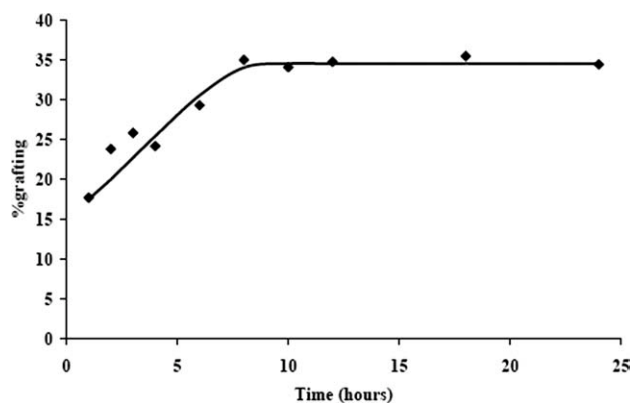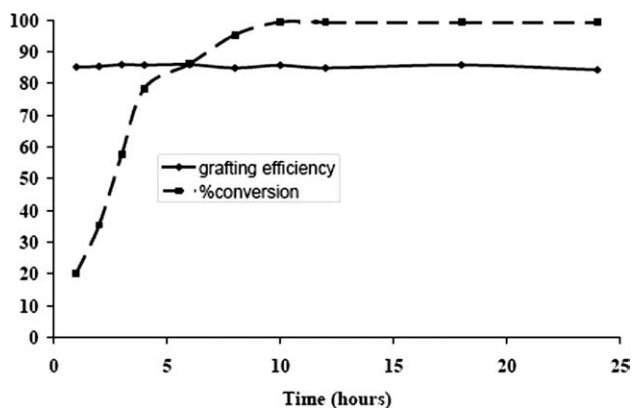

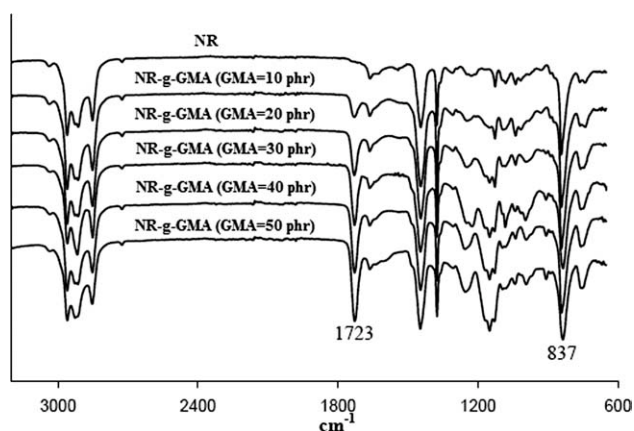**Figure 8** %Grafting at various reaction times.

the initiator decomposition. Therefore, an increased number of radicals and rate of polymerization occurred.[35] Moreover, it was found that grafting efficiency was not affected by the reaction temperature between 10 and 70°C.

Effect of reaction time on grafting efficiency, %grafting, and %conversion

To study the effect of reaction time on grafting efficiency, %grafting, and %conversion, the graft reaction was carried out at 30°C using GMA content at 40 phr. The graft samples were trapped from the reactor at different times. The reaction was terminated by using hydroquinone. The effect of reaction time on %grafting is shown in Figure 8. The %grafting increased with increasing reaction time and %grafting remained constant with the reaction time longer than 8 h. Figure 9 shows the effect of reaction time on %conversion and grafting efficiency. The %conversion increased from 20 to 99% with increasing reaction time from 1 to 8 h. This indicated that the reaction might be completed at reaction time of 8 h. So the appropriate condition for the preparation of the graft copolymer was found to be a reaction

Figure 9 Grafting efficiency and %conversion of GMA at various reaction times.

**Figure 10** FTIR spectra of NR and NR-*g*-GMA at various GMA contents.

temperature of 30°C with reaction time of 8 h, which led to a high %conversion and high %grafting. Moreover, it was observed that grafting efficiency is not affected by the reaction time.

Effect of GMA content on grafting efficiency, %grafting, and %conversion

GMA contents were varied from 10 to 50 phr to study the effect of GMA content on grafting efficiency, %grafting, and %conversion. The grafting reaction was prepared at 30°C for 8 h. The FTIR spectra of NR and NR-*g*-GMA at various GMA contents are shown in Figure 10. The single peak at 837 cm^{-1} was attributed to = C-H stretching (837 cm^{-1}) of NR which was used as an internal standard. The single peak at 1723 cm^{-1} was attributed to the carbonyl groups of GMA (C = O). The result showed that the area of this characteristic peak increased with increasing GMA content. The level of the grafted GMA was estimated by using the absorbance ratio of IR peaks at 1723 cm^{-1} to 837 cm^{-1}. Figure 11 shows the %grafting obtained from the gravimetric method and the absorbance ratio at various GMA contents. It can be seen that the %grafting and ab-
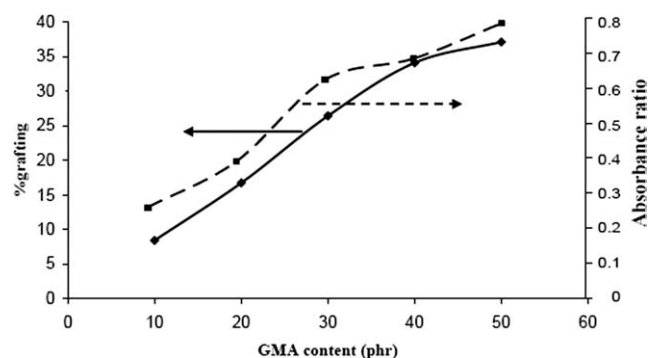
Figure 11 %Grafting and absorbance ratio at various GMA contents.
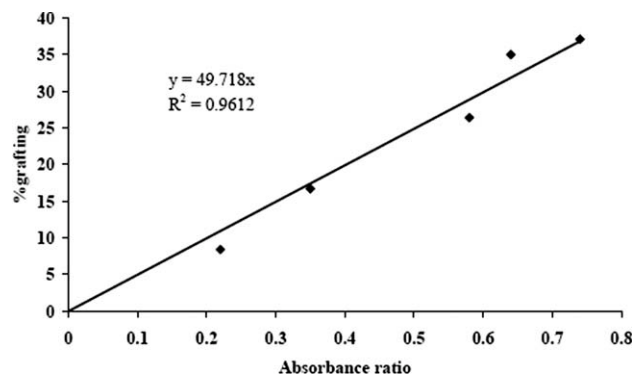

**Figure 12** Calibration curve of absorbance ratio and %grafting.

sorbance ratio showed the same trend. Figure 12 shows the calibration curve of absorbance ratio and %grafting. The absorbance ratio is linearly related to the quantity of GMA on NR-*g*-GMA and can be expressed by the equation $y = 49.718X$. X is the absorbance ratio and y is %grafting. Moreover, the coefficient of determination (R^2) is 0.9612. This indicated that the simple absorbance ratio method can be used to determine the %grafting of NR-*g*-GMA. Figure 13 shows the effect of GMA content on grafting efficiency and %conversion. The %conversion of GMA at the content of 10 to 50 phr were about 99% indicating the good polymerization reaction of GMA from this grafting method. Furthermore, it can be seen that %grafting and grafting efficiency increased with increasing GMA content. Whereas, above 40 phr of GMA, grafting efficiency decreased. This might be attributed to the chain transfer reaction of radicals to monomer leading to the formation of homopolymer during the grafting reaction.[36]

Effect of %grafting on mechanical properties

Figure 14 represents the tensile stress-strain curve of NR and NR-*g*-GMA at various %grafting. All NR-*g*-GMA samples show higher stress level than NR.
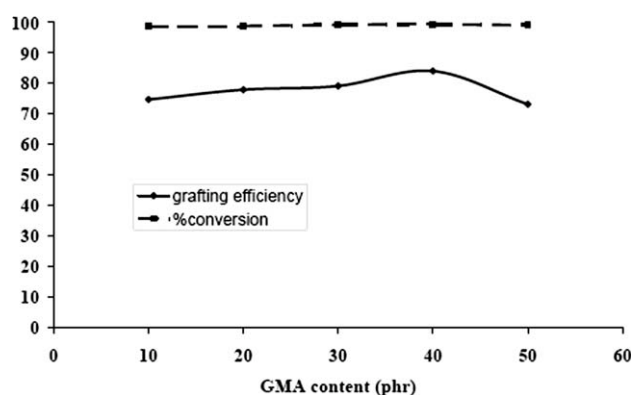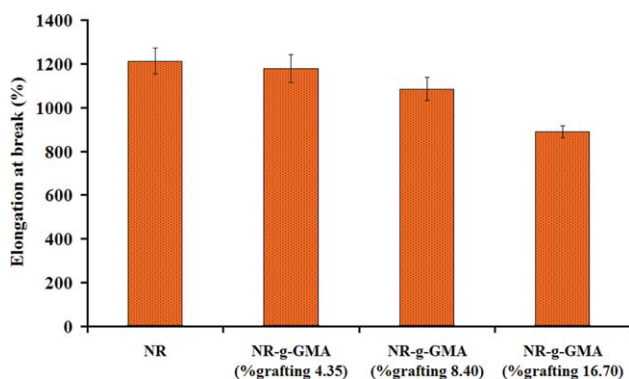

Figure 13 Grafting efficiency and %conversion of GMA at various GMA contents.
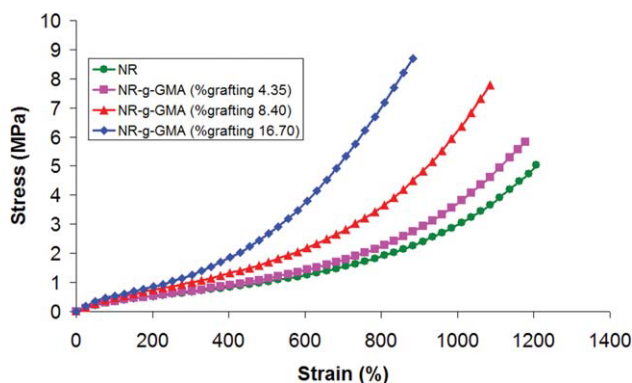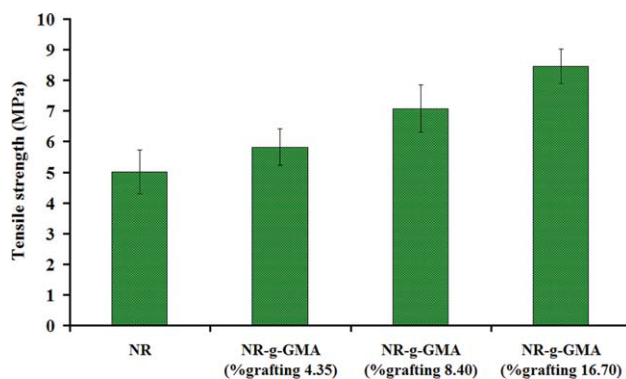
Figure 14 Tensile stress-strain curve of NR and NR-*g*-GMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This may be related to the higher crosslinking density of NR-*g*-GMA than that of NR caused by epoxy moiety from GMA. This can be observed by the increase in the diffrence in maximum torque (MH) and minimum torque (ML) of MDR curing curve of NR-*g*-GMA at %grafting of 16.70 (25 dN·m) compared with that of NR (12 dN·m). Oliveira et al. also reported the higher stress level of NR graft polydimethylaminoethyl methacrylate (NR-*g*-PDMAEMA) than that of NR.[6] They mentioned that this effect might be enhanced by the crystallization of the NR during the stretching, which is known to depend on the crosslink density and to increase the stress level at large deformation. Elongation at break and tensile strength of NR and NR-*g*-GMA obtained from Figure 14 are shown in Figure 15 and 16 respectively. With increasing %grafting up to 16.70, tensile strength was significantly increased about 70% compared with that of NR whereas elongation at break slightly decreased. The decrease of elongation at break at high %grafting was due to the restriction of molecular chain movement of NR on stretching caused by GMA. Figure 17 shows 100% modulus, 300% modulus, and 500% modulus of NR and NR-*g*-
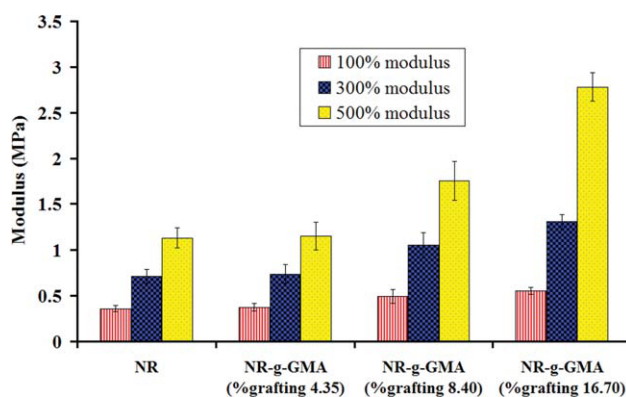

Figure 16 Tensile strength of NR and NR-*g*-GMA at various %grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

GMA. The modulus of NR-*g*-GMA dramatically increased compared with that of NR. This may be attributed to the higher crosslinking density of NR-*g*-GMA as mentioned above. Moreover, by grafting GMA onto NR the attractive force between latex particles in dry film was increased contributing to the high modulus of film. It is noteworthy to point out that NR-*g*-GMA prepared in this study exhibited excellent improved tensile strength and modulus with insignificant loss in elongation at break compared with NR. With this superior mechanical properties, NR-*g*-GMA can be used in various applications such as seal, adhesive, and coating.

CONCLUSIONS

GMA can be grafted onto NR by emulsion polymerization method using cumene hydroperoxide (CHP) and tetraethylenepentamine (TEPA) as the initiators. It was observed that %grafting and grafting efficiency were increased with increasing GMA content. However, above 40 phr of GMA content, grafting efficiency decreased. Grafting efficiency was not

Figure 15 Elongation at break of NR and NR-*g*-GMA at various %grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 17 Hundred percent modulus, 300% modulus, and 500% modulus of NR and NR-*g*-GMA at various %grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

affected by reaction time and reaction temperature between 10 and 70°C. The %grafting and %conversion increased with increasing reaction time and remained constant with the reaction time longer than 8 h. The %conversion at the reaction temperature of 10°C was 73% and increased to 99% at the reaction temperature of 30°C. This indicated that the appropriate condition for preparation of the graft copolymer was found to be a reaction temperature of 30°C with the reaction time of 8 h. With increasing %grafting, the tensile strength and modulus significantly increased with insignificantly decrease in elongation at break.

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