Improvement of polypropylene (PP)-modified bitumen through lignin addition

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Abstract. Polypropylene (PP) is usually added to bitumen to improve its mechanical properties, however, both of them have different chemical properties. To achieve best mechanical properties of the mixture, coupling agent such as lignin is importantly required. Lignin is an amorphous biopolymer, has bipolar characteristic due to its distinct chemical function which has carbonyl, carboxyl, hydroxyl and phenol chemical function. Otherwise, bitumen and PP have polar and non-polar characteristic, respectively. In the previous research, it is found that lignin is potential to be used as coupling agent. In order to confirm the potential of lignin as a coupling agent, there are various compounds of lignin on PP-bitumen mixtures used in this research. This experiment consists of several stages, ranging from sample preparation, characterization of raw materials, mixing, and characterization of the PP-Modified Bitumen. This experiment used hot melt mixing to mix lignin, PP, and bitumen. The result of this experimental was analyzed by using FTIR and FESEM. The addition of lignin make Polymer Modified Bitumen (PMB) getting better mixing and increase mechanical properties. Furthermore, FESEM characterization indicated that the addition of lignin gave better mixing of PP-Bitumen. FTIR showed a new chemical structure due to the addition of lignin. From this experiment, the addition of lignin can improve mixing between PP and Bitumen. So, we can use lignin as coupling agent.

1. Introduction

Bitumen is material which has been used for over century. The applications of bitumen as matrix material have a weakness such as plastic deformation when receiving pressure such as a vehicle. For countering that weakness, bitumen material should be added as filler. In order to obtain bitumen with better quality, an increasing number of research began to focus on bitumen modification.

Bitumen modification commonly used polymer materials. Polymer for bitumen modification include polyethylene waste (WPE), PP, tire crumb rubber [1-5]. From the research result, it shows a positive effect, which solves the waste problem in the beginning of this part. But when it is viewed chemically, bitumen has a hydrophilic characteristic that is polar and polymer is the opposite, hydrophobic and is non-polar, which make the two the exact opposite making them hard to interact with one another. What needed for the two of them to become one is the presence of coupling agent that acts as a bridge.
between these two. The condition that this coupling agent need is that it needs to be both hydrophilic and hydrophobic.

Seeing lignin that has both of the conditions and have not been used optimally becomes a solution to this problem. Lignin is amorphous, aromatic biopolymer and the part of lignocellulose that is based on natural material such as wood and plants. Lignin also a phenolic polymeric compound that is the derivative of three hydroxynamel alcohol which is p-coumaryl alcohol, coniferyl alcohol, and synapylalcohol, has hydroxyl, carbonyl and carboxyl substituents [6-8]. Based on these compound lignin has unique characteristics, which is hydrophobic and hydrophilic. Because of it, we can use the characteristics as a coupling agent from different characteristics of other material. Previous research has shown the result that PP-modified bitumen with lignin have passed the penetration requirement for construction application [9]. In this work, we did research for further study of the compatibility level of lignin especially the composition of lignin to combine with PP plastic bag and bitumen from the chemistry bond and morphological characteristics.

2. Materials and Methods

2.1. Materials

In this experiment, bitumen with a penetration grade of 60/70 was used as base material for the modification. Details of properties are shown in Table 1. PP from plastic bag and lignin from paper mill waste were used as modifier and compatibilizer, respectively.

| Table 1. Mechanical Properties of Bitumen (10) |
|-----------------------------------------------|
| **Testing Item** | **Unit** | **Result** | **Specifications** |
| Hardness at 25°C, 100g, 5 | 0.1mm | 68 | 60-79 |
| Softening Point | ºC | 49.9 | 48-58 |
| Ignition Point COC | ºC | 310 | Min. 232 |
| Ductility 25°C, 5 cm/minute | cm | 140 | Min. 100 |
| Density | g/cm³ | 1.03 | Min. 1.0 |
| Solubility at CH₂Cl₂ | % | 99.09 | Min. 99 |
| Weight Loss TFOT | % | 0.26 | Max. 0.4 |
| Hardness after TFOT | % | 80.8 | Min. 75 |
| Ductility TFOT | cm | 24.5 | Min.50 |
| Parafin Concentration | % | 0.5 | Max. 20 |
2.2. Methods

First, new PP plastic bag (purpose to minimize impurities) was crushed in to small part and prepared 4% w/w of bitumen. Secondly, lignin was prepared 0.1, 0.3 and 0.5% w/w of bitumen, respectively and then bitumen 60/70 was modified with 4% PP and lignin with those variables. Bitumen modification was performed at 180°C in 30 min using stirrer. Finally, PP-modified bitumen will go through for characterization, FE-SEM images were taken at an accelerated voltage of 20 kV, FTIR (Fourier Transform Infrared) were recorded using a Perkin-Elmer FTIR spectrometer, each sample recording consisted of 30 scans recorded from 500 to 4000 cm\(^{-1}\).

3. Result and Discussion

3.1. Base Material Characteristic

Bitumen is the precursor material and the matrix of the mixture that has the color of black or dark brown and at room temperature has the shape of solid or semi-solid. Figure 1 indicates bitumen on FE-SEM testing to shows its base shape. Furthermore, Figure 2 shows the peak when bitumen is tested with FTIR. Peak 3349 cm\(^{-1}\) shows –OH functional group.

![Figure 1. Bitumen Morphological Surface](image1)

![Figure 2. FTIR Spectra of Bitumen](image2)

Peak 2918 cm\(^{-1}\) and 2848 cm\(^{-1}\) shows C-H alkane chain. Peak 1650 cm\(^{-1}\) shows C=C alkane chain. Peak 1453 cm\(^{-1}\) and 1371 cm\(^{-1}\) shows CH\(_3\) chain. Peak 1033 cm\(^{-1}\) shows functional group C=O carboxylic. Whereas, peak 850, 723, and 548 cm\(^{-1}\) shows functional group aromatic para, meta, and ortho. On the other hand, lignin is material which consist of hydroxyl (-OH), carboxylic (C=O), and aromatic group [6,
and shows peak 2292 cm$^{-1}$. Moreover, peak 2922 cm$^{-1}$ is shown also in the FTIR characterization of polypropylene (Figure 4). From this characterization, lignin has possibility to become a bridge or link and approach to induce compatibility between bitumen and polypropylene.

3.2. Polymer Modified Bitumen (PMB) Morphology

Figure 3 is depicted morphology of PP, lignin, and bitumen mixtures. On Figure 3(a), it shows bitumen matrix and PP filler. PP filler has a border with matrix and coloured black. In Figure 3(b) shows the same bitumen matrix and PP filler, however, there’s new white material. This white material is lignin that as can be seen in Figure 3(b). Furthermore, in the Figure 3(a) PP distribution on bitumen is not even and has poor dispersion because they form an agglomerate. In the other hand, in the Figure 3(b) PP and lignin distribution is better than in the Figure 3(a), however, the dispersion is still poor because they form agglomerate too. Agglomerate formed as a result of non-optimal mixing. Hence, to have a good mixing result, there are needs for raising the temperature and stirring the mixture during the mixing process. Future study is required so that the mixing can be optimized. This research will be done in the next project.

![Figure 3. FE-SEM Image of PMB (a) without lignin, (b) with 0.3% lignin](image)

3.3. Compatibility between Raw Materials in Polymer Modified Bitumen

Figure 4 indicates the different of functional groups possessed by non-lignin and lignin bitumen modification. On bitumen modification with lignin peak in 2921 and 2851 cm$^{-1}$ shows the alkane C-H chain. Peak 1582 cm$^{-1}$ shows the CH$_2$ chain. Peak 1466 and 1376 cm$^{-1}$ showed CH$_3$ chain. Peak 1016 cm$^{-1}$ shows the functional groups of ether C-O hydrogen bonding. Peak 863 cm$^{-1}$ shows the aromatic functional groups. Peak 731 cm$^{-1}$ shows the meta-aromatic functional groups. Assuming the existence of a hydrogen bond in the ether peak indicated a decline from 1055 into 1016. This, in line with the reports given by
Stéphanie Laurichesse [10]. Functional groups -OH on lignin PMB lost due -OH in the lignin and bitumen interact to bind together and bring H₂O gas. In this PMB too, appears a new group that is group C-O ether hydrogen bonds, this occurs due to the result of the reaction between the -OH lignin and bitumen. Possible reactions that create new groups can be seen in Figure 5. In Figure 4 spectra of PMB without lignin its look like spectra of PP, this condition because mixing between bitumen and polypropylene is not really good. In addition, PMB without lignin didn’t show new chemical function group.

Possible reactions in Figure 5 shows that the reaction occurs in -OH groups. This is according to research conducted by Stéphanie Laurichesse who saw polar groups OH lignin potentially form the functional group ether [11,12]. On bitumen modification without lignin, peak formed only 2921, 2851, 1582, 1466 and 1376 cm⁻¹, so that the chains that were formed then only C-H alkanes, CH₂, and CH₃. In PMB without lignin is also -OH is reduced due to the interaction between bitumen with PP, but not forming ether. Peak FTIR that are formed from PMB without lignin also tend to be the same as the peak on the PP, so it is possible that mixing of PMB is not optimal. So, based on the result of mixing PMB without lignin is to confirm that with the addition of lignin resulted in the formation of a new cluster of ether. The cluster is indicated as an ether bond between bitumen with lignin. This shows that the lignin and bitumen have been compatible.
Figure 4. FTIR Spectra of Bitumen, Lignin, PP, PMB without and with Lignin

Figure 5. Possible Reaction (Interaction) between bitumen and lignin
Figure 6 shows the effect of the addition of lignin composition of the functional groups is formed. From this figure, it can be seen that the difference does not change the composition of the bond, but increase the intensity of the peak. With the addition of lignin in PMB, it can increase the intensity of the ether bond that is formed. Therefore, it can be assumed that the interaction between bitumen and PP increased hand in hand with the increase in the number of lignin in PMB.

**Figure 6.** FTIR Spectra of PMB with Variation of Lignin Composition

4. Conclusion

Lignin can be influential as a coupling agent between the PP plastic bag with bitumen which was indicated by the formation of ether peak and the loss of hydroxide peak. The increasing amount of lignin added to the mixture, increase the amount of ether produced. FE-SEM result indicated that with the addition of lignin, it can produce a better mixture between PP and bitumen. In addition, it also showed that the compatibility of the bitumen and PP with lignin was getting better.

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