
PRELIMINARY STUDY OF EMULSION COPOLYMERIZATION OF STYRENE ON NATURAL RUBBER LATEX

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Abstract

Polystyrene-graft-natural rubber was prepared by emulsion copolymerization using potassium persulfate and sodium dodecyl sulfate as an initiator and emulsifier respectively. Ratios of monomer styrene to natural rubber were 80:20; 60:40; 50:50, and 40:60 % (v/v). Grafting efficiency could be investigated by extracting the dried sample with methyl ethyl ketone and petroleum ether and then weighting the left over dried sample. The copolymers composition of the polystyrene-graft-natural rubber was obtained using ¹H-NMR spectroscopy and the occurrence of styrene-graft-natural rubber was identified by FTIR spectroscopy.

Keywords: Graft Efficiency, natural rubber, emulsion polymerization, copolymerization.

Introduction

Natural rubber is a polymer of isoprene-most often cis-1,4-polyisoprene – with a molecular weight of 100,000 to 1,000,000. Typically, a few percent of other materials, such as proteins, fatty acids, resins and inorganic materials are also found in natural rubber [[http://en. Wikipedia](http://en.wikipedia.org)].

Natural rubber is an elastomer, an elastic hydrocarbon polymer that was originally derived from a milky colloidal suspension, or latex. It is an unsaturated elastomer with excellent physical properties includes high resilience, high strength, high elongation at breaks and good fatigue resistance. The fact that it is a renewable resource together with the good properties means that it is a very important elastomeric material. Especially with the current increasing awareness of environmental issues which has created a high level of interest in natural rubber and its derivatives as compared to its synthetic counterparts which are mostly manufactured from non renewable oil based resources [Che Man, 2006].

However, natural rubber is quite sensitive to heat and oxidation due to the presence of the double bond on its chains. These inherent drawbacks of natural rubber have limited its application in industry. In efforts to extend it's application, various methods were developed in order to modify its properties, through physical and chemical modification.

Modification of natural rubber has been performed in different ways since 1801 [George, 1999]. Some modification processes used emulsion technique to obtain the particle size of less than 0.6 micron with effective heat transfer [Charmondusit, 1998]. One of the chemical processes to modify natural rubber is graft copolymerization. Small amount of latex was put into emulsion polymerization of styrene to produce plastic [Nampitch, 2006].

Graft copolymers are important technological materials, because they can greatly influence the interfacial region in polymer blends and composites. The graft copolymerization would effectively combine the desirable properties of natural rubber with vinyl monomer in order to produce tough, hard, and impact resistant materials with easy processibility [Charmondusit, 1998].

The general structure of rubber graft copolymer can be indicated as follows :

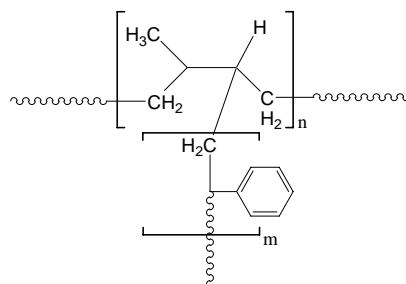


Figure 1. Structure of polystyrene grafted natural rubber

The influences of the graft copolymerization process parameters such as emulsifier concentration, initiator concentration, monomer content, and polymerization temperature on the grafting efficiency and graft ratio have been investigated [Nampitch 2006]. The purpose in this work is to prepare the graft copolymer of styrene onto natural rubber, and to study the influences of styrene monomer ratio to natural rubber to the grafting efficiency.

Experimental

Materials

Natural rubber latex was obtained from PT. Sinar Plastik and deproteinized before use. Sodium dodecyl sulfate was purchased from Aldrich. Styrene was gift from PT. Styrenemono Indonesia. Potassium persulfate and methyl ethyl ketone were purchased from EMerck. Petroleum ether was purchased from APS Ajax Finechem. Distilled water was produced at Research Center for Chemistry.

Preparation of styrene–Natural Rubber Emulsion Copolymerization

The graft copolymerization was conducted in a three necked 1000 mL round bottom reactor, equipped with thermometer, condensor and impeller. Natural rubber latex and distilled water were charged into the reactor. The dissolved oxygen present in the mixture was removed by purging nitrogen gas under continuous stirring for 30 minutes. The mixture of styrene monomer was added to the reactor dropwise. The initiator (potassium persulfate) was quickly added when the desired temperature inside the reactor was achieved. The reaction temperature was recorded immediately after the addition of initiator was completed. Then sodium dodecyl sulfate was added as emulsifier. The reaction was carried out by stirring the latex at 300 rpm for 8 hours at 60°C. Ratio of styrene monomer to natural rubber were 80:20; 60:40; 50:50, and 40:60 % (v/v). In the product system, there are three components. They are ungrafted polystyrene, ungrafted natural rubber, and grafted polystyrene-rubber. Ungrafted polystyrene and natural rubber were extracted out from product system by using methyl ethyl ketone and petroleum ether respectively. The polymer product (graft polystyrene-rubber) was recovered and dried in a vacuum oven.

Characterization of Grafted Natural Rubber

The ¹H-NMR spectroscopy measurement was carried out with the rubber samples either being dissolved or swollen in CDCl₃. ¹H-NMR spectra were obtained on a JEOL 500 spectrometer (500 MHz for ¹H). Infrared spectra of polystyrene grafted onto natural rubber were studied by FT-IR using IR Prestige-21 Shimadzu (Shimadzu Co. Japan). The graft polystyrene-rubber were mixed with KBr and pressed to a plate for measurement. All of the spectra were measured 16 scans at a resolution 4 cm⁻¹. A background spectrum containing no sample was subtracted from all spectra.

Determination of Grafting Efficiency

The free styrene homopolymer was extracted by using methyl ethyl ketone for one hour at room temperature while free natural rubber was extracted by light petroleum ether. The grafting efficiency (GE) was calculated by based on remined dried solid polymer the following equations [Charmondusit, 1998]:

$$GE = \frac{\text{Total weight of monomer grafted}}{\text{Total weight of monomer polymerized}} \times 100\%$$

Result and Discussion

The grafting of styrene monomer onto natural rubber was prepared by emulsion polymerization using sodium dodecyl sulfate and potassium persulfate as emulsifier and initiator respectively. The grafting efficiency is readily defined as the mass of the grafted polystyrene divided by total mass of styrene polymerized [Arayapranee, 2001].

Graft copolymerization of styrene onto natural rubber for 8 hours reaction time produced a grafting efficiency of 43.75%. Grafting efficiency was depended on styrene monomer to natural rubber ratio in which a maximum value was obtained at 60:40 % (v/v). When styrene monomer to

rubber ratio was added until 80:20 % (v/v), the grafting efficiency was decreased as shown in Figure 2. This indicated that the grafting reactions occur mainly on the surface of the latex particles. The addition of excess amount of styrene monomer during the graft copolymerization does not affect anymore to the grafting efficiency. Ratio of styrene monomer to natural rubber during the polymerization influenced the grafting efficiency.

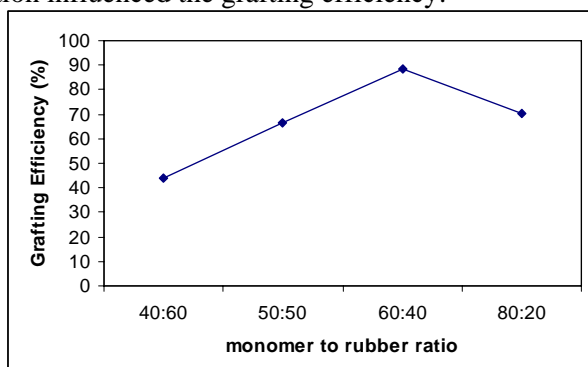


Figure 2. Effect of styrene monomer to rubber ratio on grafting efficiency

During the polymerization, samples of the polymerized latex were taken at certain time intervals for the determination of degree of conversion. The degree of conversion of monomer to polymer was determined gravimetrically and calculates as equation:

$$\text{Conversion (\%)} = (A-B)/A \times 100\%$$

Where: A is mass of monomer used for polymerization reaction (g), and B is mass of non reacted monomer (g)

The final conversion of monomers grafted to latex was varied between 73.75-88.67%. The maximum conversion styrene monomer when the monomer to rubber ratio was 60:40 % (v/v).

To confirm the occurrence of polystyrene graft natural rubber, the product was identified by FT-IR and ¹H NMR spectroscopy. Figure 3 illustrated the FT-IR spectra of the polystyrene (A), natural rubber (B), and polystyrene graft natural rubber (C).

The spectrum obtained compared favorably to those in literature [Charmondusit, 1998]. The characteristic absorption bands of R₂C=CHR of isoprene was confirmed at 839 cm⁻¹. The peaks at 3095 and 2939 cm⁻¹ was assigned to the aromatic C-H stretching ring of polystyrene. The signal at 1440 and 1364 cm⁻¹ were attributed to the aliphatic C-H stretching in natural rubber. The peak of grafted natural rubber, which was appeared at 1600 cm⁻¹ was C=C stretching of the benzene ring of styrene. This confirmed the existence of grafting polystyrene onto the natural rubber back bone.

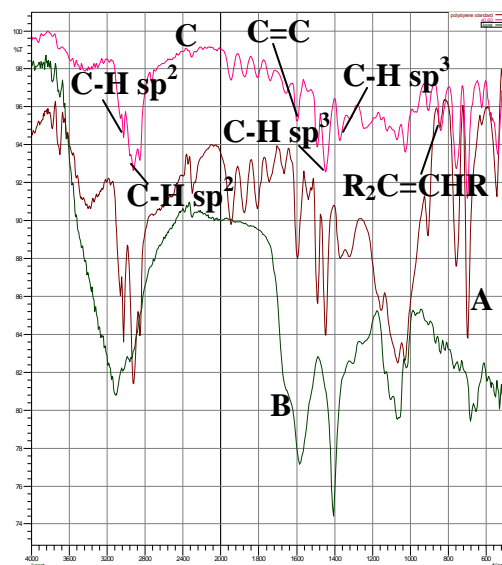


Figure 3. FTIR spectra of A. Polystyrene; B. Natural Rubber; C. Polystyrene

grafted Natural Rubber where (Styrene to Natural Rubber ratio is 40:60 % (v/v))

Qualitative analysis of the effect of rubber ratio on the polystyrene graft rubber product was conducted by using FT-IR analysis. FTIR spectrum showed that when the rubber ratio was 80:20 % (v/v), absorption peak at 1584 cm^{-1} was higher than ratio 50:50 and 40:60 % (v/v). This data showed that increasing of rubber ratio will affect the increasing of grafting.

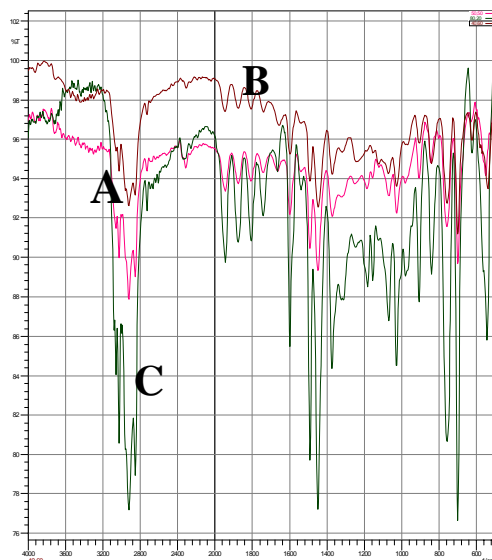


Figure 4. FTIR spectrum of polystyrene graft natural rubber

- A. Styrene to natural rubber ratio 50:50 % (v/v)
- B. Styrene to natural rubber ratio 40:60 % (v/v)
- C. Styrene to natural rubber ratio 80:20 % (v/v)

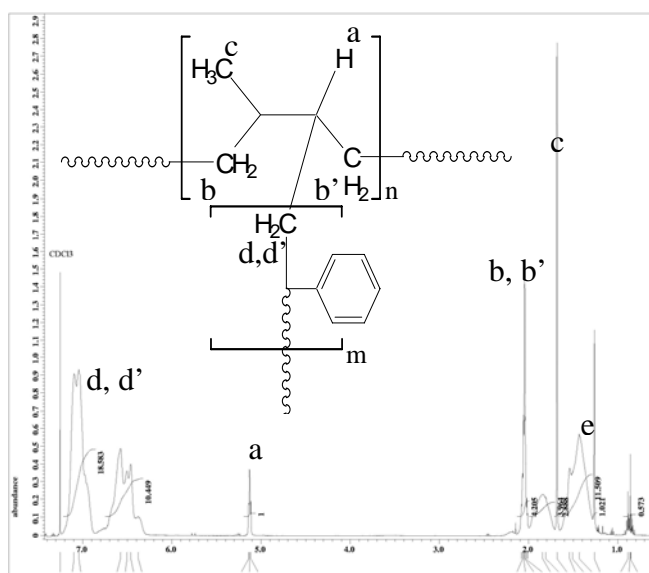


Figure 5. ^1H NMR Spectrum of polystyrene grafted natural rubber (Styrene to Natural Rubber ratio is 40:60 % (v/v))

The copolymer composition of grafted natural rubber was determined by ^1H NMR. The grafted natural rubber samples were dissolved with CDCl_3 . The ^1H NMR spectrum of polystyrene graft natural rubber appears the unsaturated methyne proton (a) of the natural rubber shows resonance at 5.15 ppm, the peak at 2.1 ppm shows the methylene protons (b,b') and than the peak at 1.7 ppm shows resonance of the methyl proton (c). The grafting of styrene onto natural rubber appeared as

peaks of phenyl group (d, d') of polystyrene, which were observed at 7.1 and 7.3 ppm and appear a new proton peak at 1.26 ppm (e). Compared to the ^1H NMR spectra of unmodified natural rubber [2], the peak of grafted natural rubber in 5.15 ppm was still exist, although slightly weakened. This peak that still occurs in grafted natural rubber showed that the grafting was not done completely. This was confirmed by the small grafting efficiency (43.75%) of the sample from styrene to natural rubber ratio of 40:60% (v/v).

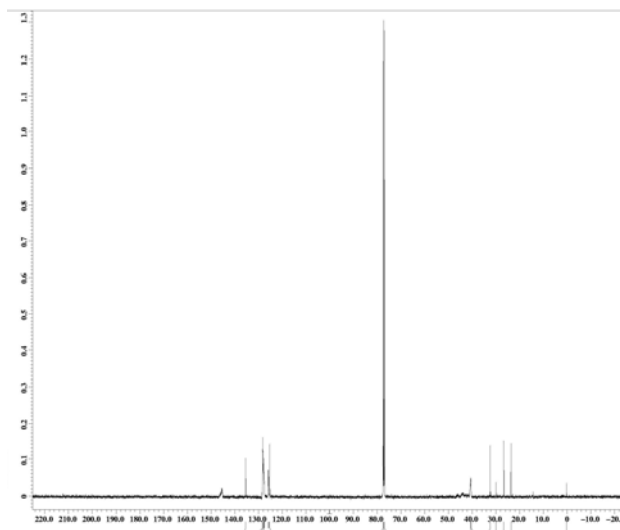


Figure 5. ^{13}C NMR Spectrum of polystyrene grafted natural rubber

Figure 5 illustrated the ^{13}C NMR spectrum of polystyrene grafted natural rubber. Exhibits the peaks at 146.02, 135.29, 128.22 and 40.53 ppm for polystyrene and the peak at 128.13, 40.53, 32.28, 26.58 and 23.61 ppm for natural rubber. This confirms the occurrence of grafting of polystyrene onto natural rubber backbone

Conclusion

Graft copolymerization of styrene onto natural rubber using potassium persulfate as initiator and sodium dodecyl sulfate as emulsifier was prepared with more than 88.67% conversion at 8 hours reaction time.

Grafting efficiency could be investigated by extracted the dried samples with methyl ethyl ketone and petroleum respectively. Grafting efficiency was depended on styrene monomer to natural rubber ratio in which a maximum value was obtained at 60:40 % (v/v).

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References

- Arayapranee, W. et al. Synthesis of Graft Copolymers from Natural Rubber using cumene hydroperoxide redox initiator. *J.Applied Polychem.Sci.* Vol 83:2993-3001 (2001).
- Che Man, S.H, Hashim, S.A, and Akil, Md, H. Preparation and characterization of styrene-methyl methacrylate in deproteinized natural rubber latex. VIth National Symposium on Polymeric Materials 2006, 13-14 December 2006, Subang Jaya, Malaysia.
- Charmondusit, K. Kiatkamjornwong, S and Prasassarakich, P. Grafting of Methyl Methacrylate and Styrene onto Natural Rubber. *J. Sci. Chula. Univ.*, Vol. 23, No. 2 (1998).
- George, F.B and P.M. Swift. The polymerization of vinyl monomers in natural rubber latex. *Journal Applied Chemical*, Vol 5: 609-616.

http://en.wikipedia.org/wiki/Natural_rubber

Nampitch, T and Vatanatham, T. Grafting Efficiency of Emulsion Copolymerization of Styrene on Natural Rubber Latex. Technology and Innovation for Sustainable Development Conference, Faculty of Engineering, Khon Kaen University, Thailand, 2006.