Asphalt Modification with LDPE Plastic Waste Treated with Glacidyl Methacrylate and Benzoyl Peroxide Initiator

Yolandha Putri1*, Tamrin1, Darwin Yunus Nasution1

1 Yolandha Putri, Kimia, Universitas Sumatera Utara, Medan, Indonesia

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Corresponding Author: Yolandha Putri
pyolandha203@gmail.com

Abstract: The aim of this research is to determine the quality of the softening point test, penetration test and deactivation of modified asphalt from garfted LDPE plasticization waste. And for grafting treatment, use the internal mixer method where GMA and BPO are added to the grafting mixture. From the grafting results obtained, we carried out an FTIR test and identified a wave number of 1728/cm indicating the presence of the C-H or benzene functional group. This can be interpreted as a grafting process which can also be seen at the wave number 1730/cm. This can be interpreted as a grafting process from GMA to LDPE. And for the wave number at 2723/cm, there is a CH3 stretching from the LDPE chain backbone so that what is obtained is the LDPE-g-GMA spectrum. As for the TGA and DSC test results obtained, namely that in DSC the peak value of the number is at a temperature of 160.60 C and the value obtained from TGA is 373.13 C. And to find out the standard of modified asphalt from mixing asphalt with waste The value of the grafted plastic that we carried out was 65.23, for the penetration test it was 53.7 and for the deactivation test it was 55.46. This can be interpreted that all three are in accordance with the 2018 Bina Marga asphalt standards.

Keywords: Asphalt; GMA; Grafting plastic waste; LDPE

Introduction

Waste is not an ordinary problem, waste is increasing day by day with the increasing number of activities carried out by the community. Waste is a quite complicated problem from the past until now. From data from the National Waste Management Information System (SIPSN) managed by the Ministry of Environment and Forestry, it can be seen as follows.

Specifically, you can see the composition of waste based on the type of waste, including 41.4% of waste and 18.3% of plastic and 18.3% of plastic and if you look at the composition of waste based on the source of the waste, the most waste comes from household waste at 37.6%, where the data is in National Waste Management Information System. The types of plastic waste that are most often found in urban waste include Low Density Poly Ethylene (LDPE), PolyPropylene (PP), High Density Poly Ethylene (HDPE), Poly Vinyl Chloride (PVC), Poly Ethylene Terephthalate (PET), Styrofoam, etc. Plastic waste of the PP and HDPE types is most commonly found. PP is used for plastic products that have high tensile strength such as plastic bags, blisters (snack wrappers) (A. Kurniawan et al., 2020). Plastic production in the world continues to increase. In the 1950s around 1.7 million tons of plastic were produced, the number increased 200-fold to 299 million tons worldwide in 2013 million tons per year (Kik et al., 2020). It is estimated that the amount of plastic produced could increase significantly and even double in the coming years (Hesler et al., 2019). Due to this, with the large amount of waste found in Indonesia, it is necessary to pay attention to how it is managed, namely by utilizing the waste so that it does not become a pile and if it is not controlled it can have a negative impact on the surrounding community.

The construction of roads in every city in Indonesia uses a mixture of aggregate and asphalt. The durability of asphalt is greatly influenced by the presence of water, because water can loosen the bond between the...
aggregate and the asphalt. When the asphalt and aggregate bonds are loose due to water, passing vehicles will apply a load which will damage the bonds and the road surface (Ritonga, 2017). Asphalt is a black or brown colored material, if heated to a certain temperature it will become soft or liquid so that it can wrap the aggregate particles when mixing asphalt concrete on road pavement (Suprayitno & Mudjanarko, 2019). Asphalt has been widely used as a road construction material as an adhesive for sand and gravel aggregates. Although, the elasticity of the material is lower which causes repeated cracks (A. Kurniawan et al., 2020).

A large amount of waste is not disposed of in proper disposal sites, not only pollutes the environment, this waste also pollutes the sea, which causes serious environmental problems. Polyolefins, which have excellent recycling properties, can make up more than 50% of non-recyclable (high density) plastics, namely polyethylene, HDPE, low density polyethylene, LDPE and polypropylene (PP) (Aumnate et al., 2019).

One effort that can be made to increase the stability value of the asphalt mixture while reducing the asphalt content in the mixture is by adding additives to the polymer mixture. The polymer used as an asphalt mixture can come from plastic waste. The use of plastic food packaging waste in making polymer asphalt as an alternative additive to increase the stability value of the asphalt mixture. Where the polymer mixing process is carried out when the hot asphalt mixture is carried out at a temperature of 145-155°C (Hadid et al., 2020). In this research, HDPE type plastic waste will be grafted with GMA. The process of grafting MAH onto HDPE initially started in 1987, through a mixing process and then continued to be applied and developed in many polymer studies such as grafting MAH onto LDPE, combining polystyrene (PS) and chloronitrile-butadiene-styrene (Rahayu et al., 2020). In the plastics industry, the raw materials are quite diverse due to the presence of various additives, such as fillers and colorants. During the recycling and depolymerization process impurities are either degraded or carried away, producing wax of various colors, primarily brown, gray, and black with a petroleum odor. This color and odor combination greatly reduces the market potential. This technical challenge means that plastics containing contaminants causing color and odor must be overcome by purification (Yao et al., 2019). Polyethylene (PE) is a thermoplastic polymer that is widely used in several industries because of its unique properties such as good chemical resistance, good thermal properties, stability, good processability, good electrical properties and low cost (Shokri et al., 2015). Because of this, waste production in Indonesia continues to increase along with economic growth and an increase in population. One of them is plastic waste, where the annual growth reaches 14.7%. As the population increases, plastic consumption will increase, which can damage the environment and disrupt the ecosystem of living things around it. Some of the plastic waste produced is made from polymer materials such as polypropylene (PP) and polyethylene (PE) as well as polyesters such as polyethylene terephthalate (PET) which are widely used for packaging products (Hadid et al., 2020).

The advantage of this method is that the polymer can be functionalized according to the desired properties (B. Kurniawan et al., 2022). Determination of the degree of grafting or degree of grafting can be done by acid-base titration of graft polyolefin maleic anhydride (GMA) and is usually carried out in aromatic solvents such as xylene or toluene, even the titration method on suspensions of polyethylene in xylene. The solvents used are pure or saturated with water leading to quantification of the anhydride or hydrolyzed groups in their respective forms. In wet organic solvents, all cyclic anhydride functions must be opened to carboxylic acid groups. The solvent is saturated with water, or added with 200 ml of water after dissolving the hydrolysis matrix carried out by refluxing in xylene solvent within 1-1.5 hours (Sclavons et al., 2000)

**Method**

The grafting process can be carried out by mixing plastic pellets, namely LDPE with glaciyl methacrylate (GMA) and assisted by the initiator Benzoyl Peroxide (BPO). Mixing is done in the internal mixer. The first thing to do was add 31.654 grams of PS polymer to the mixing chamber after melting with a melting point of 270°C, after that followed by adding 2.04 grams of GMA after 5 minutes and finally adding 0.306 BPO after 5 minutes. Mixing was carried out at temperature 270 0 C, speed 100 rpm with a total stirring time of 15 minutes. After mixing, the material is removed and cooled. The results were washed with xylene, filtered and then scraped and carried out an FTIR test, DSC test and TGA test. Mixing Asphalt with Plastic, in the initial stage, put asphalt pen 60/70 into a stainless steel cup, then heat it for 10 minutes until it melts, then add LDPE plastic which has been filtered, stir the mixture at a speed of 45-60 minutes. The results obtained were carried out by penetration tests, softening point tests and ductility tests

**Result and Discussion**

The results and discussion of this research using DSC (Differential Scanning Calorimetry) analysis can be seen in the picture below. In this research, DSC was used to test thermal properties. DSC is an analytical technique that measures the difference in heat entering the sample and comparison as a function of temperature.
samples analyzed were dry. If the sample is wet it will interfere with the analysis by appearing undesirable thermogram peaks.

**Figure 1.** Results of DSC Analysis Characterization

Differential Scanning Calorimetry or DSC is one of a series of instrument analyzes called thermal analysis. This technique can be used to characterize the physical properties of various materials and how they change with temperature (Thomas, 2005). DSC is the final model used in quantitative studies of thermal transitions in thermals (Stevens, 2001).

Determination of melting temperature and degradation temperature using the DSC method. This aims to determine the process temperature to produce HDPE-g-GMA. The temperature requirement is that it must be done at a temperature between the melting temperature of each component and the degradation temperature. The results of the thermal analysis of the HDPE-g-GMA component can be seen in Figure 2.

The picture shows a thermogram for the initial sample which shows a peak at a temperature of 160.6°C. Where this temperature is identified as the melting temperature of the initial sample, while the enthalpy is the energy required to change the initial sample from solid to liquid. And the reaction that occurs is an endothermic reaction which is shown by a downward peak.

**Figure 2.** TGA Analysis Characterization Results

Apart from the results and discussion above, researchers also carried out characterization tests with TGA on a type of HDPE plastic waste grafted by GMA. TGA functions to measure changes in the weight of a substance during the heating and cooling process of a sample. Where you can see the graphic results obtained in the TGA characterization test as Figure 3.

In the picture, it can be seen in the red line that the temperature peak is at 249.7 Cel and it can also be interpreted that the graphic model in the picture above means that the initial mass is lost quickly with the drying characteristics. As for the blue graph, at a temperature of 132.3 Cel there is decomposition of the mass contained in it and with the graphic model above it can be interpreted that there is decomposition of mass on the surface. And as for the black graph, the peak temperature decomposition is at a temperature of 3731.3 Cel and with this graphic model, this means that the oxidation products are decomposed again at a higher temperature, and this is very rare.

Most organic polymers cannot be mixed with each other, so many new products involve melting polymer mixtures to achieve better properties that are not found in a single polymer, namely a compatibilizer (Fink, 2017). Compatibilizers act through reactive processes, such as grafting techniques or through hydrogen bonds based on the polarity of a material. Compatibilizers also play a role in stabilizing different mixtures such as water-oil or mixtures that have different polarities (Stevens, 2001). Grafting reactions usually occur at locations that can accept transfer reactions, such as on the carbons adjacent to the double bond or on the carbon adjacent to the carbonyl group (Stevens, 2007).

FT-IR analysis was carried out to determine changes in functional groups that occurred in LDPE before and after grafting. As well as comparing the differences in grafting results with LDPE. The FT-IR spectrum results can be seen at Figure 3.

**Figure 3.** Results Of FTIR

The success of grafting GMA monomer with LDPE chains was demonstrated by the formation products;
LDEP-g-GMA can be identified from the emergence of new absorption peaks and friction of absorption peaks in the FTIR spectrum. Characterization can be classified into three absorptions. The first area is called the C-Cl Stretch area with a length of 600-700 cm. the second area is called the C-C Stretch area with a wavelength of 900-1200/cm and the third area is C-H with a wavelength of 1250-2970/cm. (Bodirlau & Teaca, 2009).

Based on the FTIR spectrum above, it shows the absorption peak in the HDPE-R and LDPE-g-GMA samples which have characteristic absorption in the spectrum showing the presence of a C-H stretch functional group with a wavelength of 2970/cm, there is also a CH2 functional group with strong stretching vibrations with a wavelength 690/cm attributed to LDPE.

The peak wave number of 1728/cm is the CH functional group on benzene. According to Jazani (2017), the peak at wave number around 1730 is the carbonyl group from GMA grafted on LDEP. Where this can be seen in the wave number at 2723/cm which is the CH3 stretching of the LDPE chain backbone found in the LDEP-g-GMA spectrum. For asphalt test results with penetration values, asphalt can be identified as a parameter for classifying the quality of asphalt in commercialization and the quality of asphalt as a road hardener. The results of penetration testing can be seen in the Table 1.

| Table 1. Result Testing Penetration |
|--------------------------------------------------|------------------|--------------|--------------|
| Testing                                      | Testing Methods  | Observation Result |
| Methods                                      | Asphalt Blanco   | Elastomer Asphalt | Modified Asphalt |
| Penetration                                  | SNI 2434:2011    | 60-70          | Min. 40      | 53.7 cm     |

Based on the data above, the modified asphalt penetration value obtained is 53.7. Where the results of this research for the value of asphalt can be interpreted as asphalt suitable for use where the results are adjusted to the 2018 Bina Marga specifications.

| Table 2. Result Testing Ductility |
|-----------------------------------|------------------|--------------|
| Testing                           | Testing Methods  | Observation Result |
| Methods                           | Asphalt Blanco   | Elastomer Asphalt | Modified Asphalt |
| Ductility                         | SNI 2434:2011    | >100 cm        | 9100 cm       | 55.46 cm    |

The modified asphalt ductility test carried out can be seen below, where the results obtained for modified asphalt were 55, 46. And this result can be interpreted as meaning that the ductility value is appropriate for the 2018 Bina Marga specifications. Where for Blank Asphalt the value is > 100 cm.

| Table 3. Result Testing Softening Point |
|-----------------------------------------|------------------|------------------|--------------|
| Testing                                | Testing Methods  | Observation Result |
| Methods                                | Asphalt Blanco   | Elastomer Asphalt | Modified Asphalt |
| Softening Point                        | SNI 2434:2011    | 748 c            | >54 C        | 65.23 cm    |

And the results of the Modified Asphalt Softening Point test can be seen below, which means the results obtained are that for the modified asphalt carried out, the asphalt is suitable and in accordance with the 2018 Bina Marga specification standards, which is 65.23 cm. which can be seen in the table for the Blank asphalt value >48 and the result obtained is 65.23. This indicates that the asphalt is good and suitable for further treatment so that it can be used and put to good use.

**Conclusion**

From the results of the DSC thermal analysis, it shows a downward peak, namely at a temperature of 160.60C. And the reaction results obtained are endothermic reactions which are shown by a downward peak. As for the characterization results using TGA, there are 3 graphs with different graphic models and temperature peaks, namely 373.3 Cells, 249.7 Cells and 132.3 Cells. For result FTIR The peak wave number of 1728/cm is the CH. the peak at wave number around 1730 is the carbonyl group from GMA grafted on LDEP. Where this can be seen in the wave number at 2723/cm which is the CH3. For asphalt test results with penetration values Based on the data above, the modified asphalt penetration value obtained is 53.7 cm. and result asphalt where the results obtained for modified asphalt were 55, 46 cm And the results of the Modified Asphalt Softening is 65.23 cm. This can be interpreted that all three are in accordance with the 2018 Bina Marga asphalt standards

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**Conflicts of Interest**

The authors declare no conflict of interest.
References


Thomas, L. C. (2005). An introduction to the techniques of differential scanning calorimetry (DSC) and modulated DSC.

