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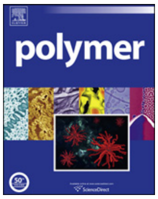

Photo-reactive particle prepared from natural rubber and 3-acryloyloxy-2-hydroxypropyl methacrylate

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ABSTRACT

Photo-reactive particle was prepared by graft-copolymerization of 3-acryloyloxy-2-hydroxypropyl methacrylate (AHM) as a bi-functional monomer onto natural rubber (NR) in latex stage with potassium persulfate (KPS) as an initiator, after deproteinization with urea in the presence of surfactant. A terminal vinyl group of AHM was used for the graft-copolymerization, while the other remained in the resulting graft-copolymer, due to different reactivities of vinyl groups in the end of the bi-functional monomer. After graft-copolymerization, the resulting latex was UV-crosslinked to make chemical linkages between the residual pendant vinyl groups of grafted polymers linking up to the rubber particle. The resulting products were characterized by ^{1}H NMR and ^{13}C NMR measurements. Effects of amount of rubber, monomer concentration and reaction time on conversion, grafting efficiency and amount of residual carbon–carbon double bond after graft-copolymerization were investigated. Under the optimum condition, high conversion of monomer and high amount of residual carbon–carbon double bond after graft-copolymerization were achieved without side reaction. A dramatic increase in modulus after UV-irradiation was associated with the connection of the functional polymer linking up to NR particle.

1. Introduction

"Photo-reactive particle" is a novel functional building block, which is indispensable to form a hierarchal structure of organic materials through photo-reaction [1]; for instance, it may enable to connect a matrix of the nano-matrix-structure [2–4] with chemical linkages. The photo-reactive particle may be prepared by introducing the photo-reactive sites into a polymer grafting onto the particle, since the nano-matrix-structure is formed by coagulating the particle to fuse the grafted polymer on its surface. In the present study, the preparation of the photo-reactive particle is made by graft-copolymerization of a bi-functional monomer onto NR particle in latex stage.

The nano-matrix-structure is a nano-phase-seperated structure consisting of a dispersoid of major rubber-component and a matrix of minor polymer-component. The rubber in the dispersoid must be crosslinked to each other and it is chemically bonded to the polymer at an interface between the dispersoid and the matrix; hence, the nano-matrix-structure is stable even after annealing the rubber above a glass transition temperature, T_g, of the polymer as a matrix. It may improve the properties of the rubber without sacrificing outstanding viscoelatic properties. In fact, a storage modulus of the rubber was viscoelastic by forming the nano-matrix-structure, while a suitable loss tangent was maintained. However, when a large deformation was imposed to the rubber with the nano-matrix-structure, its geometry was not reverted due to flow of the rubber. In order to maintain the geometry, thus, it is necessary to make crosslinking junctions into the matrix of the nano-matrix-structure. In this regard, we take a notice of the photo-reactive particle, since it may consist of the rubber particle linking up to the rigid polymer having photo-reactive pendant groups, which are useful for inter-particle crosslinking after forming the nano-matrix-structure.

The photo-reactive particle may be prepared by graft-copolymerization of bi-functional monomers onto the rubber particle in latex stage. However, when the bi-functional monomers with equally reactive sites are used, the crosslinking may occur during graft-copolymerization to cover the rubber particle with three-dimensional network polymer. In the previous work [5], 1,9-nonandioldimethacrylate (NDMA) was grafted onto deproteinized natural rubber (DPNR) in latex stage. In such a case, all carbon–carbon double bonds are used for graft-copolymerization and

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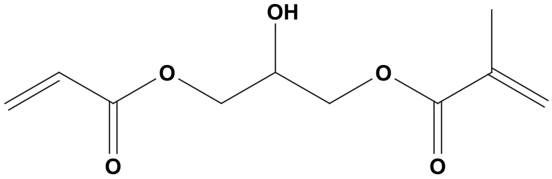

Fig. 1. Structure of AHM.

crosslinking, so that the photo-reactive sites are consumed before forming the nano-matrix-structure. Thus, to prepare the photo-reactive particle, it is necessary to react only one vinyl group present in an end of the bi-functional monomer without reacting the other, in order to prevent the crosslinking during graft-copolymerization.

3-Acryloyloxy-2-hydroxypropyl methacrylate (AHM) is a unique bi-functional monomer, which consists of hydrocarbon chain having one hydroxyl group, methacylate group and acrylate group, respectively, as shown in Fig. 1. It is anticipated to introduce the photo-reactive sites after graft-copolymerization of the monomer onto the rubber particle under a suitable condition, due to a difference in the reactivity between the methacrylate and acrylate groups present in the ends. In fact, in the previous work, Martinez et al. [6] found that a ratio of 2-hydroxyethyl methacrylate (HEMA) unit to *t*-butyl acrylate (TBA) unit in HEMA/TBA copolymer was higher than that of HEMA/TBA feed, while large amounts of unreacted TBA existed in the system. The difference in the ratio of HEMA/TBA between the copolymer composition and the feed was well associated with monomer reactivity ratios, i.e. high reactivity ratio for HEMA and low reactivity ratio for TBA. On the basis of the previous result, it is possible to distinguish the polymerization of methacrylate group from that of acrylate group.

In the present study, the photo-reactive particle is prepared by graft-copolymerization of AHM as a bi-functional monomer onto DPNR particle with KPS as an initiator, after deproteinization with urea in the presence of surfactant [3,7,8], as shown in Fig. 2. Before graft-copolymerization, a rate of reaction for the vinyl groups of AHM is investigated to distinguish the rate of methacrylate group from the rate of acrylate group in the graft-copolymerization. Effects of amount of rubber, monomer concentration and reaction time on amount of residual carbon–carbon double bond, conversion and grafting efficiency of AHM are investigated for the graft-copolymerization. The resulting latex was mixed with a photo-initiator and it was crosslinked by UV-irradiation. The resulting products are characterized by NMR measurement.

2. Experimental

2.1. Materials

Natural rubber latex used in the present study was commercial high-ammonia natural rubber (HA-NR) latex (Golden Hope, Malaysia) of about 60% dry rubber content (DRC). AHM was purchased from NOF Corporation. Sodium dodecyl sulfate (SDS) (98%) was purchased from Kishida Chemical Co., Ltd. KPS (95.0%) and chloroform-*d* ($CDCl_3$) (99.8%) were purchased from Wako Pure Chemical Industry Ltd. Urea (99.5%), methanol (99.5%), acetone (99.5%) and potassium bromide were purchased from Nacalai Tesque Inc. 2-Hydroxy-2-methyl-1-phynylpropane-1-one (DAROCUR 1173) was purchased from Ciba Co., Ltd. The reagents were used without further purification.

2.2. Deproteinization of natural rubber [7,8]

HA-NR latex was sieved with a stainless 200 mesh before usage. 300 g of HA-NR latex placed in a 1 L beaker was diluted with 300 g of 1.0% w/w SDS aqueous solution to make 30% DRC latex before deproteinization. The diluted latex was mixed with 0.6 g of urea and stirred for 1 h at room temperature and it was subjected to centrifugation at about 10^4 rpm and 288 K for 30 min to separate the rubber cream fraction from serum fraction. The resulting cream fraction, which mainly contains rubber, was added into 200 g of

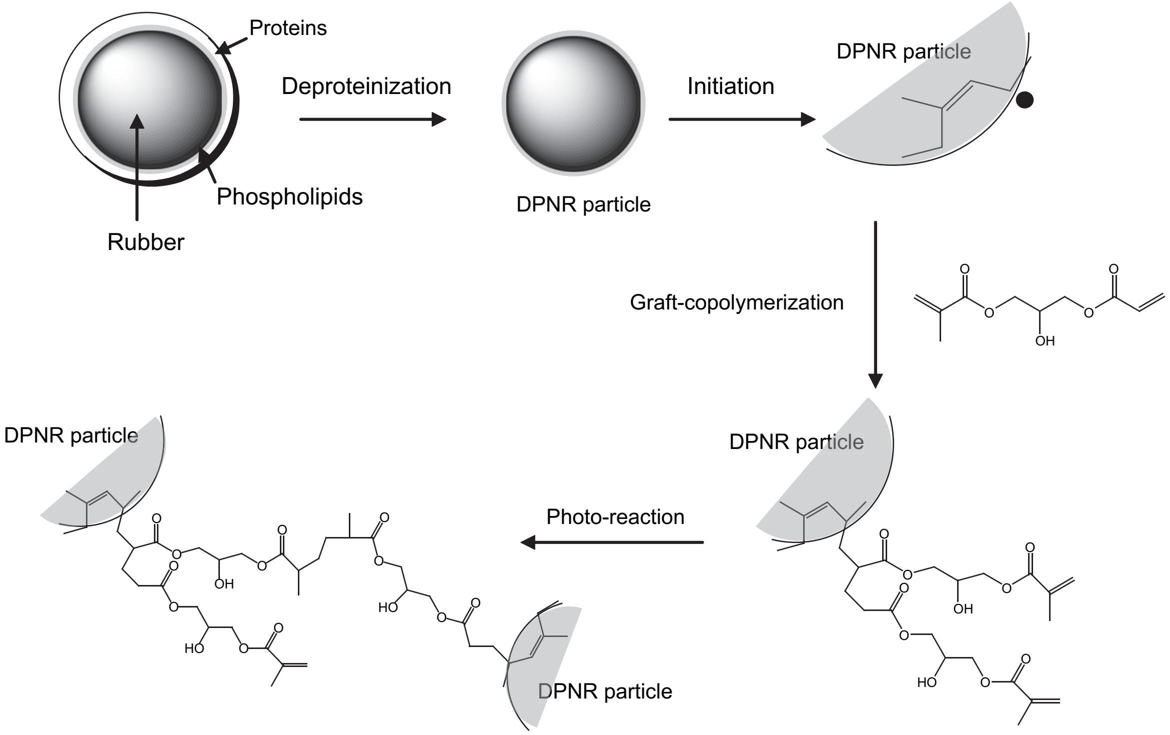

Fig. 2. Schematic representation for the graft-copolymerization of AHM onto DPNR particle in latex stage.

0.5% w/w SDS aqueous solution in a 1 L beaker. The mixture of the cream fraction and the SDS aqueous solution was stirred slowly at room temperature for 1 h to re-disperse the rubber particle. The resulting latex was sieved with a stainless 200 mesh and it was subjected to the centrifugation and the re-dispersion twice to purify natural rubber. For the last time of re-dispersion, the concentration of SDS was decreased to be 0.1% w/w SDS aqueous solution. The resulting DPNR latex was kept in a 500 ml glass bottle in the dark at room temperature.

DRC of the DPNR latex was measured as follows; 1 g of DPNR latex was poured into a small metal container and it was dried in an oven at 323 K until a constant weight was reached. The DRC was estimated from the weight of the latex and dried rubber.

2.3. Homopolymerization of AHM

Homopolymerization of AHM was carried out through emulsion polymerization. Before homopolymerization, nitrogen gas was purged into the reactor for 1 h. 0.56 mol/L of AHM, aqueous solution of SDS and ion-exchanged water were added in the reactor and stirred for 1 h. 1.5×10^{-3} mol/L of KPS used as an initiator was dissolved in small amount of ion-exchanged water and it was added into the reactor. Polymerization was carried out for 3 h at 353 K. The emulsion was poured in methanol to precipitate out the polymer. The polymer was dried in vacuum oven for 1 week at 323 K.

2.4. Graft-copolymerization of AHM onto DPNR particle

Graft-copolymerization of the DPNR latex was carried out with AHM, using KPS as an initiator. DPNR latex was charged with N_2 gas for 1 h at 333 K. 3.3×10^{-5} mol/g rubber of KPS was dissolved in small amount of water and it was added into the reactor. After adding initiator for 5 min, AHM was slowly dropped into the reactor. The graft-copolymerization was carried out by stirring the latex at about 400 rpm at 333 K. A condition of the graft-copolymerization is shown in Table 1. After graft-copolymerization, the resulting latex was subjected to the centrifugation to remove unreacted AHM. The obtained graft-copolymer was dried in vacuum oven at 323 K for more than a week. The dried graft-polymer was extracted with acetone in a Soxhlet apparatus under nitrogen atmosphere in the dark and dried under reduced pressure for 24 h in order to remove unreacted monomer and free-polymer which is isolated from natural rubber.

2.5. UV-crosslinking reaction

The graft-copolymer latex was mixed with 0.2% w/w of DAROCUR 1173 for 1 h at room temperature. The latex mixed with DAROCUR 1173 was moderately dried in vacuum oven at 353 K for 24 h and it was pressed to be a film specimen at 363 K for 5 min. Both sides of the film surfaces were exposed to UV-irradiation by using a UE031-262-01CS UV curing system, Eye Graphics Co., Ltd., at 140 mW/cm^2 in intensity of UV ray for 2 min.

Table 1
Conditions of graft-copolymerization of AHM onto DPNR in latex stage.

Code	DPNR (%DRC)	Monomer (mol/kg-rubber)	Initiator (mol/g-rubber)	Temp. (K)	Reaction time (h)
DPNR-graft-PAHM1	10	2.5	3.3×10^{-5}	333	1
DPNR-graft-PAHM2	10	2.5	3.3×10^{-5}	333	2
DPNR-graft-PAHM3	10	2.5	3.3×10^{-5}	333	3
DPNR-graft-PAHM4	20	0.3	3.3×10^{-5}	333	3
DPNR-graft-PAHM5	20	1.5	3.3×10^{-5}	333	3

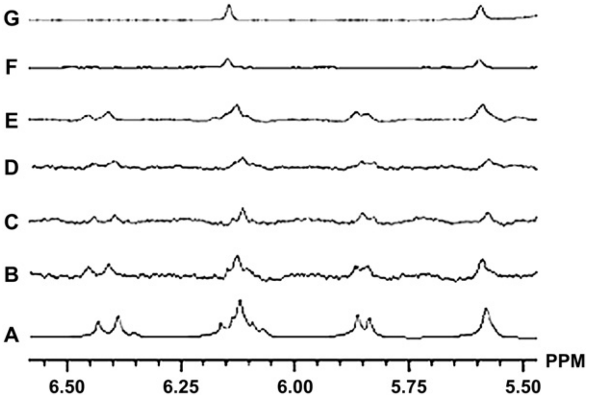

Fig. 3. ^{1}H NMR spectra of (A) AHM and DPNR-graft-PAHM prepared from 10% DRC DPNR, 2.5 mol/kg-rubber of AHM for (B) 10, (C) 20, (D) 30, (E) 40, (F) 50 and (G) 60 min at 333 K in $CDCl_3$.

2.6. Characterization

NMR measurements were carried out using a JEOL EX-400 NMR spectrometer operating at 399.65 and 100.40 MHz for ^{1}H NMR and ^{13}C NMR, respectively. The sample was dissolved into $CDCl_3$ without tetramethylsilane (TMS). Chemical shifts were referred to $CHCl_3$ in $CDCl_3$. ^{1}H NMR and ^{13}C NMR measurements were carried out at 323 and 298 K at the pulse repetition time of 7 and 5 s, respectively.

Modulus was measured by 3365Q5414 Instron (Instron Safety Standard ICP-CS503) at a crosshead speed of 200 mm/min with load cell of 5 KN. The preparation of the test sample was carried out by SDL-100 Dumb bell, Dumb bell Ltd.

3. Results and discussion

3.1. Reactivity of vinyl groups of AHM unit

To distinguish reactivity of the methacrylate group from that of the acrylate group, the graft-copolymerization of AHM onto DPNR particle was carried out and the graft-copolymer latex was taken out at each 10 min interval.

Fig. 3 shows typical ^{1}H NMR spectra for AHM and DPNR-graft-PAHM prepared by graft-copolymerization of 2.5 mol/kg-rubber AHM onto DPNR for 10, 20, 30, 40, 50 and 60 min at 333 K, respectively. As for AHM, singlet and two doublet signals appeared at 5.58, 5.80 and 6.43 ppm, respectively, whose intensity ratio was 1:1:1. On the other hand, a multiplet signal appeared at 6.15 ppm. An intensity ratio of the signal at 6.15 ppm to the signal at 5.58 ppm

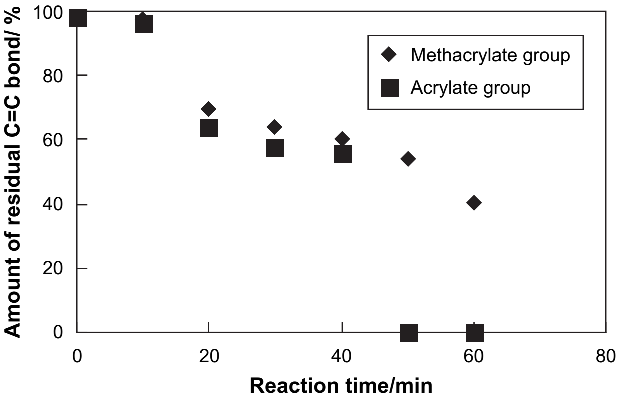

Fig. 4. A plot of reaction time versus amount of carbon–carbon double bond of methacrylate and acrylate groups present at the end of monomer unit after graft-copolymerization onto rubber particle.

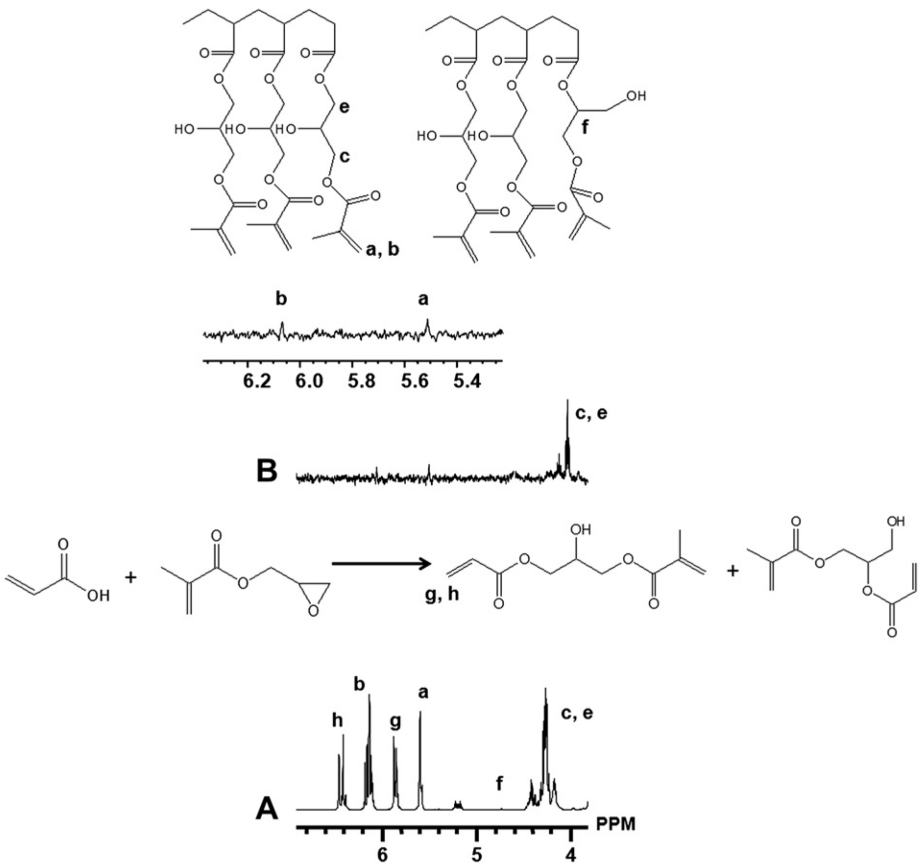

Fig. 5. ^{1}H NMR spectra of (A) AHM and (B) PAHM in CDCl$_3$.

was estimated to be 2. Thus, the multiplet signal was considered to overlap 2 signals to each other. According to the previous literature [9–14], the signals were assigned, as follows: the singlet signal at 5.58 ppm to unsaturated methylene proton of methacrylate group, the doublet signal at 5.80 ppm to unsaturated methylene proton of acrylate group, the multiplet signal at 6.15 ppm to unsaturated methine proton of acrylate group and unsaturated methylene proton of methacrylate group, the doublet signal at 6.43 ppm to unsaturated methylene proton of acrylate group. Intensity of the four signals at 5.58, 5.80, 6.15 and 6.43 ppm was dependent upon a reaction time. The singlet signal remained to appear at 5.58 ppm, whereas the doublet signals at 5.80 and 6.43 ppm disappeared. The multiplet signal at 6.15 ppm became singlet after 50 min reaction. The two signals of methacrylate group at 5.58 and 6.15 ppm moved a little to higher magnetic field, i.e. 5.52 and 6.07 ppm. This may be explained to be due to an effect of “molecular weight”.

The amount of the residual carbon–carbon double bond was estimated from the intensity ratio of signals at 5.58, 5.80, 6.15, 6.43 and 4.10–4.20, as follows,

$$\text{Amount of residual methacrylate group}\,(\%) = \left(\frac{(I_{5.58}/(I_{4.10-4.20}/4))_{\text{graft-copolymer}}}{(I_{5.58}/(I_{4.10-4.20}/4))_{\text{monomer}}}\right)\times 100$$

$$\text{Amount of residual acrylate group}\,(\%) = \left(\frac{(I_{5.80}/(I_{4.10-4.20}/4))_{\text{graft-copolymer}}}{(I_{5.80}/(I_{4.10-4.20}/4))_{\text{monomer}}}\right)\times 100$$

where I is the intensity of the signals and subscript numbers represent chemical shift (ppm) which was estimated by ^{1}H NMR spectroscopy.

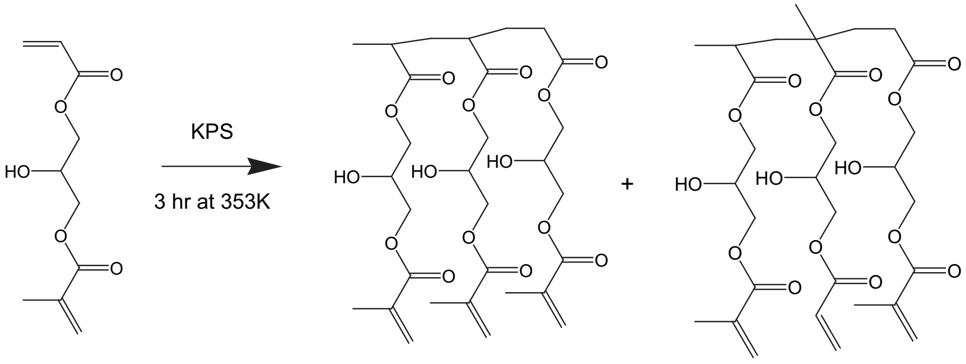

Fig. 6. Assumed mechanism of homopolymerization of AHM.

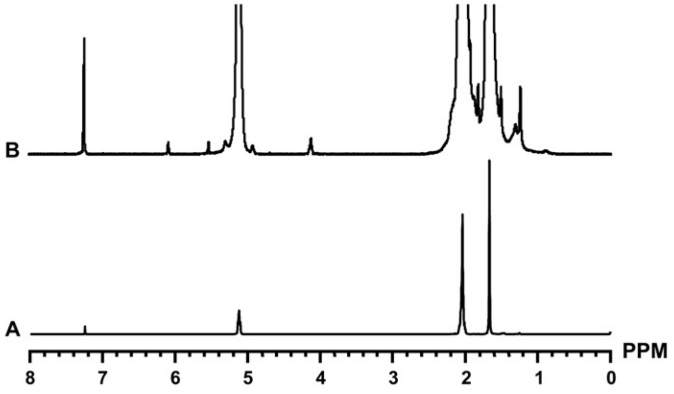

Fig. 7. ^{1}H NMR spectra of (A) DPNR and (B) DPNR-graft-PAHM5 in $CDCl_3$.

Fig. 4 shows a plot of the amount of the residual carbon–carbon double bond of methacrylate and acrylate groups versus reaction time. It was found that the amount of the residual carbon–carbon double bond of methacrylate and acrylate groups decreased with reaction time. The amount of the residual carbon–carbon double bond of acrylate group was lower than that of methacrylate group, i.e. about less than 1% for acrylate group and about 40% for methacrylate group. This suggests that the carbon–carbon double bonds of acrylate group were consumed more rapidly than that of methacrylate group during the graft-copolymerization.

3.2. Homopolymerization of AHM

Fig. 5 shows typical ^{1}H NMR spectra for AHM and PAHM, respectively. As for AHM, four signals appeared at 5.58, 5.80, 6.15 and 6.43 ppm. Signals at 4.10–4.40 ppm were overlapped to each other. The overlapped signals at 4.10–4.20 ppm were assigned to methylene protons adjacent to ester group, while the signals at 4.20–4.40 ppm were assigned to methine proton linking to hydroxyl group. The unknown signals appearing in the spectrum were assigned to signals of starting material and by-products in the monomer, as mentioned in Fig. 5, according to Nayak and co-workers [15].

After homopolymerization, small signals appeared at 5.52, 6.07, 4.10 and 4.15 ppm. The two signals at 5.52 and 6.07 ppm were assigned to the unsaturated methylene protons of methacrylate group present in the graft-copolymer. The signals at 4.10 and 4.15 ppm were assigned to methylene proton and methine proton linking to hydroxyl group, respectively. The intensity of the signals at 5.58, 5.80, 6.15 and 6.43 ppm decreased significantly after homopolymerization. Thus, the amounts of the methacrylate and acrylate groups of AHM were estimated, as follows:

$$\text{Amount of residual methacrylate group}\,(\%) = \left(\frac{(I_{5.52}/(I_{4.10-4.20}/4))_{\text{graft-copolymer}}}{(I_{5.52}/(I_{4.10-4.20}/4))_{\text{graft-copolymer}}}\right) \times 100$$

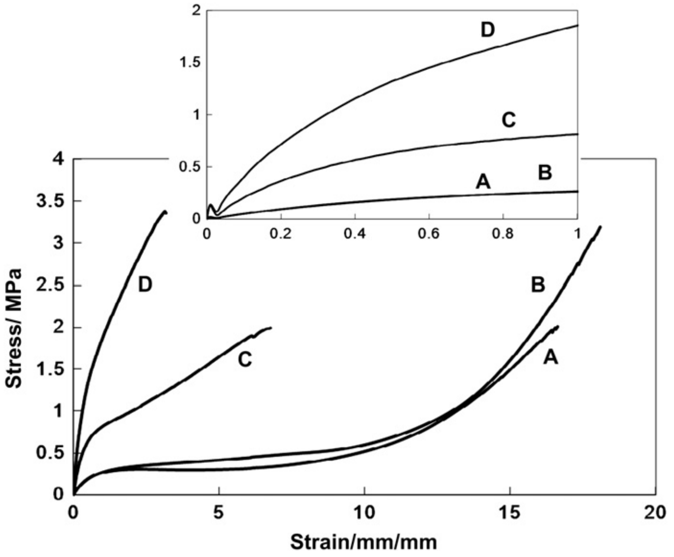

Fig. 8. A plot of stress versus strain for (A) DPNR, (B) UV-crosslinked DPNR, (C) DPNR-graft-PAHM1 and (D) UV-crosslinked DPNR-graft-PAHM1.

$$\text{Amount of residual acrylate group}\,(\%) = \left(\frac{(I_{5.80}/(I_{4.10-4.20}/4))_{\text{graft-copolymer}}}{(I_{5.80}/(I_{4.10-4.20}/4))_{\text{monomer}}}\right) \times 100$$

where I is the intensity ratio of the signals and subscript numbers represent the chemical shift (ppm) of the signals.

The estimated value of the residual methacrylate group was about 65.6% and that of acrylate group was less than 1%. In the previous paper [16–18], the bulky methacrylate group was reported to be difficult to access the reaction site. Therefore, the acrylate group of AHM reacts mainly for the polymerization, but the methacrylate group does not, as shown in Fig. 6.

3.3. Graft-copolymerization of AHM onto DPNR particle

Fig. 7 shows typical ^{1}H NMR spectra for DPNR and DPNR-graft-PAHM, respectively. As for DPNR, three signals at 1.68, 2.05 and 5.10 ppm appeared in the ^{1}H NMR spectrum. These signals were assigned to methyl, methylene, and unsaturated methine proton of *cis*-1,4-isoprene unit, respectively. In contrast, for DPNR-graft-PAHM5, small signals appeared at 4.10, 5.52 and 6.07 ppm, in addition to the signals at 1.68, 2.05 and 5.10 ppm. The signals at 5.52 and 6.07 ppm were assigned to unsaturated methylene proton of methacrylate group of AHM unit, according to the assignment in Fig. 5. It is, thus, confirmed that, after graft-copolymerization of AHM, the carbon–carbon double bond remain in the resulting graft-copolymer, as in the case of the homopolymerization of AHM.

The conversion of AHM grafted on DPNR particle and amount of residual carbon–carbon double bond of methacrylate group in

Table 2
Conversion of acrylate and methacrylate groups, amount of residual C=C bond and grafting efficiency of AHM for the graft-copolymerization of the bi-functional monomer onto DPNR in latex stage.

Code	Conversion (%)	Amount of residual acrylate group (%)	Amount of residual methacrylate group (%)	Grafting efficiency (%)	Remark
DPNR-graft-PAHM1	59.8	<1%	40.2	97.1	No coagulation (<1%)
DPNR-graft-PAHM2	62.1	<1%	37.9	97.2	Little coagulation (~10%)
DPNR-graft-PAHM3	64.0	<1%	36.0	97.4	More coagulation (~20%)
DPNR-graft-PAHM4	76.9	<1%	25.6	97.1	No coagulation (<1%)
DPNR-graft-PAHM5	79.6	<1%	22.4	97.4	Coagulation (>90%)

AHM were estimated from the intensity ratio of the signals at 5.52 and 5.80 ppm to that at 4.10–4.20 ppm, as in the following equation:

$$\text{Amount of residual carbon—carbon double bond}(\%) = \left(\frac{(I_{5.52}+I_{5.80})_{\text{graft-copolymer}}/(I_{4.10-4.20}/4)_{\text{graft-copolymer}}}{(I_{5.52}+I_{5.80})_{\text{monomer}}/(I_{4.10-4.20}/4)_{\text{monomer}}}\right)\times 100$$

$$\text{Conversion of AHM}\,(\%) = 100 - \text{C}{=}\text{C}(\%)$$

where I is the intensity ratio of the signals and subscript numbers represent the chemical shift (ppm) of the signals.

Grafting efficiency of AHM was estimated, as follows:

$$\text{Grafting efficiency}\,(\%) = \left(\frac{\text{Weight of graft} - \text{copolymer after acetone extraction}}{\text{Weight of graft} - \text{copolymer before acetone extraction}}\right)\times 100$$

The estimated values of conversion of acrylate group and methacrylate group, amount of residual C=C, grafting efficiency are shown in Table 2. The conversion, grafting efficiency of AHM and amount of residual carbon–carbon double bond were dependent upon the AHM concentration, reaction time and DRC.

Based upon the table data, when the graft-copolymerization was carried out at 10% in DRC and 2.5 mol/kg-rubber in monomer feed at 333 K for 1 h, the amount of the methacrylate group was 40.2% and the amount of acrylate group was less than 1%. This is corresponding to the result of homopolymerization of AHM. The amount of the residual methacrylate group decreased, as the reaction time and DRC increased. Furthermore, when the monomer feed was reduced, the amount of the residual methacrylate group decreased, significantly. Thus, a suitable condition to prepare the photo-reactive particle was determined to be 10% in DRC, 2.5 mol/kg-rubber in monomer feed, 3.3×10^{-5} mol/g rubber in initiator concentration, 1 h in reaction time and 333 K in reaction temperature.

3.4. Mechanical property

Fig. 8 shows a plot of stress versus strain for DPNR, UV-crosslinked DPNR, DPNR-graft-PAHM1 and UV-crosslinked DPNR-graft-PAHM1, respectively. Stress of DPNR increased gradually with increasing strain. The stress–strain curve for DPNR did not change after UV-irradiation. The stress increased about three times, after graft-copolymerization of AHM. Furthermore, the stress of UV-crosslinked DPNR-graft-PAHM1 was about 10 times as high as that of DPNR and UV-crosslinked DPNR. Since the stress at the strain of 1:5 proportional to modulus and stiffness, the mechanical property of DPNR was significantly improved by graft-copolymerization of AHM followed by UV-crosslinking.

4. Conclusion

Photo-reactive particle was formed by graft-copolymerization of AHM onto DPNR particle in latex stage with KPS as a radical initiator. High conversion, high grafting efficiency and high amount of residual carbon–carbon double bond without side reaction were achieved at 10% DRC of DPNR, 2.5 mol/kg-rubber of AHM and 3.3×10^{-5} mol/g-rubber of KPS at 333 K for 1 h. The modulus was enhanced due to chemical linkage of pendant vinyl group of PAHM linking up to rubber particle after UV-reaction.

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