Songklanakarin J. Sci. Technol.
31 (4), 453-457, Jul. - Aug. 2009

Songklanakarin Journal
of Science and Technology

http://www.sjst.psu.ac.th

Original Article

Grafting copolymerization of natural rubber with 2-hydroxyethyl methacrylate for plywood adhesion improvement

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Received 2 July 2008; Accepted 12 November 2008

Abstract

The graft copolymer of natural rubber (NR) and 2-hydroxyethyl methacrylate (HEMA) was prepared by seeded emulsion polymerization using cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA) as an initiator system. The structures of the copolymers were characterized by FT-IR and ^{1}H-NMR spectroscopy techniques. The adhesion properties of NR-*g*-HEMA were examined. The effects of monomer concentration, initiator concentration, reaction temperature, reaction time and the agitation speed on grafting and grafting efficiency were investigated. It was found that the optimum conditions for preparing NR-*g*-HEMA when 5 phr of HEMA with 0.15mol% of initiator was used were 60°C for 90 min under agitation speed of 50 rpm. Furthermore, the adhesion properties to plywood of the graft copolymers are higher than those of original NR.

Keywords: natural rubber, emulsion polymerization, 2-hydroxyethyl methacrylate, adhesion property

1. Introduction

The chemical constitution of natural rubber (NR) is mostly *cis*-1,4-polyisoprene. The excellent physical properties of NR include resilience, strength and fatigue resistance. Natural rubber does not perform well when exposed to chemicals and petroleum derivatives including sunlight, ozone, oxygen or heat aging. In order to extend its use, many efforts have been developed to improve its properties. These modifications have been directed not only towards the enhancement of certain properties characteristic of NR, but also towards introducing new properties not usually associated with NR (Oliveira *et al.*, 2005).

The extension of the applications of NR can be carried out by the grafting of a secondary polymer (Arayapranee *et al.*, 2002; Arayapranee *et al.*, 2003; Nakason *et al.*, 2004; Oliveira *et al.*, 2005; Prasasassarakich *et al.*, 2001 and Saelao and Phinyocheep, 2005) within an NR particle with the well-established technique of emulsion polymerization of artificial polymer (Chern, 2006).

In this work, natural rubber was used as a polymer backbone for the grafting reaction with HEMA in emulsion polymerization. Effects of monomer concentration, initiator concentration, reaction temperature, reaction time and agitation speed on percentage of grafting and grafting efficiency were investigated. Adhesion properties to plywood of NR-*g*-HEMA were also preliminarily studied.

2. Materials and Methods

2.1 Materials

Natural rubber latex (NRL) used in this study was a commercial high ammonia natural rubber latex with dry rubber content of 60% purchased from Pattani Industry Co., Ltd, Pattani, Thailand.

The 2-hydroxyethyl methacrylate (HEMA) monomer, cumene hydroperoxide (CHP) and tetraethylene pentamine

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(TEPA) co-initiator were purchased from Fluka, Switzerland. Toluene, ethanol, ammonia and dichloromethane were purchased from Merck, Germany. The sodium dodecyl sulphate (SDS) surfactant was purchased from Riedel-de Haen, Germany.

2.2 Preparation of NR-*g*-HEMA

The graft reactions were carried out in a 500 mL five neck glass reactor under agitation and nitrogen atmosphere, using distilled water as a continuous phase. The pH of the reaction medium was adjusted to 9.0 by adding ammonium hydroxide solution (1.5% w/w). In each reaction NRL was added first, then distilled water and NH_4OH solution. HEMA was then added followed by SDS, CHP and TEPA. The reactions were allowed to proceed under agitation and then the reactor was discharged. The parameters studied for the graft copolymerization are shown in Table 1.

Table 1. Parameters of various experiments

Parameters	Variable
HEMA amount	5, 10, 20, 30 (phr)
CHP/TEPA (1:1) amount	0.1, 0.15, 0.2, 0.25 (%mol)
Reaction temperature	40, 50, 60, 70 (°C)
Reaction time	30, 60, 90, 120, 150, 180 (min)
Agitation speed	50, 100, 150, 200 (rpm)

2.3 Determination of grafting and grafting efficiency

The dry copolymer was subjected to soxhlet extraction for 24 hours using ethanol as a solvent for extracting ungrafted PHEMA. The grafting (G) and grafting efficiency (GE) were calculated by the following equations. (Ghosh *et al.*, 1998)

$$\%\,\text{Grafting} = \frac{M_2 - M_0}{M_0} \times 100 \qquad (1)$$

$$\%\,\text{Grafting efficiency} = \frac{M_2 - M_0}{M_1 - M_0} \times 100 \qquad (2)$$

Where M_o, M_1 and M_2 denote mass (in grams) of NR, the weight of the dried sample before extraction and the weight of the sample after extraction, respectively.

2.4 Fourier transform IR spectroscopy

FT-IR spectra of the NR-*g*-HEMA were recorded using an Omnic ESP Magna-IR 560 in the range of 4000-400 cm^{-1} with a resolution of 2 cm^{-1}. The rubber sample was obtained by casting films of rubber solution on a KBr disc.

2.5 ^{1}H-NMR spectroscopy

^{1}H-NMR spectroscopic analysis was carried out using samples which were swollen in deuterated chloroform at 20°C. A Varian Mercury 300 MHz NMR spectrometer was used.

2.6 Testing of adhesion properties

The adhesion properties of NR-*g*-HEMA compared with the original natural rubber was preliminarily investigated. The experiment was performed by applying grafted copolymer or natural rubber for bonding plywood pieces. The wood joints were kept at room temperature and at a relative humidity (RH) of 50±5 for 7 days prior to be tested. These wood joints were tested for the cleavage peel strength and the shear strength using a tensile tester according to ASTM D3807-04 and ASTM D2339-04.

3. Results and Discussion

3.1 Preparation of NR-*g*-HEMA

The cumene hydroperoxide in the dilute aqueous solution was decomposed to cumiloxy radical (RO•) by the action of the base tetraethylene pentamine. The cumiloxy radical might react with either the monomer or the rubber molecule-producing macroradical, which initiates grafting. During the formation of the graft copolymers, the surface of the latex particles became the locus of polymerization. It is possible for the α-methylenic hydrogen atoms in the natural rubber, which are more active, to become the sites of graft copolymerization. The cumiloxy radical not only can abstract the α-methylenic hydrogen atoms to produce polyisoprene radicals, which initiate monomers to form the graft copolymer, but can also initiate monomer to form free polymer radicals, which combine with polyisoprene radicals to terminate or transfer to natural rubber to form graft copolymer. Moreover, some of the free polymer radicals still terminate to form free homopolymers on the latex particles (Arayapranee *et al.*, 2002). The possible structure of NR-*g*-HEMA is shown in Figure 1.

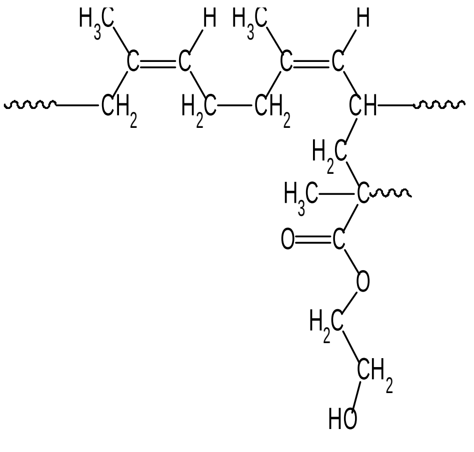

Figure 1. Possible structure of NR-*g*-HEMA

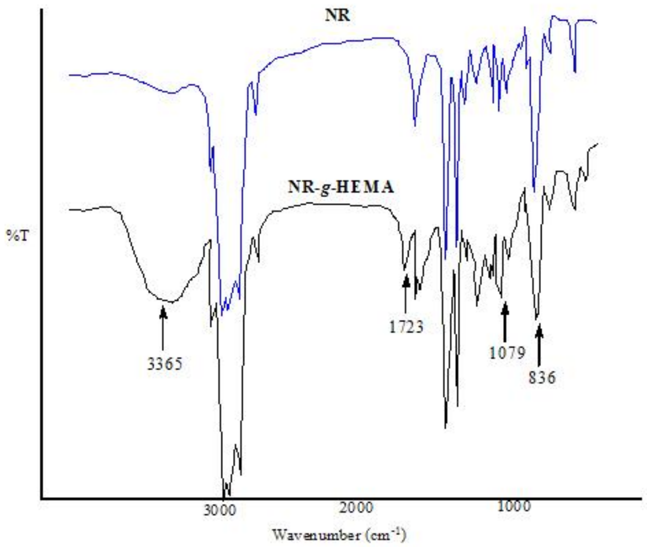

Figure 2. FT-IR spectra of NR and NR-*g*-HEMA

To determine the presence of the graft copolymer, the products were extracted with ethanol. After the solvent extraction, the graft copolymers were analyzed by FT-IR and ^{1}H-NMR spectroscopic techniques. Figure 2 illustrates the FT-IR spectrum of the graft copolymer. The peaks at 3365 cm^{-1} are assigned to the hydroxyl group (OH), at 2961-2854 cm^{-1} to the C-H stretching in -CH_3 and -CH_2, at 1723 cm^{-1} to the C=O stretching in HEMA, at 1664 cm^{-1} to the C=C stretching in *cis*-R_2C=CHR, 1447, at 1374 cm^{-1} to the C-H bending in alkyl chains, at 1079 to the C-O stretching in HEMA and at 836 cm^{-1} to the C-H out of plane bending in *cis*-R_2C=CHR. Figure 3 illustrates the ^{1}H-NMR signals of the graft copolymer. The peaks at 5.13 ppm are assigned to the olefinic proton in natural rubber. The signals at 3.31 and 3.72 ppm are attributed to the methylenoxy proton resonance of the grafted HEMA. These FT-IR and ^{1}H-NMR analyses confirm that the latex prepared in this emulsion polymerization contains graft copolymers.

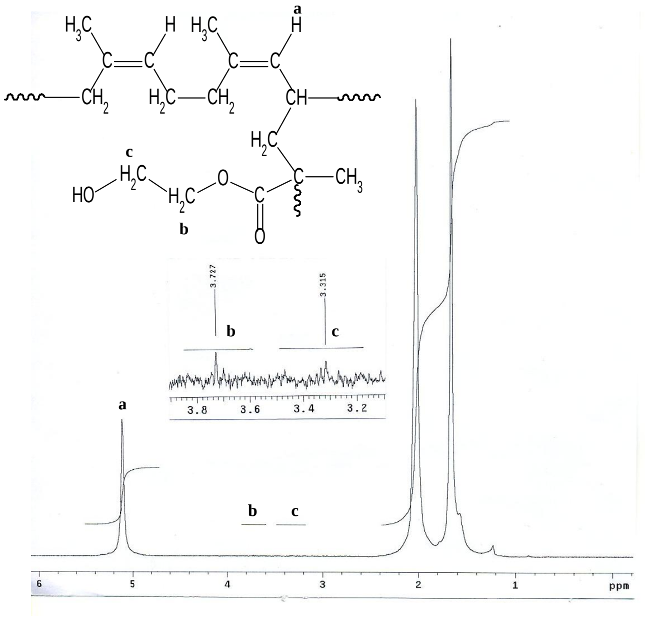

Figure 3. ^{1}H-NMR signals of NR-*g*-HEMA

3.2 Effect of HEMA concentration

The effect of HEMA concentration on %G and %GE was studied in the range of 5-30 phr at the fixed concentrations of initiator (0.2%mol) and SDS (3 phr) at 50°C for 90 mins under an agitation speed of 150 rpm. It was observed that both %G and %GE increased with the increase in concentration of HEMA as shown in Figure 4. This indicated that when the amount of HEMA was increased, a more favorable condition to produce graft copolymers rather than free homopolymers was obtained. It can be concluded that both high %G and high %GE were achieved at a high level of HEMA/NR because the amount of graft copolymers depends on the amount of the monomer used (Chern, 2006).

3.3 Effect of reaction temperature

The rate of decomposition of the initiator depends on the reaction temperature. With an increase in reaction temperature, more cumiloxy radicals are produced. It is also known that the transfer of cumiloxy radicals to the rubber chain produces the graft copolymer. So, perusal of the results indicate that the %G and %GE increase as the polymerization temperature is increased up to 60°C (Figure 5) then both %G and %GE decrease with further increases in the reaction temperature. This may result from the rapid decomposition of the initiator, yielding a high instantaneous radical concentration.

3.4 Effect of initiator concentration

The effect of the amount of initiator on the %G and %GE was investigated over a range of approximately 0.1 to

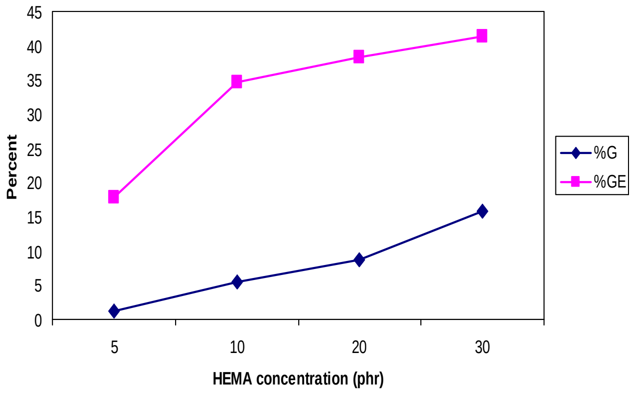

Figure 4. Effect of HEMA concentration on grafting (%G) and grafting effiency (%GE). SDS = 3 phr, [I] = 0.2 %mol, T = 50°C, Time = 90 mins, Agitation speed = 150 rpm.

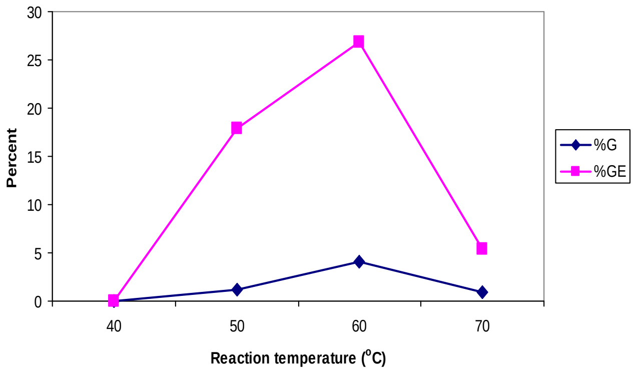

Figure 5. Effect of reaction temperature on grafting (%G) and grafting effiency (%GE). SDS = 3 phr, HEMA concentration = 5 phr, [I] = 0.2 %mol, Time = 90 mins, Agitation speed = 150 rpm.

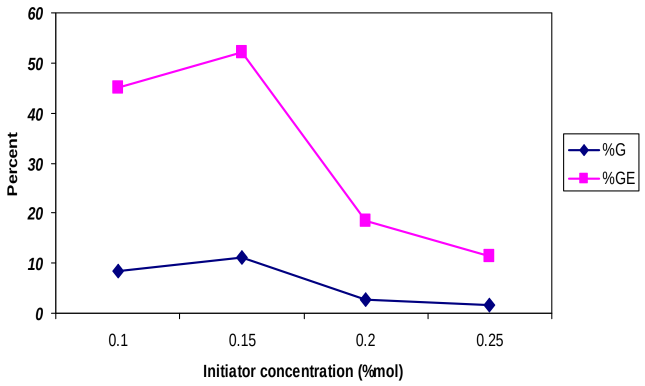

Figure 6. Effect of initiator concentration on grafting (%G) and grafting effiency (%GE). SDS = 3 phr, HEMA concentration = 5 phr, T = 60°C, Time = 90 min, Agitation speed = 150 rpm.

0.25 %mol while keeping the concentration of all other reagents constant (Figure 6). The %G and %GE increased with an increase in the amount of initiator from 0.1 to 0.15 %mol. This can be explained by the fact that radical transfer to either rubber or monomer produces macroradicals, and this is enhanced on increasing the initiator, thus resulting in an increase in grafting. However, increasing the initiator concentration beyond a concentration of 0.15 %mol, results in a decrease in the %G and %GE decrease, which results from the conversion of free copolymers increasing again over 0.15 %mol. Under this condition, the chain length of grafts has hardly anything to do with the free polymer radical. The excessive free polymer radicals react with each other to form free homopolymers more than to graft on the natural rubber and decrease the chain length of the graft. Therefore, the production of free polymers is promoted more at high initiator concentrations (Arayapranee *et al.*, 2002).

3.5 Effect of reaction time

The %G and %GE increased extremely rapidly during the initial period (30-90 min) before reaching a plateau level **(**Figure 7). This is shown by the rapid increase of %G and %GE between 30 and 90 min. After 90 min, %G and %GE of the HEMA monomer in reactor was high and remained constant. This result may be explained by a mechanism involving a surface controlled process; that is, the graft reaction occurs mainly on the surface of the latex particles or mainly in the shell of the particles. As grafting proceeds at a certain shell thickness the second-stage polymer is reached and the contact area between monomer and rubber decreases. Therefore, it is more difficult for graft copolymerization to occur through diffusion of the monomer to the rubber chain (Chern, 2006), compared to the copolymerization of monomer. As a result the %G and %GE increased during the initial phase and remained constant after this.

3.6 Effect of agitation speed

The %G and %GE were also influenced by agitation speed, as shown in Figure 8. A reduction in agitation speed to 50 rpm leads to earlier attainment of acceleration in the

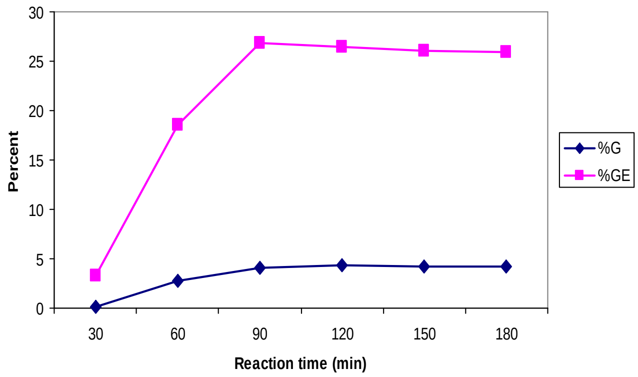

Figure 7. Effect of reaction time on grafting (%G) and grafting effiency (%GE). SDS = 3 phr, HEMA concentration = 5 phr, [I] = 0.2 %mol, T = 60°C, Agitation speed = 150 rpm.

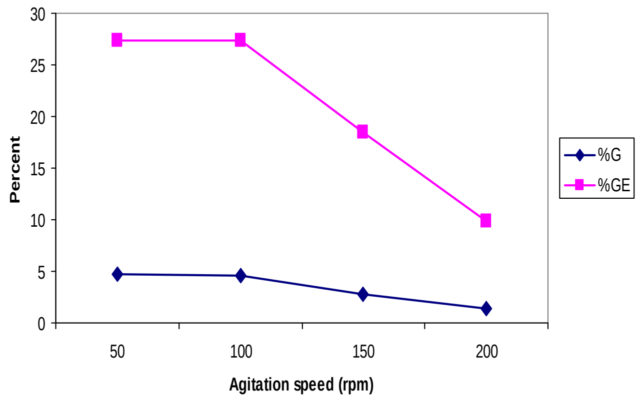

Figure 8. Effect of agitation speed on grafting (%G) and grafting effiency (%GE). SDS = 3 phr, HEMA concentration = 5 phr, [I] = 0.2 %mol, T = 60 °C, Time = 90 min.

Table 2. The effect of variation of %G on the graft copolymer on the cleavage peels strength and the shear strength.

Sample	Shear strength (N/m^2)	Cleavage peel strength (N/mm)
NR	0.86 ± 0.04	0.96 ± 0.20
NR-*g*-HEMA 2.78 %G	0.93 ± 0.32	0.99 ± 0.26
NR-*g*-HEMA 4.10 %G	1.38 ± 0.26	1.12 ± 0.12
NR-*g*-HEMA 8.35%G	1.41 ± 0.30	1.21 ± 0.23

polymerization. This can be explained by considering a monomer mass transfer from monomer droplets to the polymer particles formed in the aqueous phase (Ni *et al.*, 2001). Thus %G and %GE decrease with increase in agitation speed.

3.7 Adhesion properties

Table 2 shows the effect of variation of %G on the graft copolymer on the cleavage peel strength and the shear strength. It was found that both the cleavage peel strength and the shear strength increase as the %G increases, and graft copolymer has a higher strength compared to the NR. The relative increase in strength is due to the increased polar component of the graft copolymer. The H-bonding between plywood and hydrophilic groups such as OH and C=O of the copolymer or mechanical interlocking may both take part in this adhesion enhancement.

4. Conclusion

The highest level of natural rubber grafted 2-hydroxyethyl methacrylate was obtained when using 5 phr of HEMA, 0.15 %mol cumene hydroperoxide and tetraethylene pentamine at 60°C for 90 mins under the agitation speed of 50 rpm. The cleavage peel strength and shear strength of plywood adhesion increase as the %grafting increases and graft copolymer has higher strength compared to the original natural rubber.

Acknowledgements

The authors thank the kind support of the Graduate School, Prince of Songkla University (PSU), and Research Fund (PSU Campus), Thailand.

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