

PREPARATION, ADHESIVE PERFORMANCE AND STABILITY OF NATURAL RUBBER LATEX GRAFTED WITH N-BUTYL ACRYLATE (BA) AND METHYL METHACRYLATE (MMA)

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Abstract

In order to study the potential of increasing the weather stability of natural rubber latex for use as a water-based contact adhesive, the natural rubber latex was modified by graft copolymerization with n-butyl acrylate (BA) and methyl methacrylate (MMA). The grafting reaction was carried out using emulsion polymerization at 60°C. Potassium persulfate was used to initiate polymerization. Four different weight percentage ratios of BA to MMA used in this work were 95:5, 90:10, 85:15 and 80:20. Percentage conversion of the monomer of all latexes prepared was $\geq 79.5\%$. The grafting efficiency of graft-modified natural rubber with a different monomer ratio tends to decrease with an increase of MMA. ¹H-nuclear magnetic resonance spectroscopy (¹H-NMR) confirmed that the latexes which were prepared contained graft copolymer. The adhesive performance was characterized by 90° peel strength tests. Only graft-modified natural rubber latex with the monomer ratio of 80:20 possessed an adhesion property enough to conduct peel testing. The peel strength value of graft-modified natural rubber was lower than that of natural rubber latex. However, graft-modified natural rubber latex tends to have a higher weather stability than natural rubber latex.

Keywords: Contact adhesive, graft-modified natural rubber, emulsion polymerization

Introduction

A significant advantage of contact adhesives is auto-adhesion, which results in an instant bond with sufficient green strength so that fixturing is unnecessary. They are dominantly used in the production of automotive trim, shoes and furniture. Most contact adhesives are solvent-based polychloroprene adhesives. Formulations are based on the variety of such

polymers available and using various resins, solvents, etc. can provide adhesives with a wide variation in the range of specific properties and applications. Although solvent-based polychloroprene contact adhesives are widely used, there are some problems associated with the organic solvents used, including inherent toxicity, general solvent hazards and flammabil-

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ity. Accordingly, there have been a number of attempts to produce environmentally friendly water-based contact adhesives (Patel, 2002; Thames *et al.*, 2003).

Natural rubber latex which is a renewable resource can also be used as a water-based contact adhesive (Adam *et al.*, 1998). However, due to its unsaturated backbone chain nature, natural rubber adhesive is not quite stable and is brittle when left for a period of time (Landrock, 1985; Pocius, 1997). Thus, it is necessary to add an antioxidant and stabilizer into the natural rubber latex adhesive. An alternative route to improve stability of natural rubber may be achieved by decreasing the amount of double bonds via graft copolymerization with a vinyl monomer. The graft copolymerization of a vinyl monomer onto the rubber can be carried out in the latex phase using emulsion polymerization (Arayaprane *et al.*, 2002; Oliveira *et al.*, 2005). In this work, the graft copolymerization of the n-butyl acrylate/methyl methacrylate mixture onto natural rubber seed latex was carried out by using potassium persulfate as an initiator. The main monomer was n-butyl acrylate which is a monomer used to produce water-based acrylic adhesive (Sanderson and Gehman, 1984). Methyl methacrylate was found to increase the glass transition temperature of the copolymer leading to improve in cohesive strength (Hamada and Ichikawa, 2003).

Materials and Methods

Materials

A high ammonia-concentrated natural rubber latex containing 62% dried rubber was supplied by Thai Hua, Ltd. of Udontani, Thailand. Butyl acrylate (BA, Aldrich, 99+%) and methyl methacrylate (MMA, Aldrich, 99+%) monomers were used after removal of the inhibitor using 2%w/w aqueous sodium hydroxide which was shaken with an equal volume of monomer in a separating funnel. This process was repeated three times. Residual sodium hydroxide was removed by washing the monomer four times with deionized water. The inhibitor-free monomer was dried over

anhydrous calcium chloride overnight and filtered before use. The stabilizer isopropanol, the buffer potassium hydroxide (KOH, Aldrich), the initiator potassium persulfate (Merck), the chain transfer agent t-dodecyl mercaptan (tDM, Fluka), and the emulsifier sodium dodecyl sulfate (SDS, Acros) were used as received. Deionized water was used throughout the work.

Preparation of Grafted Natural Rubber

Graft copolymerization was carried out in a 500 ml five-necked round-bottomed flask. Natural rubber latex, NR, (50 g), distilled water (100 g), isopropanol (3 g), KOH (0.12 g) and SDS (0.16 g) were charged to the flask and the flask was set up in the water bath. The flask was purged with nitrogen while the temperature was brought to 60°C. After 30 min, the monomer mixture (0.75 × amount of dried natural rubber) and tDM (0.05 g) were fed to the flask. The natural rubber seed latex was swollen with the monomer for 1 h before adding the initiator (0.6 g). The reaction was performed for 6 h under continuous stirring. At 1 h intervals during the preparation samples were removed to evaluate the percentage conversion of the monomer using the gravimetric method. Four different weight percentage ratios of BA to MMA used were 95:5, 90:10, 85:15 and 80:20. For comparison of the adhesive performance, the controlled natural rubber latex (CNR) was also prepared using the same conditions as the preparation of graft-modified natural rubber latex except for the addition of the monomer mixture, tDM and the initiator. The nomenclatures used to describe the latex preparation are listed in Table 1.

After the reaction was finished, the latex was coagulated using a 5%w/w CaCl_2 aqueous solution. The coagulum was separated and dried to a constant weight in a vacuum oven at 40°C. A Soxhlet extraction was used to wash out the ungrafted NR with petroleum ether and the free copolymer with acetone. The weight difference between the initial sample and the extracted samples was taken. The free copolymers (FP) and the grafting efficiency (GE) were calculated using the following relationships:

$$\%GE = \frac{\text{weight of monomers grafted}}{\text{weight of monomers polymerized}} \cdot 100$$

$$\%FP = \frac{\text{weight of free copolymers}}{\text{weight of the gross polymers}} \cdot 100$$

The monomer conversion is defined as the weight of the monomer polymerized (grafted and free) divided by the initial weight of the monomers.

Nuclear Magnetic Resonance

¹H-NMR spectra were run on a Varian NMR spectrometer (model Inova 3000) using a 5 - 10%w/w solution in deuterated chloroform (CDCl₃).

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (Perkin-Elmer DSC 7) was used to determine glass transition temperature (*T_g*) of dried latex samples.

Samples were heated from -100 to 50°C at the rate of 10°C min⁻¹ in nitrogen atmosphere.

Measurement of 90° Peel Strength

Peel strength was measured according to ASTM D1876-95 using a 90° peel test as shown in Figure 1. Cotton Duck cloth strips (25 × 280 mm) were coated three times with latex. The final coating was allowed to dry for 60 min before being folded in half lengthways. A 25 × 100 mm area was then immediately pressed using a pressure of 50 kg cm⁻² for 30 s. Peel strengths were measured at a rate of 100 mm min⁻¹ after 3 h, 3 days and 7 days conditioning at 25 ± 1 °C and 50 ± 5% relative humidity and also after 45 days left in the open air.

Thermogravimetric Analysis (TGA)

Thermo-oxidation of CNR and GNR-80:20 latexes were determined on ~10 mg dried latex samples in a Perkin Elmer model TGA 7 with a heating rate of 20°C min⁻¹ in air flow.

Table 1. The nomenclatures of graft-modified and controlled natural rubber latexes

Latex	Monomer mixture used in latex preparation (%w/w)	
	BA	MMA
CNR	-	-
GNR-95:5	95	5
GNR-90:10	90	10
GNR-85:15	85	15
GNR-80:20	80	20

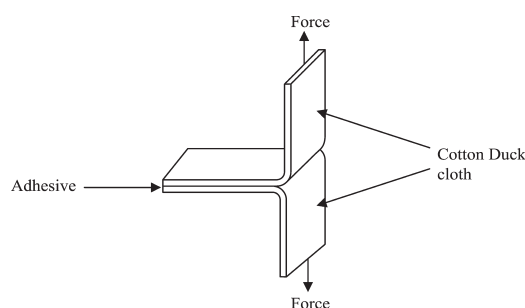


Figure 1. Schematic diagram of the 90° peel strength test method

Results and Discussion

Percentage Conversion, Free Copolymer and Grafting Efficiency

The final %conversion of monomers, free copolymer (%FP) and grafting efficiency (%GE) for each latex sample are shown in Table 2.

The final %conversion of monomers for latexes prepared is varied between 79.5 - 90%. However, there is no definite trend in %conversion with the different ratio of BA to MMA.

The grafting efficiency of the graft-modified natural rubber latex produced using a different weight percentage ratio of BA to MMA tends to decrease with an increase of MMA. This might be because MMA has a higher water solubility than BA [the water solubility of MMA and BA at 50°C is 0.15 and 0.0064 mol L⁻¹ respectively (Gilbert, 1995)]. The higher the water solubility, the higher chance of free polymer particles occurred in the water phase (El-Aasser and Sudol, 1997) which agrees with the amount of free copolymer present in the latex as shown in Table 2.

¹H-NMR Spectra

To confirm the occurrence of graft copolymer, the ¹H-NMR spectra of NR latex, latex GNR-80:20 and poly(n-butyl acrylate)-co-poly(methyl methacrylate), PBA-co-PMMA, are compared in Figure 2. The unsaturated methyne proton of NR shows a singlet resonance signal at 5.12 ppm. The signal at 4.03 ppm is attributed to the OCH₂ group of PBA. The methoxy proton of the acrylic group of the grafted MMA unit appears at 3.60 ppm. The peak which appeared at 0.94 ppm is due to the aliphatic hydrogen of

PBA. These ¹H-NMR analyses indicate that the latexes prepared contained graft copolymer. Figure 3 illustrates the ¹H-NMR spectrum of the graft-modified natural rubber which can be seen that four different latexes prepared have slightly different spectrum. The clarity of signal at 3.60 ppm increases when the amount of methyl methacrylate used in the preparation increases. This indicates that the chain composition of the grafted copolymers may not be the same.

Transition Behavior of the CNR and GNR-80:20

Contact adhesives must be in the rubbery state at application temperature, i.e. room temperature. Thus, it is necessary to evaluate their glass transition temperature (T_g's). In this work, four different latexes were prepared but only latex GNR-80:20 shows adhesive property enough to determine adhesive performance. Accordingly, transition behavior of dried latex GNR-80:20 were studied compared with that of dried latex CNR.

Figure 4 shows DSC curves of dried latexes GNR-80:20 and CNR. Dried latex CNR has a single glass transition temperature at -65°C. Dried latex GNR-80:20 shows two different glass transitions, one at -65°C corresponding to NR and other at -25°C corresponding to poly(n-butyl acrylate)-co-poly(methyl methacrylate). The results illustrate that T_g's of both latexes are well below room temperature.

Adhesive Performance of Graft-Modified Natural Rubber

As state above, only latex GNR-80:20 possesses an adhesive property enough to determine adhesive performance. The possible

Table 2. Final Latex solids content, percentage conversion, percentage free copolymer and grafting efficiency for the grafted-modified and controlled natural rubber latex

Latex	%solid content	%conversion	%FP	%GE
CNR	29.0	-	-	-
GNR-95:5	28.0	84.7	16.9	58.4
GNR-90:10	27.0	80.5	21.1	46.9
GNR-85:15	26.5	79.5	22.6	43.4
GNR-80:20	28.4	89.9	26.8	41.7

explanation for the result obtained might be the difference in the chain composition of the graft copolymer and the amount of free copolymer. The peel strength of GNR-80:20 and CNR latexes are shown in Table 3. Under conditioning at $25 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity, the peel strength of both latexes increased with increasing time from lamination. This can be explained in terms of the molecular diffusion processes. Initially, the bonds formed at the interface between the two adhesive films are relatively weak because of limited molecular entanglement. As contact time increases more polymer molecules diffuse across the interface due to their glass transition temperature (T_g) being below room temperature, and the degree of entanglement increases (Allen, 1992).

The peel strength of latex GNR-80:20, however, was lower than that of latex CNR. This

may have occurred because the polymer chain of latex GNR-80:20 did not sufficiently wet the substrate. The wetting ability of the polymer chain in this latex may have decreased due to short branching (Jovanovic and Dube, 2005). In addition, the number of graft copolymers presented in the latex may not be high enough. Therefore, the diffusion process may be inefficient because the interdiffusion of polymer chains across the interface will occur well only if the two materials are thermodynamically compatible (Wake, 1978). Inefficient diffusion leads to lower cohesive strength.

Peel strength results of the specimens left in the open air for 45 days are shown in the last

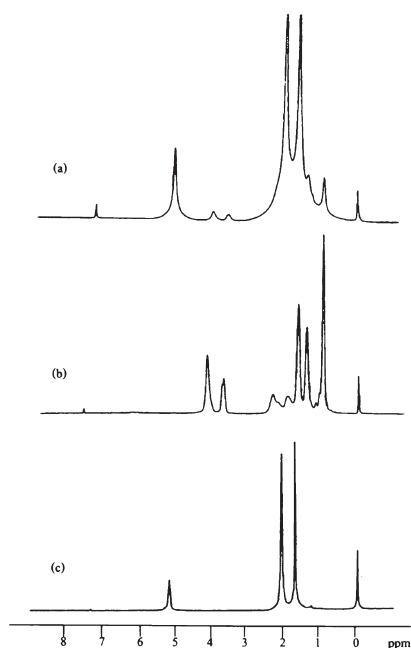


Figure 2. ^1H -NMR spectra of polymers (a) GNR-80:20 (b) PBA-co-PMMA and (c) CNR

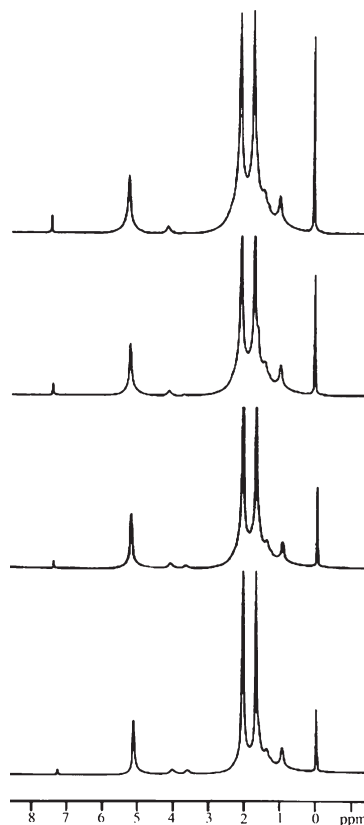


Figure 3. ^1H -NMR spectra of graft-modified natural rubber: (a) GNR-95:5 (b) GNR-90:10 (c) GNR-85:15 and (d) GNR-80:20

column of Table 3. The peel strength of latex CNR decreased significantly whereas the peel strength of latex GNR-80:20 increased about 58%. This may be because of the chain scission of NR molecules due to oxidation reaction (Barbin and Rodgers, 1994). On the other hand, the graft-modified natural rubber contains less of a double bond resulting in less of an oxidation reaction. Moreover, free copolymer, i.e. the poly(n-butyl acrylate)-co-poly(methyl methacrylate), in the latex has high weather stability.

Thermo-Oxidation

In order to compare the oxidative stability of dried latexes CNR and GNR-80:20, thermal degradation in air was studied. The TGA curves of CNR and GNR-80:20 are shown in Figure 5. The 10% weight loss temperature of dried latex CNR is about 280°C and that of dried latex GNR-80:20 is about 310°C. This implies that the latex

GNR-80:20 has a higher oxidative stability than latex CNR. The results obtained confirm the explanation given above.

Conclusion

The graft copolymerization of n-butyl acrylate and methyl methacrylate mixture onto natural rubber latex using potassium persulfate as the initiator was carried out by varying the monomer mixture ratio. The percentage conversion of the monomer of all latexes prepared was $\geq 79.5\%$. The grafting efficiency of graft-modified natural rubber with a different monomer ratio tends to decrease with an increase of MMA.

Characterization of the graft copolymers by ^1H -nuclear magnetic resonance spectroscopy (^1H -NMR) indicates the occurrence of grafting on the natural rubber backbone in the latex particle.

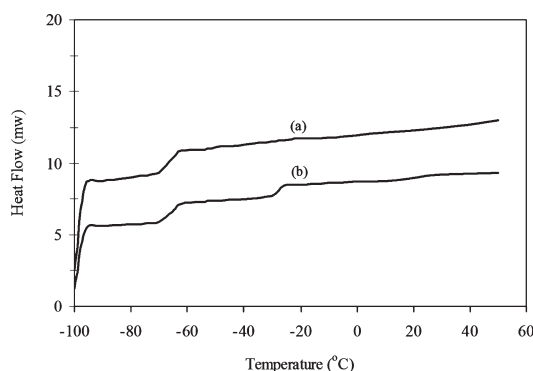


Figure 4. DSC curves for (a) CNR and (b) GNR-80:20

Table 3. Peel strength values obtained for CNR and GNR-80:20 latexes

Latex	90° Peel strength / N mm ⁻¹			
	3 hours	3 days	7 days	45 days ^a
CNR	1.33 ± 0.10	1.82 ± 0.13	2.33 ± 0.30	0.74 ± 0.12
GNR-80:20	0.42 ± 0.05	0.52 ± 0.15	0.71 ± 0.04	1.12 ± 0.05

^a Leave in open air

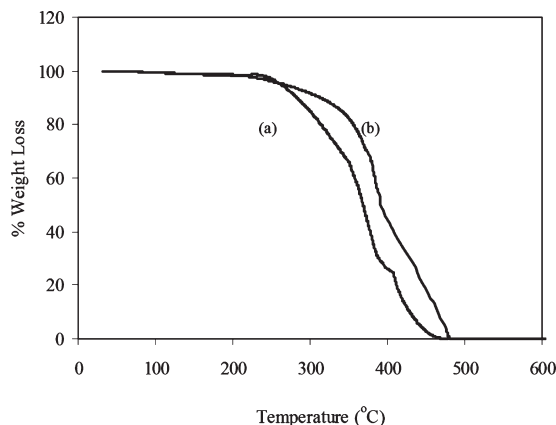


Figure 5. TGA curves in air on heating ramp of 20°C min⁻¹ of the (a) CNR and (b) GNR-80:20

The adhesive performance was characterized by 90° peel strength tests. Only latex GNR-80:20 possessed adhesion properties enough to conduct peel testing. The peel strength values of GNR-80:20 were lower than that of natural rubber latex. However, graft-modified natural rubber latex tends to have higher weather stability than natural rubber latex.

Acknowledgement

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