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PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER LATEX GRAFTED WITH ETHYLACRYLATE (EA) – METHYLMETHACRYLATE (MMA) MONOMERS MIXTURE

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ABSTRACT

Weather stability is a critical factor in the service life of natural rubber latex as a water-based contact adhesive. To enhance its weather stability, natural rubber latex was modified by graft copolymerization with ethyl acrylate (EA) and methyl methacrylate (MMA) monomers mixture. The grafting reaction was carried out by emulsion polymerization at 60^0*C using ceric ammonium nitrate as initiator. Four different weight percentage ratios of EA to MMA used in this study were 90:10, 85:15, 80:20, and 75:25. The grafting efficiency of graft-modified natural rubber latex was found to decrease with increase in MMA.* ^{1}*H-nuclear magnetic resonance (*^{1}*H-NMR) spectroscopy confirmed that the latexes prepared contained graft copolymers. The adhesive performance was evaluated by 90*^{0} *peel strength tests. Only graft-modified natural rubber latex with monomer ratio of 75:25 gave significant results. The peel strength value of graft-modified natural rubber latex was lower than that of natural rubber latex. However, graft-modified natural rubber latex showed higher weather stability than natural rubber latex.*

Keywords: natural rubber latex, graft copolymerization, contacts adhesive, emulsion polymerization.

INTRODUCTION

Graft copolymerization provides a unique technique for modifying polymers to meet end-use requirements. Graft copolymers of natural rubber latex are of interest because natural rubber is a renewable resource, and can also be used as a water-based contact adhesive (Adams et al, 1998). A significant advantage of contact adhesive is auto-adhesion, which results in an instant bond with sufficient green strength so that fix-Turing is unnecessary. Accordingly, they are dominantly used in the production of shoes, furniture and automotive trims.

Most contact adhesives are solvent-based poly chloroprene adhesives. Although solvent-based poly chloroprene contact adhesives are widely used, there are some problems associated with the organic solvents used, including inherent toxicity, general solvent hazards and flammability. Accordingly, there have been a number of attempts to produce environmental friendly water-based contact adhesives (Patel, 2002; Thames et al, 2003). Natural rubber latex is a potential alternative to poly chloroprene as a water-based contact adhesive because of its advantages of low cost and renewability, especially with the substantial depletion of petroleum resources in the last decade worldwide. However, due to its unsaturated backbone chain nature, natural rubber adhesive is not quite stable and it is brittle when left for a period of time (Landrock, 1985; Pocius, 1997). Thus, it is necessary to add an anti-oxidant and stabilizer into natural rubber adhesive. An alternative route to improve the stability of natural rubber may be achieved by decreasing the amount of double bonds via graft copolymerization with a vinyl monomer. Graft copolymerization of a vinyl monomer onto the rubber can be carried out in the latex phase using emulsion polymerization (Aryapranee et al, 2002; Oliveira et al, 2005). In this study, graft copolymerization of ethyl acrylate/methyl methacrylate monomers mixture onto natural rubber latex was carried out by using ceric ammonium nitrate as the initiator. Ethyl acrylate was used as the main monomer because it is one of the monomers 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 improvement in cohesive strength (Patil and Fanta, 1993).

MATERIALS AND METHOD

Materials

Concentrated natural rubber (NR) latex containing about 60% dry rubber was obtained from Federal Research Institute, Umudike, Abia State, Nigeria. Ethyl acrylate (EA, BDH) and methyl methacrylate (MMA, Aldrich) 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 five times with de-ionized water. The inhibitor-free monomer was dried over anhydrous calcium chloride overnight and filtered before use. The stabilizer (isopropanol), the buffer (potassium hydroxide) (KOH, BDH), the initiator (ceric ammonium nitrate) (BDH), the chain transfer agent (t-dodecyl mercaptan) (tDM, Aldrich), and the emulsifier (sodium lauryl sulphate (Aldrich) were used as obtained. De-ionized water was used throughout the study.

Preparation of Graft-Modified Natural Rubber

Graft copolymerization was carried out using constant amounts of natural rubber latex (50g), and four different weight percentage ratios of ES to MMA of 90:10; 85:15; 80:20; and 75:25. The polymerization procedure was based on the method described by Okieimen and Egharevba, 1989. For comparison of the adhesive performance, the unmodified natural rubber latex was used as the controlled natural rubber latex (CNR). The monomer mixtures used in latex preparation (%w/w) are listed in Table 1. After completion of graft copolymerization the latex was coagulated using a 5%w/w aqueous calcium chloride solution. The coagulum was separated and dried to a constant weight in a vacuum oven at 50^0C. A Soxhlet extraction was used to wash out the un-grafted NR with petroleum ether, and the free copolymer with acetone. The monomer conversion (MC), free copolymers (FCP), and the grafting efficiency (GE) were calculated using the following relationships:

%MC = (Weight of monomer polymerized (graft and free)/Initial weight of monomers) × 100.
%FCP = (Weight of free copolymers/Weight of gross polymers) × 100.
%GE = (Weight of monomers grafted/Weight of monomers polymerized) × 100.

Table 1: Monomer mixtures used in latex preparation (%w/w)

Latex	Monomer mixture used in latex preparation (%w/w)	Monomer mixture used in latex preparation (%w/w)
	EA	MMA
CNR	-	-
GNR-90:10	90	10
GNR-85:15	85	15
GNR-80:20	80	20
GNR-75:25	75	25

Nuclear Magnetic Resonance

Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra of the controlled natural rubber (CNR) and graft-modified natural rubber (GNR) samples were obtained on NMR spectrometer (Model Inova 3000) using a 10%w/w solution in deuterated chloroform ($CDCl_3$).

Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) of dried latex samples were determined by Differential Scanning Calorimeter (Perkin-Elmer DSC 7). Samples were heated from -100 to 50^0C at the rate of 5^0C min^{-1} in nitrogen atmosphere.

Thermo-Gravimetric Analysis (TGA)

Thermal stability of CNR and GNR-75:25 latex samples were determined on 10mg dried latex samples by Thermo-gravimetric analysis (Perkin-Elmer model TGA 7) in air flow with a heating rate of 10^0C min^{-1}.

Measurement of Peel Strength

90^0-Peel strength was measured according to ASTM D1876-95 using cotton cloth strips measuring 25mm x 250mm. Peel strengths were measured at the rate of 80mm/min after 5hr, 5days, and 10days and 50days exposure in open air.

RESULTS AND DISCUSSION

Percentage Monomer Conversion, Grafting Efficiency and Free Copolymer

The percentage monomer conversion (%MC), grafting efficiency (%GE) and free copolymer (%FCP) for each latex sample are presented in Table 2. The results show that there is no definite trend in % monomer conversion with the different ratio of EA to MMA. On the other hand, the grafting efficiency decreased with an increase in MMA. This is attributed to higher water solubility of MMA (the water solubility of EA and MMA at 50^0C is 0.0043 and 0.15mol/l respectively (Gilbert, 1995). Thus, the higher the water solubility the higher the chance the chance of free polymer particles occurring in the water phase (Li, Z ; and Fu,J, 1988) which is in agreement with the amount of free copolymer present in the latex (Table 2).

Table 2: **Latex Solids Content, Percentage monomer conversion, Percentage grafting efficiency and Percentage free copolymer for graft-modified and controlled natural rubber latex**

Latex	% Solids contents	% Monomer conversion	% GE	% FCP
CNR	23.0	-	-	-
GNR-90:10	22.0	75.5	47.5	19.7
GNR-85:15	21.0	70.0	38.6	22.3
GNR-80:20	20.5	68.5	32.4	23.8
GNR-75:25	22.5	79.8	30.1	28.6

^{1}H-NMR spectra

The occurrence of graft copolymer was confirmed by comparing the ^{1}H-NMR spectra of CNR, GNR-75:25 and poly (ethyl acrylate)-co-poly (methyl methacrylate) as shown in Figure 1. The singlet resonance signal at 5.12ppm is due to the unsaturated methyne proton of natural rubber. The signal at 4.03ppm is attributed to the OCH_3 group of poly (ethyl acrylate). The ethoxy proton of the acrylic group of the grafted MMA unit appeared at 3.60ppm. The peak at 0.94ppm is due to the aliphatic hydrogen of poly (ethyl acrylate). These results indicate that the prepared latexes contained graft copolymer. The ^{1}H-NMR spectrum of the graft-modified natural rubber is presented in Figure 2. The results show that the four different latexes prepared have slightly different spectra. As the amount of MMA used in the preparation increased, the clarity of signal at 3.60ppm increased. This suggests that the chain compositions of the grafted copolymers are not the same.

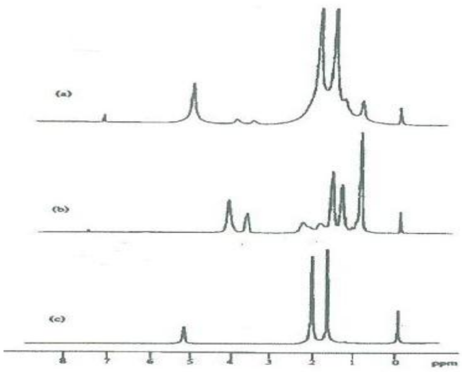

Figure 1. ^{1}**H-NMR spectra of polymers (a) GNR-75:25 (b) PEA-co-PMMA and (c) CNR.**

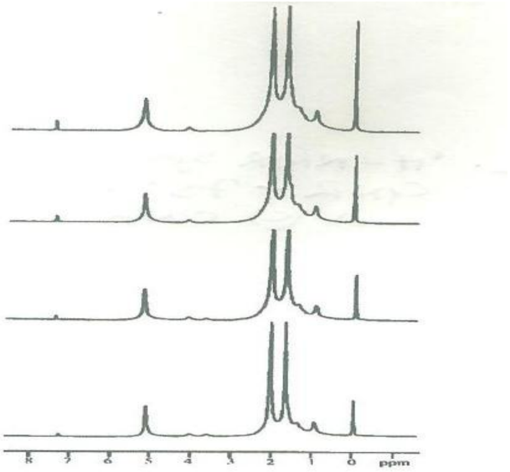

Figure 2. ^{1}**H-NMR spectra of graft-modified natural rubber: (a) GNR-90:10 (b) GNR-85:15 (c) GNR-80:20 and (d) GNR-75:25.**

Glass Transition Temperature (Tg) Of CNR And GNR-75:25

Among the four different latexes prepared, only latex GNR-75:25 gave significant results. Accordingly, the glass transition temperatures of dried latex GNR-75:25 and dried latex CNR were determined and compared as shown in the DSC curves (Figure 3). The results show that the dried latex CNR gave a singlet glass transition temperature at -65^{0}C, whereas the dried latex GNR-75:25 gave two different transitions, one at -65^{0}C is corresponding to natural rubber and the other at -25^{0}C corresponding to poly (ethyl acrylate)-co-poly (methyl methacrylate). These results indicate that the glass transition temperatures of both latexes are well below room temperature. It is important to note that contact adhesives must be in the rubbery state at application temperature, i.e. at room temperature.

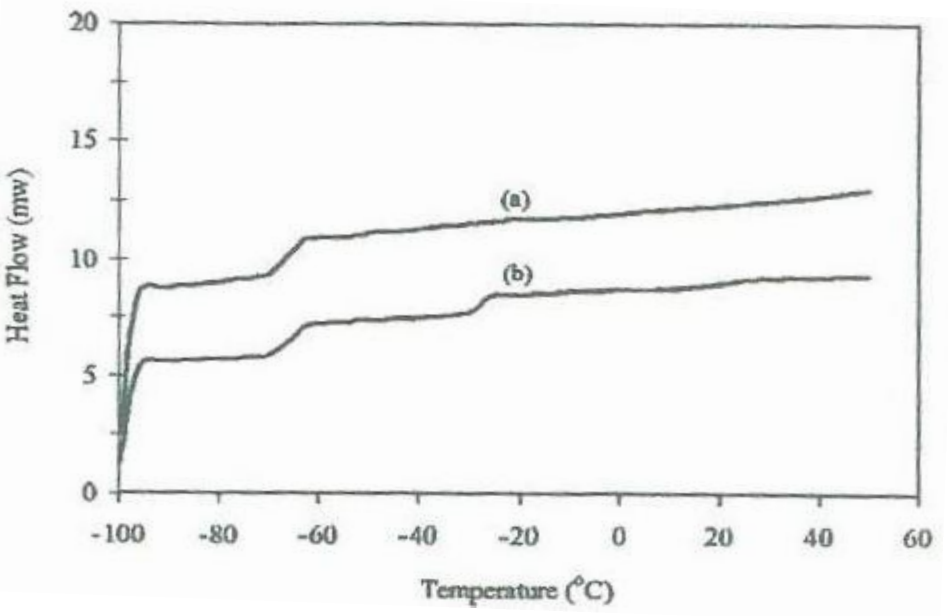

Figure 3: DSC curves for (a) CNR and (b) GNR-75:25.

Peel Strength of Graft-Modified Natural Rubber

As earlier stated, only latex GNR-75:25 gave significant results in adhesive property. Thus, the peel strength of latexes GNR-75:25 and CNR are presented in Table 3. From the results, the peel strength of latex GNR-75:25 were found to be lower than that of latex CNR. This may be due to insufficient wetting of the substrate by the polymer chain of latex GNR-75:25.

Table 3: Peel Strength values for CNR and GNR-75:25 Latexes

Latex	90^0 Peel Strength (N/mm)			
	5 hours	5 days	10 days	50 days
CNR	2.25	1.38	0.97	0.85
GNR-75:25	0.30	0.48	0.65	0.65

The decrease in the wetting ability of the polymer chain in this latex may be due to short branching (Jovanovic and Dube, 2005). In addition, the number of graft copolymers present in the latex may not be high enough. Insufficient diffusion leads to lower cohesive strength. Inter-diffusion of polymer chains across the interface will only occur freely if the two materials are thermodynamically compatible (Wake, 1978). The peel strength of latex CNR decreased significantly, whereas the peel strength of latex GNR-75:25 increased with increasing time of exposure. This is attributed to chain scission of NR molecules due to oxidative degradation reaction (Barbin and Rodgers, 1994). On the other hand, the graft-modified natural rubber contains less double bond which gives rise to less oxidative degradation reaction. In addition, the free copolymer, i.e., poly (ethyl acrylate)-co-poly (methyl methacrylate) in the latex has high weather stability.

Oxidative Stability of Dried CNR and GNR-75:25 Latexes

Thermal stability of CNR and GNR-75:25 latexes in air were studied by Thermo-gravimetric Analysis (TGA) in order to compare their oxidative stability. The TGA curves of the two latexes are presented in Figure 4.

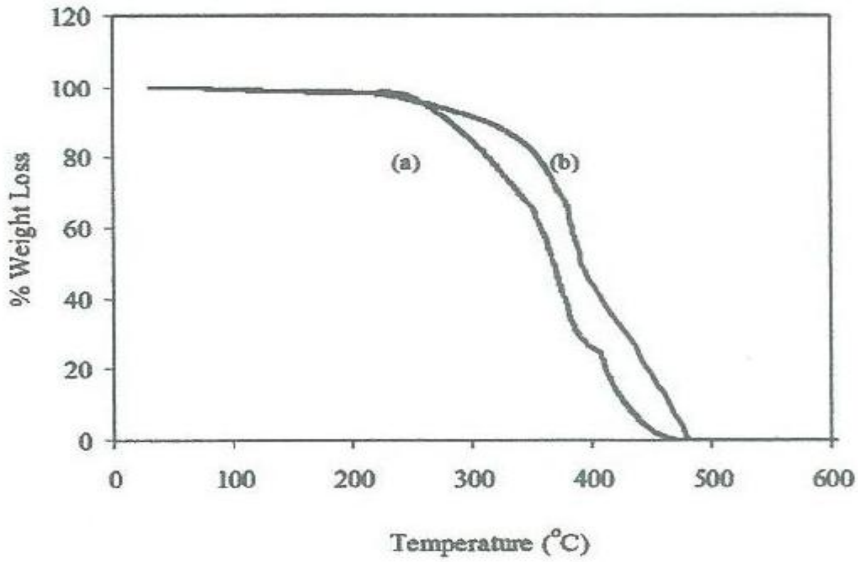

Figure 4: TGA curves of (a) CNR and (b) GNR-75:25

As shown in Figure 4, weight loss of latex CNR occurred at a temperature of about 270^{0}C while that of dried latex GNR-75:25 occurred at about 320^{0}C. This indicates that latex GNR-75:25 have a higher oxidative stability than latex CNR.

CONCLUSION

The graft copolymerization of ethyl acrylate and methyl methacrylate mixture onto natural rubber latex using ceric ammonium nitrate as the initiator was carried out by varying the monomer mixture ratio. The grafting efficiency of graft-modified natural rubber decreased with an increase in methyl methacrylate. ^{1}H-NMR spectra for the controlled natural rubber (CNR) and graft-modified natural rubber latexes indicate the occurrence of grafting onto the natural rubber backbone chain. 90^0 Peel Strength tests were conducted to assess the adhesive strength of the graft-modified natural rubber latex. Only latex GNR-75:25 possessed enough adhesion property for peel testing. The peel strength values of GNR-75:25 were lower than those of natural rubber latex. However, graft-modified natural rubber latex gave higher weather stability than natural rubber latex.

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