Grafting of Maleic Anhydride onto Cyclized Natural Rubber by Reactive Processing: the Effect of Maleic Anhydride Concentrations

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Abstract
Grafting of Maleic Anhydride onto Cyclized Natural Rubber has been performed in the Internal Mixer at 150°C and 80 rpm. The grafted product were analysed by Fourier Transformed Infra Red to determine the presence of Maleic Anhydride onto Cyclized Natural Rubber and Differential Scanning Chalorimetry and Thermogravimetric Analysis to investigated their thermal properties. Fourier Transformed Infra Red spectra confirmed that the grafted product accured by appearance of characteristic band at 1720 cm^{-1}. The higher concentration of Maleic Anhydride reacted the higher of grafting degree of Maleic Anhydride by means of carbonyl index. Futhermore, the glass transition temperature values increase with increasing the grafting degree of Maleic Anhydride and Thermogravimetric Analysis thermogram showed the thermal properties of grafted product did not change significantly compared with the Cyclized Natural Rubber blank.

Keywords: grafting, cyclized natural rubber, reactive processing, maleic anhydride

1. Introduction

Chemical modification by grafting of functional group onto polymers have been widely used to obtain the expected specifications product. Maleic Anhydride (MA) is one of the most common monomers in the polymer modification. Chemical structure of this monomer can be used in grafting onto synthetic and natural polymers. Grafting of MA onto various polyolefins and rubbers and preparation of high performance engineering materials and nanocomposites by using reactive extruder systems have been significantly developed, some results of which are employed in commercial applications (S. Cimmino et al, 1986).

Grafting of MA onto non-polar backbone of polyolefins and rubbers has overcome the disadvantage of low surface energy of these polymers, improving their surface hydrophilicity for the benefit of printing and coating applications, and adhesion with polar polymers, metal, and glass fibers Maleated polymer is also used as compatibleser in polymer blends (Y. Kayano, H. Et al, 1998; Fenouillot F. Et al, 2007; Zakir M. O. Rzayev, 2011).

Grafting with reactive processes in the melt phase using an extruder or an internal mixer has been developed by many researchers on grafting AM onto polypropylene (S. N. Sathe et al 1994; S. H. P. Bettini and J. A. M. Agnelli, 1999; J. Cha, J. And L. White, 2001; Jaehyug Cha dan James L. White, 2001; Yılser Guldogan et al, 2004; B. M. Dorscht and C. Tzoganakis, 2003; Eddyanto, 2007), polyethilene (W. Heinen et al, 1998; N. G. Gaylord and R. Mehta, 1988) and natural rubber (Nakason,C. A. Et al, 2001).

Cyclized natural rubber (CNR) is a product modification that obtained by treatment of natural rubber with strong acids (Mirzatheri, M., 2000). In these reactions, the rubber loses its elasticity properties and turns into a hard and brittle material. CNR has a weak adhesion properties with the polar surface (Riyajan, S., Sakdapipanich, J.T., 2006). To improve the adhesion properties of CNR and its stability it is necessary to perform chemical modification of the structure so that the product can be used in the wider field applications.

Research on grafting of MA onto CNR in the melt phase has not been reported so far. Grafting MA was intended to increase the polarity of the CNR. In this paper we reported the grafting of MA onto CNR in the melt phase. In our work, the grafting reactions were carried out in an Internal Mixer. The amount of reacted MA were determined by means of Fourier Transformed Infra Red (FTIR) spectroscopy.

2. Experimental

2.1 Materials and Methods

CNR used was the commercial grade, Resiprena 35, manufactured by PT Industi Karet Nusantara (Nusantara Rubber Industry), Medan, Indonesia. MA used to prepare the maleated Cyclized natural rubber was manufactured by Riedel-deHaen, Seelze, Germany. For the determination of the grafting degree of maleated Cyclized natural rubber used in this work, different reactants were used toluene, aceton were acquired from Merck, Germany Scharlau (Barcelona, Spain), used without any prior purification.

2.2 Grafting Procedure

The grafting of MA onto CNR was carried out in an internal mixer, Brabender Plasticorder PLE 331 (Duisberg, Germany) type batch mixer. The amount of 30 g CNR loaded into the chamber slowly. The internal mixer was then used to melted CNR at 150 ^{o}C with a rotor speed of 80 rpm for 4 minutes. A predetermined quantity of MA was then incorporated into the internal mixer. The mixing was continued for 8 min and the process was then stopped by pressing the STOP button. Furthermore, in hot conditions the product quickly removed from the chamber and the product was then granulated. Various concentrations of MA (i.e., 0, 2, 4, 8 and 16 phr) were each used to prepare the maleated cyclized natural rubber (MCNR) in this work.

2.3 Purification of grafted pruducts

The amount of 1.0 g crude blend product was first dissolved in 50 ml of toluene. The mixture was heated at 60 ^{o}C under reflux condition to complete the solubility. The solid undissolved content was separated out by filtration. Then the product solution was added slowly into the excess acetone to precipitate the grafted product. The solid product obtained was washed with acetone. The product was dried in a vacuum oven at 120 ^{o}C for 24 h. The dried and purified grafted product stored in desiccator.

2.4 Characterizations

2.4.1 Fourier Transformed-Infra Red (FT-IR)

The dried and purified grafted product molded into tablets with KBr powder. The Fourier Transformed Infra Red spectra were determined on a GALAXY 5000 Fourier Transformed Infra Red Spectrometer.

2.4.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed with a TA INSTRUMENTS Q2000 thermal analyzer in nitrogen atmosphere. Samples were heated from 50 to 120°C at a heating rate of 10°C min^{-1} and then cooled at the same rate. Thermal properties, such as glass transition temperature was determined by used a Thermal Analysis Universal Software.

2.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was performed with a Mettler Toledo TGA850 thermal analyzer in nitrogen atmosphere. Samples were heated from 50 to 650^{o}C at a heating rate of 10^{o}C min^{-1}.

3. Result and Discussions

3.1. Fourier Transformed-Infra Red (FT-IR)

To investigate the effect of the MA concentration, this research performed with various concentrations of MA: 0, 2, 4, 8 and 16 phr. By using Microsoft EXCELL software the FT-IR spectra of grafted products with various concentrations of MA is shown in Figure 1. In Figure 1 it can be seen that the grafting reaction MA onto CNR is successful produce grafted product (MA-g-CNR). It is confirmed on the appearance of the absorption peak at the wave number 1720 cm^{-1} which is a typical absorption of carbonyl groups (C = O) of MA molecules (S. H. P. Bettini and Agnelli, 1999; Demin Jia et al., 2000; C. Nakason et al., 2004 and Eddiyanto, 2007).

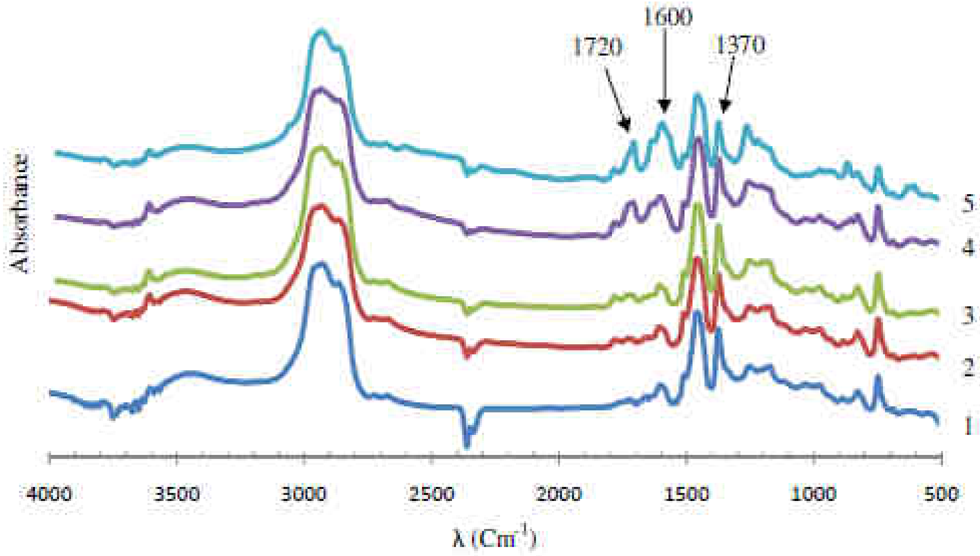

Figure 1. Overlay FT-IR spectra grafted CNR, without addition MA/blank (1), with addition MA 2 phr (2), 4 phr (3), 8 phr (4) and 16 phr (5).

Furthermore, by using OMNIC software can be determined a peak area absorption at 1720 cm^{-1} for each product of MA concentrations. Then based on the peak area can be determined Carbonyl Index (CI) for each FT-IR spectra were generated. Carbonyl Index is a peak area at 1720 cm^{-1} (typical carbonyl absorption) compared with peak reference. Carbonyl Index can be determined by using the equation (1).

$$CI = \frac{A_{1720}}{A_{1370}} \qquad (1)$$

where: A_{1720} is the absorbance at 1720 cm-1, characteristic of carbonyls from cyclic anhydrides with a five-member ring; and A_{1370} is the absorbance at 1370 cm-1, characteristic of CH3 groups, proportional to the amount of CNR

The peak reference is the absorption peak that is always appeare and theoretically peak area remained for all samples of research design. In this study a peak reference was used as the peak absorption at 1370 cm^{-1} which is a typical absorption -CH3. Theoretically -CH3 in the CNR structure did not change with treatment in this study.

Carbonyl index of all grafted product with variation of MA concentration as shown in Figure 2. In Figure 2 can be seen that with increasing MA concentrations the carbonyl index is increased.

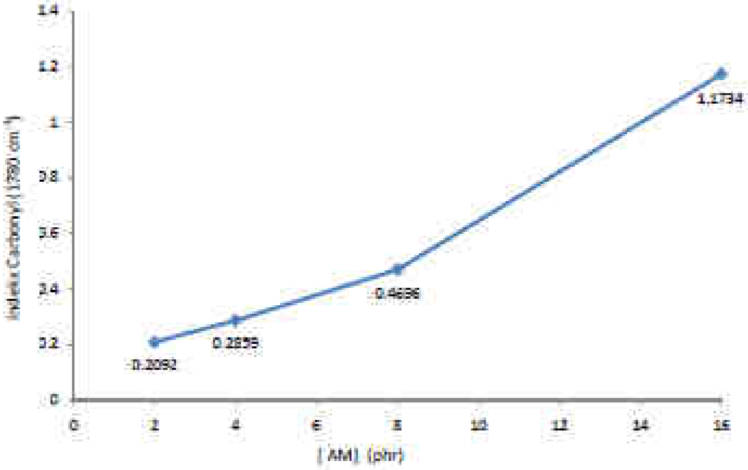

Figure 2. Carbonyl Index of grafted product CNR with variations of MA consentration.

Based on the carbonyl index at Figure 2, it can be seen that the higher MA concentration reacted, the more MA grafted on CNR. Increasing in MA concentrations will increase the number of MA molecules reacted, increasing the contact MA with makroradikal, further increase the amount of MA that reacts to form a grafted product.

Some researchers have reported that with increasing MA concentrations, it will increase the percentage of AM that grafted on the polymer, namely: polypropilena (S. H. P. Bettini and J. A. M. Aquelli, 1999), natural rubber (Nakason C. et al., 2004).

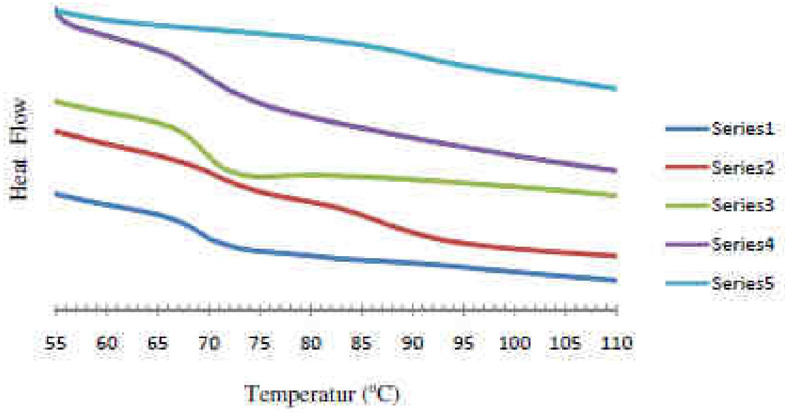

Figure 3. Overlay DSC Thermogram grafted product, without addition of AM (1), the addition of MA 2 phr (2), 4 phr (3), 8 phr (4) and 16 phr (5).

The overlay thermogram grafted product of CNR and MA can be viewed as in Figure 3. The glass transition temperature (Tg) has a tendency to increase with the grafting MA onto CNR. The glass transition temperature graft products increased compared to CNR blank. Increased the MA concentrations to increase the glass temperature (Tg) of grafted products. It also shows that there has been grafting maleic groups in CNR. The more MA groups grafted onto CNR then the product becomes more bulky or rigid, polar and increasing the mass of the molecule.

The glass transition temperature (Tg) is also increased with the grafting MA onto CNR. The glass transition temperature of the grafted product increased compared with CNR blank, be increased from 69oC 73oC. It also shows that there has been grafting of MA onto CNR. The more MA grafted onto CNR then the grafted product becomes more bulky, rigid, polar and increasing the mass of the molecule.

The glass transition temperature (Tg) is the temperature at which the amorphous polymer release properties of the glass. When the polymer is heated, the kinetic energy of the molecules increases, but the motion is still limited to short regions of vibration and rotation along the polymer continuously able to maintain the structure of the glass. Thus Tg is a function of rotational freedom, anything that limits the rotation should raise the Tg. The more bulky / bulky substituent groups attached to the polymer backbone, the freedom of rotation is reduced and becomes higher Tg.

Polarity can also affect Tg. More polar group raises Tg greater due to increased dipole-dipole interaction. Freedom of rotation decreases with the presence of intramolecular hydrogen bonds. The bulky structure and increased polar nature and the increase in the molecular mass of a substance will increase the glass transition temperature of a substance (FW Fifield and D. Kealey, 2000 and Stevens, MR, 2001).

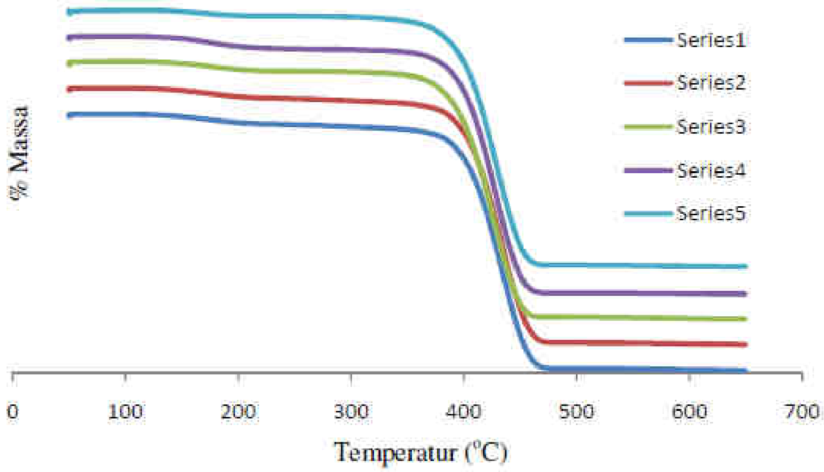

Figure 4. Overlay thermogram grafted product, without addition of AM (1), the addition of MA 2 phr (2), 4 phr (3), 8 phr (4) and 16 phr (5).

In general it can be said that the thermal properties grafted product does not change significantly compared with the blank CNR. Samples and standards were already experiencing grafting reaction in the internal mixer has the same thermal properties, no thermal properties change with the grafting reaction in the internal mixer. Likewise grafted product samples with different concentrations of AM did not show different thermal properties of the product. Different MA concentration was not significantly effect on the thermal properties of grafted CNR, as can also be seen in Figure 4.

4. Conclusions

Grafting of MA onto CNR can be done by reactive processing in the Internal Mixer at 150°C and 80 rpm. Fourier Transformed Infra Red spectra confirmed that the grafted product accured by appearance of characteristic band at 1720 cm^{-1}. The higher concentration of Maleic Anhydride reacted the higher of grafting degree of Maleic Anhydride by means of carbonyl index. The glass transition temperature values increase with increasing the grafting degree of Maleic Anhydride and the thermal properties of grafted product did not change significantly compared with the Cyclized Natural Rubber blank.

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