Addition of divinyl benzene comonomer to glycidyl methacrylate grafting to cyclic natural rubber

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Abstract. The process of thermally grafting glycidyl methacrylate (GMA) on cyclic natural rubber (CNR) compared to the addition of an initiator of organic peroxide, dicumyl peroxide (DCP) and using cross-linker divinyl benzene (DVB) has been carried out by means of melt processing. The main aims of the modified GMA grafted to CNR was to increase the polarity of the polymer to be used as a compatibiliser agent in asphalt modification. The addition of DVB comonomer in the processing was to increase the amount of GMA implanted in cyclic rubber as measured by the degree of GMA grafting. The grafting method was carried out by melting polymer (melt processing) at high temperatures in the reactor internal mixer (Brabender model). The grafting reaction took place at a temperature of 160°C, 60 rpm rotor rotation for 10 minutes of mixing. To determine the GMA grafting reaction on cyclic rubber, characterization was carried out with Fourier Transformed Infra Red (FT-IR) while the degree of GMA grafting on natural rubber was determined by acid-base titration method in organic solvents. It was found that the GMA grafting process on cyclic natural rubber could easily occur in the melting phase at high temperatures and increase with the addition of dicumyl peroxide (DCP) peroxide. Although the addition of divinyl benzene (DVB) comonomer can increase the degree of grafting of GMA on CNR, the addition of comonomer can cause high cross-linking.

1. Introduction

Cyclic Natural Rubber (CNR) which is a natural resin made from cyclisation of cis-1,4-polyisoprene has many desirable properties such as good adhesivity, and outstanding resilience but also with some shortcomings such as high sensitivity to heat and oxidation, low paintability due to still presence of double bonds in its chains and its high molecular weight. In many cases, molded product made of a polyolefin such as polyethylene, polypropylene are used in the state that the surface is painted with a paint in order to improve the beautification property, endurance and other properties. However, polyolefin is low in polarity and is poor in adhesiveness to the paint, so as to result in a problem that the painted film is easily peeled.

It is well known that a paint comprising a cyclised product of conjugated diene polymer such as polyisoprene adheres well to polyolefin (Japanese Patent Application Laid-Open (JP-A) No. 51-12827). CNR has also low solubility, mixibility, and poor compatibility unless it is lowered its
molecular weight and functionality. Therefore, the major problems encountered during paint manufacture, for example, is the poor mixibility between CNR and polyamide, polyalkyd, polycarbonate resin, and others surface. To overcome this drawback, adhesion-promoting systems, it is important to manipulate its molecular weight and functionalisation with reactive monomer such as glycidyl methacrylate (GMA).

Graft copolymerisation of GMA onto cyclic natural rubber could be an attractive technique to enhance adhesion without drastically altering the original properties of the cyclic rubber. The objective of this work is to provide a or functionalised or polar-group-containing cyclized rubber with lower molecular weight making it possible to improve remarkably its solubility, adhesiveness, and compactibility between paint ingredients either in oil or emulsion paint, and a process for producing the same.

In previous work, different chemical modifications have been performed in natural rubber (NR) in order to increase its useful properties; this includes preparation of graft copolymers of NR with various types of vinyl monomers such as maleic anhydride (MA) and glycidyl methacrylate (GMA) [1]. The copolymer products have been used extensively in the area of polymer reactive blending as compatibilisers for certain incompatible polymer pairs [2]. However, there is a limited amount of work in the literature on the grafting of GMA (I) onto cyclic natural rubber (CNR).

In this research, cyclic natural rubber was functionalised with GMA. The grafting of GMA onto the cyclic natural rubber was carried out in a melt processing system by thermal and free radical initiation. In the case of free radical initiation system, organic peroxides dicumyl peroxide (DCP) 2,4-dimethyl-2,5-bis(tert-butyl peroxy)hexane was used to initiate the reactions.

In this study, the addition of DVB comonomer was also carried out to increase the degree of grafting of GMA on cyclic natural rubber in the molten state in the internal mixer. At the end of this research, it is targeted to obtain a glycidyl methacrylate grafting product on cyclic natural rubber with increased polarity so that its adhesion to compounds and/or polar surfaces increases for use as a binder asphalt modification.

The problems in this research are: how is the role of the divinyl benzene comonomer in the grafting reaction of glycidyl methacrylate on cyclic natural rubber and what are the physico-chemical and thermal characteristics of the grafting product of glycidyl methacrylate at CNR-35. Meanwhile, the purpose of this research is to produce a grafting product of glycidyl methacrylate at CNR, which has a higher degree of grafting which will improve its adhesion to polar compounds/surfaces and understand the physico-chemical characteristics of glycidyl methacrylate grafting products on CNR.

2. Experimental methods

2.1. Materials

The grafting process was carried out in a Brabender type internal mixer reactor with a processing temperature of 160°C and its rotor rotational speed of 60 rpm for 10 minutes. The main material used was CNR-35, a cyclic natural rubber obtained from PT. IKN PTPN 3 North Sumatra. Glicidyl
methacrylate, dicumil peroxide, divinyl benzene were purchased from Sigma and Fluka and used directly without prior purification.

2.2. Preparation of CNR-g-GMA
Grafting of Glycidyl methacrylate (GMA) on cyclic natural rubber (CNR) was carried out in an internal mixer Brabender Plasticorder PLE 331 (Duisberg, Germany), either by heat initiation or free radical initiation using dicumyl peroxide. In heat-initiated grafting, GMA is mixed with cyclic natural rubber in a chamber in the absence of peroxide. In another process the addition of dicumyl peroxide as an initiator was added together with the GMA monomer after the CNR had melted in the internal chamber of the mixer. An internal mixer was used to melt 30 grams of cyclic natural rubber at a temperature of 160 °C with a rotor rotation speed of 60 rpm for 2 minutes. Then added GMA, dicumyl peroxide with a certain concentration into the chamber so that it was mixed, and left for 8 minutes. Furthermore, the mixing product was taken and granulated into a granular form.

2.3. Purification of Product
An amount of 10 g of the copolymerised CNR with GMA were put in a bottom flask containing 100 mL of xylene and then heated to 135°C upto all the products were completely dissolved. The undissolved solids that are still present are separated by filtration. Then the solution of this product is added slowly to the acetone to form a precipitate. The precipitated product was then separated from means of filtration. The precipitated product was rinsed by pouring acetone for three times and then dried in an oven at 80°C for 24 hours.

2.4. Characterisation of CNR-g-GMA Product By FTIR
The entire modified polymer samples (purified and unpurified) were also characterised by Fourier Transform Infrared (FTIR) analysis. The modified CNR were made into thin films. A Perkin Elmer Spectrum-1 FTIR spectrometers were used to analyse the rubber films with spectra obtained over the range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) for 64 scans with a resolution of 4 cm\(^{-1}\). Semi quantitative analysis of the extent of grafting was also obtained from IR absorption area ratio of a characteristic group peak (e.g. carbonyl peak of GMA) relative to a polymer reference peak (used as internal standard) in order to eliminate experimental error due to variation in film thickness. In the FTIR instrument systems, it has been equipped with a menu called ‘normalised scale’ in data processing whose function was to normalise the absorbance measurement or absorbance subtraction in order to eliminate the problem of differences in thickness.

2.5. Determination of GMA on CNR by Titration
An acid-base, non-aqueous back titration method was established to determine the grafting degree of GMA [3]. A modified procedure of the literature employing trichloro acetic acid (TCA)-xylene method was used in this work to determine the epoxy content in CNR-g-GMA as follows: 1 g of the purified reaction product (CNR-g-GMA) was dissolved in 100 ml of hot xylene (120-130°C) in a two-neck flask, connected to a condenser and maintained under nitrogen atmosphere. After the CNR-g-GMA had completely dissolved (15-30 min) the condenser was removed. The flask was stoppered and placed in an oil bath maintained at lower (stable) temperature of 105-110°C. It was very important to keep the system at this temperature (thermometer was placed in the oil bath) before addition of 5 ml (excess) of 0.3 N trichloro acetic acid (TCA) and the reaction was allowed to continue for 90 min in order to achieve complete ring opening of the epoxy group by its reaction with the acid. The hot solution was then titrated with 0.1 N KOH (standard solution) in methanol. In the presence of indicator (five drops of 1 % w/v phenolphthalin in ethanol), endpoint was reached when the colour (pink) had formed and remains for at least 30 seconds.
3. Results and Discussion

3.1. Result
Cyclic natural rubber (CNR) was a modified natural rubber product by cyclisation in batch reaktor with phenol and phosphor pentoxide (P₂O₅) as solvent and catalyst, respectively [4].

![Molecular structure and appearance of SIR-20 and CNR](image)

The use of infrared spectroscopy (FTIR) in polymer research includes two aspects, namely qualitative aspects and quantitative aspects. This study emphasizes the qualitative aspect because it is in the form of determining the structure by observing the typical frequency or wavelength of the functional group FTIR spectra obtained by comparing the spectra of pure cyclic rubber processed at high temperatures with the spectra of a mixture of cyclic rubber mixed with glycidyl methacrylate without and with dicumyl peroxide. In addition, divinyl benzene comonomer was added as a comonomer in the grafting reaction of CNR-GMA-DCP.

The results of FTIR spectra show that there has been an interaction between CNR and GMA which was processed at high temperature. The presence of GMA in the CNR was indicated by the appearance of a specific peak at a wavelength of 1718 cm⁻¹ (Figure-2). The absorbance area in the CNR sample spectra with GMA processed in the presence of DCP shows a wider peak. The presence of DVB in the CNR-GMA-DCP grafting process showed a sharper and wider carbonyl peak. Figure 2 shows the comparison of the FTIR spectra of the different composition of grafting mixtures. Table 1 shows their FTIR spectra of different composition and list of their infrared assignment.

From the titration results, the degree of grafting of GMA on CNR can be seen in Table 2. The thermal process shows that GMA was easily grafted on CNR. However, the degree of GMA grafting on CNR with thermal initiation was still low at 0.57%. The use of peroxide initiator increased the degree of grafting more than twofold to 1.85%. Furthermore, GMA grafting process on CNR with DCP initiator and the addition of 0.5 weight ratio divinyl benzene (DVB) to GMA showed an increase in grafting degree to 2.27%. However, the presence of DVB can increase the cross-linking reaction which increases in the cyclic rubber chain which is indicated by the grafting product into powder.
Figure 3. Spectra of CNR thin film processed at high temperature, CNR/GMA (thermal initiation), CNR/GMA/DCP, CNR/GMA/DCP/DVB system.

Table 1. The intensity of peaks absorbance of each wave number and its assignment of FTIR spectra of CNR and CNR-g-GMA.

| Name            | Peak (cm⁻¹) | Intensity | Assignment               |
|-----------------|-------------|-----------|--------------------------|
| CNR             | 3669        | strong    | ν(O-H)                   |
| and             | 2918        | very strong | ν(CH₂, CH₃) sym. and asym |
| CNR-g-GMA       | 1718        | medium    | ν(C=O)                   |
|                 | 1606        | medium    | ν(C=C)                   |
|                 | 1452        | very strong | δ(CH₃), ν(CH₃ ), δ(CH₂)   |
|                 | 1374        | strong    | δ(CH₂)                   |
|                 | 1309        | medium    | τ(CH₂)                   |
|                 | 1226        | medium    | τ(CH)                    |
|                 | 1127        | medium    | ν(C-C)cis                |
|                 | 1053        | medium    | τ(CH₂)                   |
|                 | 889         | medium    | ν(CH), ν(CH=CH₃)          |
|                 | 745         | medium    | τ(CH₂)                   |

Tabel 2. Volume (ml) Titration and Grafting Degree GMA on CNR

| Sample                  | CNR-g-GMA (g) | Volume KOH (mL) | Grafting Degree of GMA on CNR (%) |
|-------------------------|---------------|-----------------|---------------------------------|
| CNR                     | 1.09          | 0.3             | 0                               |
| CNR-GMATHermal          | 1.03          | 0.7             | 0.57                            |
| CNR-GMA-DCP             | 1.05          | 1.6             | 1.85                            |
| CNR-GMA-DCP-DVB         | 1.07          | 1.9             | 2.27                            |
3.2. Discussion

In the preparation of the GMA grafted-CNR, initiation of grafting reaction is due to free radicals produced by the interaction of peroxide, GMA and CNR. In the CNR/GMA/T-101 system, for example, the peroxide DCP decomposes to yield alkoxyl and alkyl radicals (RO·) formed in the ‘molten’ CNR system, which might interact with the monomer GMA or the rubber molecule producing a macroradical that initiates grafting. Figure 4 gives a proposed mechanism for the graft copolymerization of GMA onto CNR via the free-radical initiation.

The success of a typical melt grafting experiment is usually measured in terms of the grafting yield dictated by the fraction of the monomer that becomes grafted onto the polymer backbone versus that which either remains unchanged or is consumed in side reactions such as homopolymerisation. In the experiments examined here, the results clearly showed that grafting glycidyl methacrylate (GMA) on cyclic natural rubber (CNR) can be achieved by both thermal and peroxide initiation in the melt, though to varying degrees, the grafting efficiency of GMA by thermal initiation was quite low compared to that achieved by free radical initiation. However, if one compares this with a typical reaction of grafted GMA on polyolefins [5, 6], then the observed grafting degree of GMA on NR by thermal initiation becomes quite meaningful.

Hu (1998) proposed that the styrene plays a role as a charge transfer complex with MA [7]. The styrene can react first with the rubber macroradical generated from the reaction of BPO initiator, followed by the reaction with MA molecules, leading to improvement of the grafting efficiency of MA. However, in this work, an attempt to add a reactive coagent, e.g. DVB resulted in excessive crosslinking because of the very high reactivity of the coagent and C=C from the cyclic natural rubber (CNR). Therefore, the use of any multifunctional and highly reactive coagent such as TRIS or DVB could not be applied successfully in the grafting of GMA onto cyclic natural rubber.

4. Conclusion

Modification of cyclic natural rubber occured by grafting process of a reactive monomer, glycidyl methacrylate (GMA) on CNR by thermal and the presence of dicumyl peroxide. The grafted GMA on CNR was relatively low due to a competitive reaction. The use of DVB comonomer in the
CNR/GMA/peroxide system has succeeded in increasing the degree of grafting higher than without the use of DVB comonomer.

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