ABSTRACT

Novolac type resin was prepared by liquefaction reaction of oil palm empty fruit bunch (EFB) in the presence of phenol at various reaction conditions. This polymer later is known as phenolated EFB (PEFB). PEFB-base board was made using PEFB as a polymer matrix phase and EFB as a filler. The effect of various liquefaction conditions and filler content on water absorption and thickness swelling of PEFB-base board was studied. The hardness of these samples also was examined before and after water absorption. The result clearly showed that the major part of water absorption and thickness swelling were due to water absorption of EFB filler. It was found that the water absorption in the PEFB-base board is slightly higher than the commercial novolac resin board. The result of hardness test showed a substantial decrease in hardness after water absorption test at higher filler content (80%). It was also found that the reduction of hardness in PEFB-base board after water absorption is lower than the commercial novolac-base board.

INTRODUCTION

Composites with common structural polymer matrices often absorb moisture and this has profound effects on their mechanical, thermal, dielectric and barrier properties and performance. It is, therefore, not surprising that experimental and theoretical works on moisture absorption in composites was and still is an active research topic across many disciplines [1-6].

The mechanisms of moisture penetration in composites are much more complex than in the case of non-reinforced matrix [7]. Moisture penetration into composite materials is partly conducted by diffusion, which involves transport of water molecules into the matrix and, in some cases, into the fibres [8,9]. Water can also diffuse rapidly into composites along the fibre-matrix interface. This capillary flow, also known as water wicking, represents the second mechanism for conveying water to the interior part of composites, which tends to occur preferentially along the interface, if wetting of the fibres by the matrix is incomplete [10]. Finally, percolating flow and storage of water in micro-cracks possibly present in the matrix constitute a third mechanism of moisture penetration into composites. Woo et al. [11] identified that the transport
behaviour of matrix voids and fibre-to-matrix interphase can have a significant effect on the value of diffusivity in a composite; they modelled these regions as having a diffusion coefficient higher than that of the bulk matrix, suggesting values as high as 10-fold for the interphase.

It should be admitted that the hydrophilicity is related to the existence of specific interactions between the water molecules and polar groups of the polymer. The hypothesis that the equilibrium water concentration is a molar additive function can lead to relationships having some predictive quality. Many authors have also suggested that the quantity of absorbed water at equilibrium is determined by the available free volume [12].

Ergun et al. [13] reported that loading the capillaries (void space in wood) with polymer reduces the rate of water diffusion into the cell walls. The decrease in water absorption is because the hydrophobic characteristic of monomers shields the wood surface and remains in the cell wall and lumen result in less water penetration into the wood.

Novolac types of phenolic resin are most commonly used in the manufacture of moulding powders as a polymer matrix phase. Recently, the preparation of novolac-type resin by liquefaction of lignocellulosic materials such as wood powder [14], oil palm empty fruit bunches (EFB) in the presence of phenol using sulphuric acid as a catalyst [15-17] have been carried out. After liquefaction reaction a large amount of phenol remains in the liquefaction mixture as the non-reacted phenol which is known as free phenol. In the preparation of phenolated EFB (PEFB) the free phenol must be removed after completion of liquefaction reaction to obtain the final product.

Preparation of PEFB
EFI and phenol at various weight ratios of (1:2, 1:3, 1:4) and sulphuric acid as a catalyst (5% based on the weight of phenol) were charged into a four-neck glass reaction flask (500 mL) equipped with a reflux condenser, thermometer and an electrical stirrer. The total amount of EFB and phenol in every reaction was 120 g. The liquefaction reaction was carried out in an electrical heating mantle from 30 min to 120 min at 110ºC, 130ºC, and 150ºC. The main product of this reaction is known as phenolated EFB (PEFB).

After the completion of each phenolation the resulting mixture was diluted with methanol and then filtered with a glass-fibre filter to separate residue of EFB (methanol-insoluble part) from methanol-soluble part. The resulting residue was oven dried and weighed, and the amount of residue determined in percent. The remaining sulphuric acid in the
methanol-soluble part was neutralized using magnesium oxide (MgO), and the neutralized solution was once again filtered with a glass-fibre filter to remove the salt produced during the neutralization process. Subsequently, methanol was evaporated from the solution at 80°C under vacuum, and the free phenol (non-reacted phenol) was distilled under a reduced pressure at 190°C to obtain condensed PEFB in a solid form.

**Preparation of Composite Board**

The resin (PEFB or commercial novolac) was dissolved in acetone and mixed with HMT (25% of the resin weight), zinc stearate (2.5% of the resin weight), calcium hydroxide (6% of the resin weight), and various amounts of EFB fibre which act as fillers. The blend ratio of resin/EFB was 80/20, 50/50, and 30/70, respectively. After mixing, the mixtures were oven dried at 70°C for 2 h to remove acetone, and then ground in an electrical grinder to make a fine powder.

For the preparation of resin-base board, the obtained powder was compression moulded in a die into sheets measuring 130×130×3.4 mm. Then, this moulding board was cut to the test specimen size appropriate for each test. The moulding conditions were as follows: temperature, 185±5°C; pressure, 100 kg/cm²; preheating time, 20 s; venting time, 20 s; curing time, 330 s; and cooling under a slight pressure to ambient temperature.

**Water Absorption and Thickness Swelling**

The moulding samples were used for the measurement of water absorption and thickness swelling. The samples were periodically taken out of water, wiped with tissue paper to remove the excess water on the surface, reweighed and dimensions remeasured and immediately placed them into water. At least five specimens for each sample were measured. Water absorption (WA) was calculated according to the following formula:

\[ \text{WA} \% = \left[ \frac{M_e - M_0}{M_0} \right] \times 100 \]  \hspace{1cm} (1)

where \( M_e \) is the mass of sample after immersion (g), and \( M_0 \) is the mass of sample before immersion (g). The value of absolute error for water absorption (WA%) is ±0.2%.

Thickness swelling (TS) was calculated as follows:

\[ TS \% = \left[ \frac{t_e - t_0}{t_0} \right] \times 100 \]  \hspace{1cm} (2)

where \( t_e \) is the thickness of sample after immersion (mm), and \( t_0 \) is the thickness of sample before immersion (mm). The value of absolute error bar for thickness swelling (TS%) is ±0.7%.

**Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) [Phillips XL 30 Oxford 6650 SEM with an acceleration voltage of 20.0 kV] was used to observe the fracture surface of the moulded material (composite) after the flexural test. The samples were coated with gold layer to provide about 200 Å thickness gold layer using a vacuum sputter coater.

**Hardness**

The test was carried out using the durometer hardness tester type Shore D (Zwick Model) by first placing a specimen on a hard and flat surface. The pressure foot of the instrument was pressed onto the specimen, making sure that it was parallel to the surface of the specimen. The durometer hardness was read within 1 s after the pressure foot was in firm contact with the specimen. Five readings were determined and the mean value was recorded as the hardness of the sample. All the measurements were performed at room temperature.

**RESULTS AND DISCUSSION**

**Water Absorption and Thickness Swelling**

Figures 1 and 2 show the effect of filler content on the thickness swelling and water absorption of PEFB-base board, respectively. Figure 1 illustrates that the thickness swelling increases sharply by increasing the filler content. Since lignocellulose fibre is hydrophilic in nature, the increased amount of EFB used as filler in the composite showed a tremendous effect on the thickness swelling result. This figure clearly shows that the majority of swelling occurred during the first 7 days. After that, the percentage of swelling is negligible. Furthermore, during the first 7 days the...
percentage of swelling for all samples from the 2nd day to the 5th day is approximately the same, around 3%. However, for these samples the amount of swelling on the 1st day differs with 1%, 7%, and 19% for the samples with 20%, 50%, and 80% of EFB filler, respectively. Figure 2 also shows an approximately similar pattern for water absorption. As shown in Figure 2, the water absorption increases sharply by increasing the filler content. This figure clearly shows that the majority of water absorption occurs during the first 7 days. After that, the amount of water absorption is also negligible. Additionally, the percentage of water absorption for all samples from the 2nd day until 7th day is approximately the same, around 7%. However, the amount of water absorption on the first day in these samples is significantly different for 2%, 7%, and 37% of the samples with 20%, 50%, and 80% of EFB filler, respectively. It can be concluded that the maximum water absorption and thickness swelling occur on the first day soaking due to the absorption of water by EFB filler. The rate of water absorption and thickness swelling in EFB is higher compared to the PEFB. It is believed that many hydroxyl reactive sites in cellulose involved during the phenolation reaction. Hence, the hydrophilicity of EFB reduces greatly during the liquefaction process.

Figures 3 and 4 show the effect of initial input phenol/EFB ratio (P/E) of liquefaction reaction on the thickness swelling and water absorption of PEFB-base board, respectively. The amount of EFB filler in all samples with different P/E ratios are 50%. As shown in Figure 3, no significant difference is found between the thickness swellings in the samples with different amounts of initial input P/E ratio. This
figure shows that the maximum difference in thickness swelling in these samples is around 3% after 21 days soaked in water. The result mentioned above can be explained using our previous findings in Figure 1. We have proved that the swelling of matrix phase is insignificant and the main reason for thickness swelling is the swelling of EFB filler. Since, the amount of EFB filler in all samples in Figure 3 is fixed at 50%; as this has resulted to similar results in thickness swelling.

Figure 4 shows the water absorption of PEFB-base board composite with various P/E ratios using 50% of EFB filler. As shown in this figure, no significant difference is observed on the amount of water absorption when the P/E ratios are 2 and 3. When the P/E ratio is 4, the amount of water absorption reduces and becomes negative. After 5 days, the amount of water absorption increases up to 1% where thickness swelling is around 12% (Figure 3). There is a possibility of losing weight during the water absorption which is due to the leaching of some low molecular weight materials in water. Our previous findings [18] which show a sharp reduction of viscosity and molecular weight in PEFB by increasing P/E ratio from 3 to 4 support the existence of some low molecular weight materials that can probably be extracted in water. It was also reported that the leaching in phenolated wood might be explained by an insufficient cross-linking between phenolated wood and HMT under the experimental conditions [14].

Figure 5 indicates the effect of liquefaction time on thickness swelling and water absorption of PEFB-base board. The amount of filler in these boards is fixed at 50%. This figure illustrates the maximum difference in water absorption and thickness swelling between PEFB-base boards whose PFEB matrix has been prepared at various liquefaction times is 4% and 3%, respectively. The reason for this small difference (4%) is not clear, because the mechanisms of moisture penetration and absorption in composites include the complex function of matrix structure, moulding condition, composite structure and some other parameters [4]. However, these results seem to agree with Alma [14], which has investigated the relationship between the amount of water absorbed and thickness swelling verses soaking time for the phenolated wood board with different amounts of combined phenol. He found that, approximately 63% increase in the amount of combined phenol causes about 8% decrease in the water absorption and 4% in thickness swelling. Furthermore, the phenolated boards with greater amount of combined phenol were found to be comparable to the commercial novolac as far as thickness swelling is concerned.

The thickness swelling between PEFB-base board and commercial novolac resin-base board (Figure 5a) does not show any significant difference. As shown earlier (Figure 1), the percentages of EFB filler in the moulded board influence the thickness swelling more than matrix phase. However, the amount of water absorption in commercial novolac resin (Figure 5b) is slightly lower than that of PEFB. This illustrates that the hydrophilicity of PEFB is higher than the commercial novolac resin. Since the starting material for the preparation of PEFB is a lignocellulosic fibre, which is hydrophilic, and as for the novolac resin, it is from petroleum base, this phenomenon is well understood.
Effect of Water Absorption on the Hardness

The effect of filler content on the hardness before water absorption (b.w.a) and after water absorption (a.w.a) is shown in Figure 6. As shown in this figure, the initial hardness slightly decreases by increasing the filler quantity. The figure shows that the hardness decreases from 87.75 to 85.6 Shore-D when the filler content increases from 20% to 80%. However, after 60 days of water absorption, the hardness sharply decreases with increasing the filler content. The figure indicates the tremendous decrease of hardness in the sample with 80% of filler. The previous findings (Figure 1) showed that the amount of thickness swelling with EFB filler is higher than the PEFB matrix. Thus during the water absorption, the amount of swelling in EFB fibre is higher than the PEFB and, in fact, the non-homogeneous swelling is observed in PEFB-base board. This non-homogeneous swelling creates a tension in composite especially between filler and matrix. Therefore, some of the bonds between filler and matrix and also cross-linking bonds in matrix are broken due to this tension. On the other hand, the water absorption could decrease the bond strength between filler and matrix due to some chemical and physical bondings between water and composite component. It has been proved that a good bonding strength between the internal reinforcements and matrix is one of the dominant factors that give outstanding mechanical properties of advanced composite structures [19].

The data in Table 1 show the effect of liquefaction time and temperature on the hardness of PEFB-base boards, respectively. The amount of EFB filler in these samples is fixed at 50%. These data indicate that the liquefaction time and temperature do not contribute an important effect on the hardness before water absorption. The amount of hardness decreases after water absorption. As shown in this table, the reduction of hardness after water absorption in the samples with 30 min of liquefaction time or 110ºC of liquefaction temperature is higher than the other samples. The results clearly show that the reduction of hardness after water absorption in other samples is less than the reduction in these two samples. It must be noted that the reduction of hardness after water absorption in other samples is approximately similar. Our previous results [16] showed that the molecular weight of PEFB increases rapidly when the liquefaction temperature rises from 110ºC to 130ºC. However,

Table 1. Effect of liquefaction condition on the hardness of PEFB-base board before water absorption (b.w.a) and after water absorption (a.w.a) at (P/E: 3).

<table>
<thead>
<tr>
<th>Liquefaction condition</th>
<th>Hardness (Shore D)</th>
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<tbody>
<tr>
<td></td>
<td>b.w.a</td>
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<tr>
<td>Time (min)</td>
<td>Temperature (ºC)</td>
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<tr>
<td>30</td>
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<td>130</td>
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<tr>
<td>90</td>
<td>150</td>
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<tr>
<td>Commercial novolac</td>
<td>88±1</td>
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</table>
there is a slight difference between molecular weight of PEFB obtained at 130°C and 150°C. It is possible to say that these results are related to the rapid increase of $M_w$ of PEFB in initial stage of liquefaction when the liquefaction time or temperature increases. Another possible reason for these results is referred to the increase of bonding strength in composite due to the increase of cross-linking density. It was found that the cross-linking density increases as the liquefaction time or temperature increases because of increasing the combined phenol [14].

As it is shown in this table, the difference between the hardness commercial novolac and PEFB-base board before water absorption is not significant. However, after water absorption the hardness decreases for novolac-base board more than most of the PEFB-base board. This phenomenon indicates that the interaction between EFB filler and phenolated EFB is higher than the interaction between EFB filler and commercial novolac. This also shows that the compatibility between EFB and phenolated EFB is better than EFB and commercial novolac. The excellent compatibility between PEFB and EFB in comparison with commercial novolac resin and EFB was reported also using SEM micrograph [18].

Figure 7 illustrates the effect of initial input P/E ratio on the hardness of phenolated EFB-base moulding before and after water absorption. As shown in this figure, the hardness decreases sharply after water absorption when the P/E ratio is 4. The reduction of hardness during the water absorption with P/E ratio of 4 is 1.5 times more than the other samples with P/E ratio of 3 or 2. As mentioned earlier (Figure 3), there is a possibility of higher amount of chemical leaching during water absorption as well as low cross-linking density in the sample with P/E ratio of 4.

Figure 8 illustrates the effect of phenol/EFB ratio (P/E) in liquefaction on the hardness of phenolated EFB-based moulding before water absorption (b.w.a) and after water absorption (a.w.a). Other reaction conditions (time: 90 min, temperature: 130°C, catalyst: 5%).

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face and fibre lumen are approximately similar. Therefore, it can be concluded that there are some interactions between fibre and matrix inside the fibre lumen. Thus the interaction between filler and matrix is not only on the surface of fibre bundle but also inside the fibre lumen.

Figure 8b shows the fracture surface after water absorption. These figures clearly show the separation between matrix and fibre after water absorption due to non-homogeneous swelling of filler and matrix. Non-homogeneous swelling creates the tension between EFB fibre and matrix. This tension helps to break the interaction bond between filler and matrix. Therefore, the hardness and mechanical properties of the sample moulded decreases after water absorption.

CONCLUSION

It is found that the main reason for water absorption and thickness swelling of PEFB-base board composites is the water absorption and swelling of EFB filler that is caused by hydrophilic nature of lignocellulosic material. Comparison of the thickness swelling between PEFB-base board and novolac-base board does not show any divergence, due to the major effect of EFB filler on the control of thickness swelling. On the other hand, the amount of water absorption in novolac resin is slightly less than that of the PEFB. This is due to the high hydrophilicity of EFB as a raw material in production of PEFB.

It was observed that the PEFB matrix and EFB fillers possess a strong interaction compared with the interaction between the novolac matrix and EFB fibre. It was also found that the lumen of fibre is filled with the resin during the hot press moulding, which yields some interactions between fibre and matrix inside the fibre lumens.

ACKNOWLEDGEMENT

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