Carboxy terminated rubber based on natural rubber grafted with acid anhydrides and its adhesion properties

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Abstract. The chemical modification of natural rubber by grafting of various polar functional molecules is an essential method, improving the versatility of rubber in applications. This research investigated the preparation of natural rubber-graft-citraconic anhydride (NR-g-CCA), natural rubber-graft-itaconic anhydride (NR-g-ICA), and natural rubber-graft-maleic anhydride (NR-g-MA), with the anhydrides grafted to natural rubber in toluene using benzoyl peroxide as an initiator. Variations of monomer content, initiator content, temperature and reaction time of the grafting copolymerization were investigated. The maximum degrees of grafting were 1.06% for NR-g-CCA, 4.66% for NR-g-ICA, and 5.03% for NR-g-MA, reached using 10 phr citraconic anhydride, 10 phr of itaconic anhydride, or 8 phr of maleic anhydride, 3 phr benzoyl peroxide, at 85, 80 and 80°C for 2, 2 and 3 hrs, respectively. Solvent-based wood adhesives were formulated from these copolymers with various contents of wood resin in the range 10-40 phr. The maximal 289 N/in cleavage peel and 245.7 KPa shear strength for NR-g-MA (5.03% grafting) were obtained at 40 phr wood resin.

1. Introduction

Natural rubber is a well-known renewable resource obtained from the tree popularly known as Hevea brasiliensis in the form of a milky white fluid, and is a versatile raw material used mainly in the manufacture of tyres. Because of being highly unsaturated, it is less resistant to oxidation, ozone, weathering, various chemicals and solvents, in comparison to synthetic rubbers. Hence, chemical modification of natural rubber is essential to overcome some of its drawbacks. Graft copolymerization is one such modification technique used with natural rubber [1]. In particular, chemical modification with diene polymers of natural rubber has improved or produced useful materials. Among the many possibilities of chemical modifiers, the monomers used include maleic anhydride [2-3], styrene and methyl methacrylate [4], styrene and acrylonitrile [5], n-butyl and methyl methacrylate [6], ethyl acrylate and methyl methacrylate [7]. However, the grafting of acid anhydrides, particularly citraconic and itaconic anhydrides, onto natural rubber, and their effects on adhesion properties have not been thoroughly studied.

The present work focused on the grafting of citraconic anhydride, itaconic anhydride and maleic anhydride in toluene, using benzoyl peroxide as the radical initiator. The effects of these polar grafted copolymers on the adhesion properties were experimentally tested with plywood.
2. Experimental

2.1 Preparation of natural rubber grafted with acid anhydrides

A 250-mL three-necked round bottomed flask equipped with a mechanical stirrer, dropping funnel and N\textsubscript{2} inlet, immersed in a water bath at desired temperature (70-85°C), was charged with the solution of 5% dried natural rubber (air dried sheet rubber) in toluene, 1-4 phr benzoyl peroxide initiator, and stirred for 15 mins. An amount of 4-10 phr maleic anhydride, citraconic anhydride or itaconic anhydride (dissolved in 10 mL toluene) was introduced slowly through the dropping funnel into the reaction mixture. The resulting mixture was allowed to react for 180 mins. The grafted product was obtained by precipitating the reaction mixture in hot methanol, separating, and drying the precipitate in an oven at 50°C. The grafted rubber was purified before further investigation by dissolution in toluene and re-precipitating in methanol.

2.2 Characterization of grafted natural rubber

The natural rubber grafted maleic anhydride (NR-g-MA), natural rubber grafted citraconic anhydride (NR-g-CCA), and natural rubber grafted itaconic anhydride (NR-g-ICA) were characterized by FTIR spectrophotometry (Bruker Tensor 27 spectrophotometer). The grafting tendency of anhydrides onto the natural rubber molecules was monitored by using the peak height ratio of absorbance peaks at 1785 cm\(^{-1}\) and 838 cm\(^{-1}\):

\[
\text{Peak height ratio} = \frac{A_{1785}}{A_{838}}
\]

Here, A\(_{1785}\) represents the absorption peak of C=O (symmetric vibration) of cyclic anhydride, and A\(_{838}\) represents \(=\text{CH}\) (out-of-plane bending) of cis-1,4-polyisoprene (natural rubber).

The precise grafting of anhydrides onto natural rubber chain can be also determined using a titration method as follows.

0.25 g NR-g-MA, NR-g-CA, or NR-g-1A, was dissolved into 25 mL p-xylene in a 250-mL Erlenmeyer flask, with stirring using magnetic bar until a homogeneous solution was obtained. The grafted rubber solution was supplemented with 1 mL distilled water and refluxed for 1 hour. The hot resulting solution was then titrated with 0.005M KOH in ethanol solution using 1% thymol blue in dimethylformamide (DMF) as an indicator. The grafting percentage of anhydrides is determined by:

\[
\text{Anhydride content (\% w)} = \frac{(v_1 - v_0) \times M \times MW \times 100}{2W \times 1000}
\]

Here, M denotes the molar concentration of KOH/ethanol solution, v\(_0\) and v denote the volumes of KOH/ethanol solution for blank and sample titrations, and W and MW denote the sample weight and molecular weight of monomer, respectively.

2.3 Adhesion properties of natural rubber grafted with acid anhydrides

In order to study the adhesion properties of these graft copolymers, solvent-based contact adhesives were formulated by varying the amount of wood resin in the range 10-40 phr (Table 1). The adhesion properties were characterized in terms of cleavage peel strength and shear strength (ASTM D3807) [8].
Table 1. Solution-based adhesive formulations based on NR-g-MA, NR-g-CCA or NR-g-ICA

| Ingredients          | Formulation (phr) |
|----------------------|-------------------|
|                      | A     | B     | C     | D     | E     |
| NR-g-CCA (%grafting=1.06) \(^a\) | 100   | 100   | 100   | 100   | 100   |
| NR-g-ICA (%grafting=4.66) \(^a\) |       |       |       |       |       |
| NR-g-MA (%grafting=5.03) \(^a\)  |       |       |       |       |       |
| 20% K-oleate         | 5     | 5     | 5     | 5     | 5     |
| Diphenylamine        | 1     | 1     | 1     | 1     | 1     |
| Toluene              | 1000  | 1000  | 1000  | 1000  | 1000  |
| Wood resin           | 0     | 10    | 20    | 30    | 40    |

\(^a\) Titration method determination

3. Results and Discussion

3.1 Synthesis and characterization of natural rubber grafted acid anhydrides

The ATR-FTIR spectra of NR-g-MA (Figure 1), NR-g-CCA (Figure 2) and NR-g-ICA (Figure 3) present two principal absorption bands, as verified in previous work \(^{2-3}\): at 838 cm\(^{-1}\), assigned to out of plane bending of =CH of cis-1,4-polyisoprene (natural rubber); and at 1785 cm\(^{-1}\) (strong peak) and 1859 cm\(^{-1}\) (weak peak) attributed to symmetric and asymmetric vibrations of C=O in a five-membered cyclic anhydride.

Figure 1. ATR-FTIR spectrum of NR-g-MA
Free-radical graft copolymerization reactions of anhydrides with natural rubber involve the allylic hydrogen atoms in natural rubber chains, and these are susceptible to abstraction by interactions with free-radicals, generating reactive sites from which copolymerization can propagate [9]. The mechanism by which natural rubber grafted acid anhydrides are formed is given in Scheme 1.
3.2 Adhesion properties of natural rubber grafted anhydrides

Figure 4 illustrates that the NR-g-MA adhesives have better cleavage peel strength than either NR-g-ICA or NR-g-CCA. The cleavage peel strength increased with wood resin content. It is clear that the maximal 298 N/in2 peel strength for NR-g-MA was obtained at 40 phr of wood resin, because NR-g-MA increased the interfacial adhesion between carboxyl groups and cellulosic plywood. This may be due to higher grafting percentage of maleic anhydride in natural rubber, relative to the other anhydrides. Therefore, natural rubber grafted by maleic anhydride had enhanced interfacial adhesion to plywood. However, the peel strength of NR-g-CCA formulation was lower than that of ungrafted natural rubber. This may due to insufficient wetting of substrate by the rubber polymer chains. Similar results have been reported earlier in the case of n-butyl acrylate and methyl methacrylate [6], and...

Scheme 1. A possible mechanism for preparation of NR-g-MA, NR-g-CCA and NR-g-ICA in the presence of benzoyl peroxide as an initiator.
grafting natural rubber with ethyl acrylate and methyl methacrylate [7]. In addition, the grafting percentage of citraconic anhydride on natural rubber was comparatively low.

Figure 5 shows that the shear strengths of these graft copolymer adhesives tended to increase with wood resin content. The NR-g-MA adhesives had better shear strengths than NR-g-ICA or NR-g-CCA. The maximal 245.7 KPa shear strength for NR-g-MA (at 5.03% grafting) was obtained with 40 phr wood resin. The lowest shear strength was found for NR-g-CCA (1.06% grafting) adhesive, and might be due to low grafting.

4.Conclusion
Natural rubber-graft-citraconic anhydride (NR-g-CCA), natural rubber-graft-itaconic anhydride (NR-g-ICA), and natural rubber-graft-maleic anhydride (NR-g-MA) were successfully prepared by graft copolymerization of natural rubber and the anhydrides in toluene, using benzoyl peroxide as the initiator. The maximum degrees of grafting were 1.06% for NR-g-CCA, 4.66% for NR-g-ICA, and 5.03% for NR-g-MA, reached using 10 phr citraconic anhydride, 10 phr of itaconic anhydride, or 8 phr of maleic anhydride, 3 phr benzoyl peroxide, at 85, 80 and 80°C for 2, 2 and 3 hrs, respectively. Solution-based wood adhesives were formulated from these copolymers, with various contents of wood resin in the range 10-40 phr. The maximal 289 N/in cleavage peel and 245.7 KPa shear strength for NR-g-MA (5.03% grafting) were obtained at 40 phr wood resin.

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References
[1] Mohapatra S and Nando G B 2013 Ind. Eng. Chem. Res. 52 5951
[2] Nakason C, Kaesaman A and Supasanthitikul P 2004 Polym. Test. 23 35
[3] Saelao L and Phinyocheep P 2005 J. Appl. Polym. Sci. 95 28
[4] Arayapranee W, Prasassarakich P and Rampel G L 2003 J. Appl. Polym. Sci. 89 63
[5] Prasassarakich P, Sintoorahat P and Wongwisetsirikul N 2001 J. Chem. Eng. 34 249
[6] Chumsamrong P and Monprasit O 2007 Suranaree J. Sci. Technol. 14 269
[7] Onyeagoro G N 2012 Acad. Res. Inter. 3 387
[8] ASTM D3807 2012 *Standard Test Method for Strength Properties of Adhesives in Cleavage Peel by Tension Loading* (Engineering Plastics-to-Engineering Plastics)

[9] Blackley D C 1997 *Polymer Latices: Science and Technology* (England: Springer) p 523