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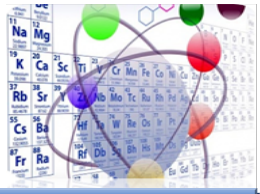

Study of Thermal Oxidative Degradation of Asphalt Modified with Cyclic Natural Rubber-g-Maleic Anhydride Reactive Polymer

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ABSTRACT

This study aims to investigate the effect of asphalt modification using a reactive polymer in the form of cyclic natural rubber grafted with maleic anhydride (CNR-g-MA) on the thermal oxidation resistance of asphalt. The modification was carried out ex situ by mixing the synthesized polymer with asphalt after the grafting process. CNR-g-MA was synthesized through a grafting reaction of maleic anhydride onto cyclic natural rubber using benzoyl peroxide as a radical initiator. The grafted product was characterized using Fourier Transform Infrared (FTIR) spectroscopy to identify functional groups and confirm the success of the grafting process. The modified asphalt was further analyzed using FTIR and Thermogravimetric Analysis (TGA) to evaluate changes in chemical structure and thermal stability. FTIR spectra showed characteristic absorption peaks corresponding to carbonyl and ester groups, indicating successful grafting. TGA results revealed that asphalt modified with CNR-g-MA exhibited higher thermal stability compared to pure asphalt, suggesting improved resistance to thermal and oxidative degradation.

Keywords: Modified Asphalt, Cyclic Natural Rubber, Maleic Anhydride, FTIR, TGA, Grafting, Thermal Oxidation.

1. INTRODUCTION

Asphalt is a complex hydrocarbon material that is viscoelastic and is widely used as a binding material in road pavement construction. The mechanical properties of asphalt are greatly influenced by temperature and oxidative aging processes over the service life. Exposure to heat, oxygen, and ultraviolet radiation can cause oxidation that alters the chemical structure of asphalt thereby increasing its rigidity and decreasing its elasticity. This process results in asphalt hardening which can ultimately cause damage such as fatigue cracking and permanent deformation of the road pavement. Therefore, increasing the resistance of asphalt to oxidative degradation is one of the important focuses in the development of modern pavement materials.[1]

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One of the approaches that is widely used to improve asphalt performance is through modifications using polymers. The addition of polymers can improve viscoelastic properties, thermal stability, as well as resistance to permanent deformation and cracking due to repetitive traffic loads. Previous research has shown that the use of elastomer polymers is able to increase complex modulus and resistance to rutting at high temperatures compared to conventional asphalt.[2] In addition, modification of asphalt with natural rubber is also reported to be able to increase the elasticity and flexibility of the asphalt mixture so that the service life of road pavement becomes longer.[3] However, the direct use of natural rubber has limited compatibility with asphalt due to the difference in polarity between the two materials.[4]

To overcome these compatibility problems, natural rubber can be chemically modified through a grafting process with reactive monomers such as maleic anhydride. This process produces modified natural rubber that has a polar group so that it is able to increase chemical interactions with asphalt components. maleic anhydride are monomers that are widely used in grafting reactions because they have reactive anhydride groups and are able to form bonds with polymer chains through free radical mechanisms.[5] The presence of anhydride groups in grafted polymers can improve adhesion, compatibility, and stability of polymer–asphalt mixtures.[6]

One form of potential natural rubber modification is cyclic natural rubber (CNR). The cyclic structure of CNR provides better thermal stability than linear natural rubber, so it has the potential to be used as a material for asphalt modification. Previous research has shown that the combination of the elastomer structure of natural rubber and the polar group of maleic anhydride can produce reactive polymers that are able to improve the chemical stability and oxidative resistance of polymer–asphalt systems.[7] However, studies on the use of CNR grafted with maleic anhydride (CNR-g-MA) as asphalt modifiers are still relatively limited, especially related to its effect on the thermal oxidation degradation of asphalt.

Based on this background, this study aims to study the effect of asphalt modification using CNR-g-MA reactive polymer on the thermal oxidation resistance of asphalt. CNR-g-MA is synthesized through a grafting reaction between cyclic natural rubber and maleic anhydride using benzoyl peroxide as a free radical initiator. The grafted products are then mixed with asphalt ex situ to produce modified asphalt. Characterization was performed using Fourier Transform Infrared (FTIR) spectroscopy to identify changes in function groups as well as Thermogravimetric Analysis (TGA) to evaluate the thermal stability of the material. The mechanism of free radical reaction includes the initiation stage by benzoyl peroxide, propagation through the formation of radicals in the CNR chain, as well as termination resulting in grafted polymers containing maleic anhydride groups. The existence of the polar group is expected to increase the interaction between polymers and the asphalt matrix so as to produce modified asphalt materials with better thermal oxidation resistance than pure asphalt.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The equipment used included Aspal PEN 60/70 from PT. Pertamina, Cyclic Natural Rubber (CNR), Maleic Anhydride (MA)(CHO), Benzoyl Peroxide (BPO)(p.a. Merck) from CV Rudang Jaya, Solvent in the form of n-hexane (p.a. Merck) and Chloroform Solvents(p.a. Merck) from CV. Rudang Jaya.

The tools used include Stand, Three-neck flask (pyrex), Stirring Stick, Beaker Glass (pyrex), magnetic stirring with hot plate, magnetic stirrer, thermometer (Fisher), measuring cup condensor, Erlenmeyer, watch glass, filter paper, glass funnel, spatula, oven, aluminum foil, vacuum pump, storage stability container and FTIR spectrophotometer (*nicolet/Perkin Elmer*).

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2.2. Research Procedure

A. Extraction Process

At this stage, the asphalt extraction process is carried out using a hexane solvent. The asphalt is weighed and then mixed with n-hexane solvent using a temperature of 150°C for 24 hours and with a stirring speed of 300 rpm After stirring, the solution was allowed to settle for 10 minutes to form deposits and solutions. Then the sediment formed is put into the oven at a temperature of 150°C for 24 hours and then cooled, while the solution is heated in an oven with a temperature of 135°C for 4 hours. The results obtained were then carried out FTIR test with the aim of finding out the difference with pure asphalt.[8]

B. Preparation CNR-g-MA

Put 5 grams; 10 grams and 20 grams of samples and 100 mL. Chloroform into a three-neck flask while heated and stirred with a magnetic stirrer. Then maleic anhydride and benzoyl peroxide were added, three variations of maleic anhydride (MA) were used, namely 0.25 grams, 1 gram, 2 grams with benzoyl peroxide (BPO) concentrations of 0.0688 grams, 0.275 grams; 0.069 grams of MA mass Mixing of MA and BPO into CNR was carried out in reflux at 150°C for 90 minutes. Then, reprecipitation is carried out using methanol so that sediment is obtained. The sediment is then dried in the oven at 100°C for 24 hours, then analyzed using FTIR.[6]

C. Cyclic Natural Rubber Asphalt and Rubber Mixing

Furthermore, the manufacture of modified asphalt was carried out. The modified asphalt is designed by mixing 100 g of 60-70 pen asphalt and 1 g of maleic anhydride grafted natural rubber into a beaker containing xylene solution, then heated for 30 minutes at 90°C at 180 rpm until melted and homogeneous. The result of mixing asphalt and cyclic natural rubber materials is referred to as modified asphalt. The mixture is then poured entirely into a mold that has been coated with aluminum foil and thin plates, and flattened with a hot compressor machine at 165°C. After the mixture is flattened, it is then released from the mold and ready to be cut according to the test needs. The results obtained are then mechanical tested with tensile strength test, then characterized to determine changes in their functional groups using FTIR spectroscopy, thermal analysis with TGA[9]

3. RESULTS AND DISCUSSION

3.1. Characterization FTIR CNR-g-MA

Characterization using Fourier Transform Infrared (FTIR) spectroscopy was performed to identify the success of the maleic anhydride grafting process in cyclic natural rubber (CNR). This analysis was carried out by comparing the spectra of FTIR spectrum of pure CNR with CNR that has undergone the process of maleic anhydride grafting. The main objective of this test is to identify functional group changes that indicate the formation of the CNR-g-MA polymer structure.

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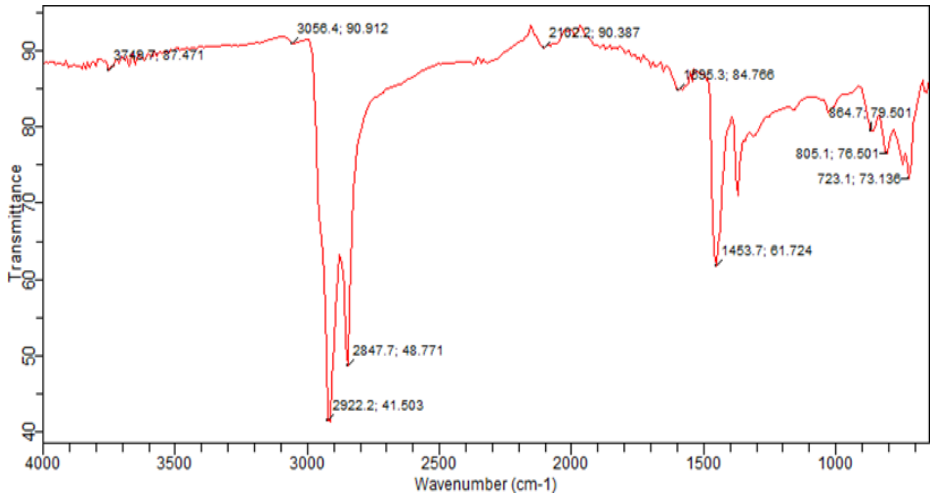

Figure 1. FTIR CNR-g-MA

The FTIR spectrum shows the presence of several characteristic absorption peaks that indicate the success of the grafting process. At wavelengths of about 2922.42 cm^{-1} and 2862.57 cm^{-1}, absorption related to the stretching of the aliphatic C–H group, which is characteristic of the hydrocarbon chain of natural rubber, was detected. In addition, the appearance of a peak at 1708.23 cm^{-1} indicates the presence of a carbonyl group (C=O) derived from maleic anhydride. This peak is an important indicator that indicates that maleic anhydride have successfully grafted onto the natural rubber polymer chain.

Other absorptions were also detected at the wave number 1655.44 cm^{-1} which indicates the presence of a C=C bond in the cyclic natural rubber structure. In addition, the appearance of peaks at 1452 cm^{-1} and 1371.66 cm^{-1} is related to the bending vibrations of the CH_2 and CH_3 groups, which suggests that the main structure of natural rubber is still maintained after the grafting process. The presence of absorption at 1213.48 cm^{-1} related to the C–O bond further strengthens the indication that the maleic anhydride group has successfully bonded to the CNR polymer chain Based on these results, it can be concluded that the process of grafting maleic anhydride in cyclic natural rubber has been successfully carried out. This success is demonstrated by the emergence of carbonyl groups and ester groups that are characteristic of maleic anhydride that are bound to the polymer structure of natural rubber.

3.2. Analysis of Asphalt Group Changes

FTIR analysis was also carried out on asphalt that has been modified with CNR-g-MA to determine changes in chemical structure due to the mixing and thermal aging process. The results of the analysis showed that in the area of wave numbers 1300–1400 cm^{-1} there was absorption related to the bending vibration of the $–CH_2$ and $–CH_3$ groups. This peak is related to the bending of the C–H bond in the asphalt hydrocarbon structure. In the asphalt aging process for 1 day, 3 days, and 5 days, no significant wave peak shifts were observed in these areas. This shows that the main structure of hydrocarbons in asphalt is relatively stable to the thermal aging process under the test conditions. This stability indicates that the addition of CNR-g-MA polymer is able to maintain the chemical structure of the asphalt during the heating process.

In addition, in an area of about 1000 cm^{-1} C–O group was identified, indicating a chemical interaction between the asphalt component and the modified polymer. This group was likely formed as a result of the interaction between the maleic anhydride group and the polar component in the asphalt during the mixing or thermal aging process. At a wave number of about 700 cm^{-1}, an absorption related to the C–H group was

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detected indicating the presence of aromatic or aliphatic structures in the asphalt. The absence of significant changes at this peak indicates that modification with CNR-g-MA did not cause major degradation of the asphalt base structure.

3.3. Thermal Stability Analysis using TGA

Thermogravimetric Analysis (TGA) was performed to evaluate the thermal stability of CNR-g-MA-modified asphalt. This method is used to observe changes in sample mass as a function of temperature during the heating process. The TGA graph shows the relationship between temperature and the percentage of remaining sample weight, so that the stages of material decomposition can be determined. In the first stage, which is in the temperature range of about 50–150°C, there is a relatively small decrease in mass, which is about 2–3% of the initial mass. This decrease is generally caused by evaporation of adsorbed water or moisture trapped in the material structure. At this stage, there is no significant peak on the DTG curve, which indicates that the evaporation process occurs gradually and does not involve significant chemical decomposition reactions.

In the next stage, the increase in temperature causes the decomposition of organic components in the asphalt material. However, asphalt modified with CNR-g-MA shows a more stable decrease in mass compared to pure asphalt. This shows that the presence of grafted polymers is able to increase the thermal stability of the asphalt system. This increase in thermal stability is suspected to be caused by the chemical interaction between the maleic anhydride group in CNR-g-MA and the polar components in asphalt, such as asphaltene and resin fractions. This interaction can form a polymer network that is more stable to high temperatures, thus being able to slow down the thermal and oxidative degradation process on asphalt.

3.4.Implication of Asphalt Modification with CNR-g-MA

Based on the results of the characterization of FTIR and TGA, it can be concluded that asphalt modification using CNR-g-MA has a positive effect on the chemical and thermal stability of the material. The presence of polar groups of anhydrous maleates increases compatibility between polymers and asphalt matrices, resulting in a more homogeneous and stable mixing system. In addition, the elastomer properties of cyclic natural rubber also play a role in increasing the flexibility of materials, thus potentially increasing asphalt's resistance to deformation and cracking during its service life. Thus, the use of CNR-g-MA as an asphalt modification material not only improves thermal stability, but also has the potential to extend the service life of road pavement through increased resistance to oxidative degradation and thermal aging.

4. CONCLUSION

The results of the FTIR analysis showed that the grafting of Maleat Anhydrous in cyclic natural rubber had been successfully carried out, which was characterized by the peak of carbonyl group (C-O) characterization at the peak of the wave with a range of 1900-1650 $^{cm-1.}$ The addition of cyclic natural rubber polymers that have been modified with Maleat Anhydrous (MA) exerts a significant effect on the thermal stability of modified asphalt. These modifications result in asphalt with better physical properties, including increased resistance to oxidation and the rate of thermal aging. This is evidenced by thermogravimetric (TGA) results that show a more stable decrease in mass at high temperatures, as well as storage stability analysis that shows an increase in asphalt resistance to phase separation.

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REFERENCES

1. Azka CN, Salimah A, Susilowati A, Handayasari I, Latifa EA, Wiyono E, et al. **(2023)**No Title. 1–236 p.
2. Airey GD. **(2004)**. Fundamental Binder and Practical Mixture Evaluation of Polymer Modified Bituminous Materials. Int J Pavement Eng. 5(3), 137–51.
3. Bahia HU, Hanson DI, Zeng M, Zhai H, Khatri MA, Anderson RM. **(2001)**. Characterization of Modified Asphalt Binders in Superpave Mix Design. 1–93 p.
4. Utami R, Suherman. **(2019)**. Temperature sensitivity effect in asphalt modification with natural rubber sir20. In: First International Conference of Construction, Infrastructure, and Materials. p. 1–6.
5. Eddiyanto, Siregar MS, Syaputra IR. **(2012)**. Grafting Maleat Anhidrat pada Karet Alam Siklis (Cyclic Natural Rubber/CNR) dengan Inisiator Dicumyl Peroksida. Agrium.17(2), 128–33.
6. Humaira T, Kurniawan B, Hasanah S, Christina E, At-Tsabiq JH. **(2022)**. Modifikasi Struktur Polistirena Menggunakan Maleat Anhidrida sebagai Pengikat Silang dan Benzoil Peroksida sebagai Inisiator. Asian J Mechatronics, Electr Eng.1(1), 25–34.
7. Hou X, Lv S, Chen Z, Xiao F. **(2018)**. Applications of Fourier Transform Infrared Spectroscopy Technologies on Asphalt Materials. Measurement [Internet].121(March), 304–16.
8. Utami HH, Yani S, Sabara Z. **(2023).** Pengaruh Proses N-Hexane Solvent Extraction pada Ekstraksi Bitumen dari Aspal Buton sebagai Bahan Baku Minyak Bumi Nonkonvensional. J Sains Teknol Lingkung.9(1), 35–43.
9. Ritonga W, Irfandi. **(2016)**. Pengaruh Karet Alam Siklik (Cyclic Natural Rubber) Terhadap Rongga Aspal Modifikasi. J Pendidik Fis Indones.12(2), 169–76.

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