Properties of unsaturated polyester composite filled with cellulose from peanut shell (*Arachis hypogea I*): the effect of filler content and compatibilizer addition

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**Abstract.** Unsaturated polyester (UPR) composite containing the powder of peanut shell fiber filler is a panel product made by compacting the particles of peanut shell powder and binding them with UPR. The purpose of this research is to investigate the effect of peanut shell fiber powder cellulose filler composition and addition of compatibilizer on the tensile properties, energy impact and water absorption of UPR composites. The composites were made of UPR as matrix and mixed with peanut shell powder as filler, with methyl ethyl ketone peroxide catalyst, and molded by using compression molding method. The result of the physical properties test supported by FTIR characterization of the composite showed that the filler was dispersed into the matrix with the formation of a new wave from 3463 to 3495 cm$^{-1}$. The best of tensile and impact properties were found on 5% filler and 4% of compatibilizer composition with the tensile strength of 26.04 MPa and an energy impact of 99.82 MPa. The results obtained have been supported by Scanning Electron Microscopy (SEM) analysis that there was resistance from the composite when the impact was applied. The water absorption of composite tended to rise with the increasing amount of filler.

1. **Introduction**

Nowadays, the use of polymers in the industrial world is growing very rapidly. This is due to the characteristics of polymers that are light, cheap, corrosive resistant and have relatively lower processing temperatures compared to metal or ceramic materials. In general, the polymer is mixed with other materials to obtain better characteristics, known as composite materials. To improve the desired characteristic in polymers such as strength, stiffness, and fire resistance, fillers are added. Those materials integrate homogeneously into the matrix [1]. Various organic materials that can be used as filler including wood such as pine, banana, and peanut shells. Peanut (*Arachis hypogea L.*) is an important oilseed crop. The composition of peanut shell consists of 18.7% hemicellulose, 35.7% cellulose, 30.2% lignin and 5.9% ash. Lignin is often considered as a cementing agent that binds individual fiber cells together, and the content of hemicellulose in peanut shells is for water absorption. The cellulose content in peanut shells consists of amorphous and crystalline parts. Crystalline cellulose is preferred to amorphous cellulose as a filler due to its organized structure that makes it stronger [2].
Composite materials are materials that are composed of a mixture or combination of two or more principal elements which are mainly different in shape and/or material composition which are inseparable. The advantage of composite materials compared to metal is their resistance to corrosion or the effect of environment and some types of composites are better in terms of strength and stiffness [3]. Unsaturated polyester (UPR) is the most widely used resin in various applications of thermoset resin, either separately or in the form of material composite. This is because the resin is easy to obtain, the price is relatively affordable and most importantly easy in the fabrication process. The type of UPR used as a composite matrix is the unsaturated one, which is a thermoset that can undergo curing from the liquid phase into a solid phase when proper treatment is applied [4].

This research aims to investigate the optimum composition of cellulose from peanut shells as a filler and the composition of the compatibilizer, so it can increase the tensile strength, energy impact, and water absorption on UPR composites produced.

2. Method

2.1 Material

The material used as a matrix was UPR blended with methyl ethyl ketone peroxide (MEKPO) catalyst were obtained as received. Meanwhile, the peanut shells for filler were acquired from traditional markets in Medan, Indonesia.

2.2 Preparation of composite matrix

UPR was mixed with MEKPO catalyst with 1% of catalyst out of the resin’s weight. The mixture was stirred with a metal mixer for 10-15 minutes until it was mixed evenly.

2.3 Preparation of composite filler

Peanut shells were washed by mineral water and sundried for 12 hours. Dried peanut shells were blended until the shells turn into powder. After that, it was sifted through a sieve to obtain the size of 140 mesh.

2.4 Composite molding process

Matrix and filler with the composition of 2.5; 5; 7.5; 10 and 12.5% (w/w) and 140 mesh of peanut shell powder were mixed in a container. The base of the iron mold of 250 mm x 250 mm x 5 mm dimension was applied with glycerin as lubricant beforehand to prevent the resin from becoming glued to the mold. The mixtures of the materials were poured into an iron mold that has been coated. Compression molding was used to apply pressure at 125 psi. The dried composites were then removed from the mold and cut according to the ASTM D 638-10 to determine the mechanical properties of composites, then a scraper and sandpaper were used to smoothen the surface. All the composite samples were made with 3 repetitions.

2.5 Analysis of the physical and mechanical properties of composite

The composites that have been formed were then analyzed using the water absorption tests with physical analysis tools. For the mechanical properties, in the form of tensile strength test of ASTM D 638-10 and energy impact test of ASTM D 4812-11.

2.5.1. Tensile properties test.

The specimens of the composites were selected and cut to form a specimen for the tensile strength test. Tensile strength test was performed using a tensometer on each specimen with a thickness of 4 mm. The tensometer was first conditioned at a load of 100 kg force at a speed of 20 mm/min and then clamped firmly. The engine is turned on and the specimen will be pulled up, until the observed specimen breaks, the maximum stress and strain are recorded.

2.5.2. Energy impact.
The impact test for the specimen is done with the Unnotched Izod method.

![Figure 1. Standard specimen size for Unnotched Izod method.](image)

2.5.3. Water absorption test of ASTM D 2842-01.
The specimens were of the dimension of 15 cm x 15 cm x 7.5 cm. The specimens were immersed in water at the height of 5.1 cm from the surface of the water at room temperature for 24, 48, and 96 hours and so on until the specimens’ weight became constant. The weight of the specimen will increase as water enters the polymer textures. In this research, the tested composites were composites which contained cellulose from peanut shell fiber powder. The following equation is to calculate the percentage of the weight gain percentage of composite:

$$W_g = \frac{W_e - W_0}{W_e} \times 100\%$$

Notes:
- $W_g$ = Weight gain a percentage of composite
- $W_e$ = Composite weight after immersion
- $W_0$ = Composite weight before immersion

2.5.4. FTIR (Fourier Transform Infra-Red).
The analyzed samples were peanut shell fiber powder and UPR filled with peanut shell fiber powder to observe whether a cross-linking or a new strain is formed.

2.5.5. SEM (Scanning Electron Microscope).
The analyzed samples were the result of the tensile strength test of UPR composite filled with peanut shell powder filler with one of the compositions that had the best properties among the four variables to observed the morphological changes that occurred in both composites.

3. Results and discussion

3.1 Tensile properties
Figure 2 indicates the effect of filler and compatibilizer addition composition on the tensile strength of UPR filled with cellulose from peanut shells.
Figure 2. The Effect of filler and compatibilizer addition composition on the tensile strength of UPR filled with cellulose from peanut shells.

The purpose of the tensile strength test is to find out the maximum resistance that the material can retain when force is applied before the material breaks. Figure 2 shows that the tensile strength of composites with 4% of compatibilizer increased by the increase of filler concentration from 2.5% to 5% and reached the highest tensile strength with 4% of maleic anhydride (MA) composition and 5% of a filler, which was 26.041 MPa. The increase of the tensile strength was influenced by the good binding force between fibers and matrix with the addition of compatibilizer as well as the addition of fiber fraction volume in the composites. Another factor that affects the increase in composite’s tensile strength was the orientation of the fibers in the composites [5]. This was because the matrix spread evenly to the filler, thus increased the composite's tensile strength. A similar result was obtained by Ramaniah et al. [6], that an increased amount of fillers increase in tensile strength. However, in the filler composition of 5% to 7.5% a decrease occurred, this was due to increased contacts among the fillers which reduced the filler's ability to withstand the stress transferred from the matrix to the filler. While at 6% and 8% of MA, the tensile strength decreased due to the occurrence of agglomeration. This was consistent with the Nasution report [7], that the increase of bindings among the interface of the filler, the matrix and the addition of the compatibilizer produced a good pressure transition, which in turn increased the tensile strength properties. Meanwhile, Figure 3 indicates the effect of filler and compatibilizer addition composition on the young modulus of UPR filled with cellulose from peanut shells.

Figure 3. The effect of filler and compatibilizer addition composition on the young modulus of UPR filled with cellulose from peanut shells.
Young Modulus analysis aimed at determining the stiffness level of a material. Figure 3 shows that the elasticity modulus value increased from the composition of 2.5% to 5% where the value of elasticity modulus was at its highest. The elasticity modulus value increased by the addition of natural filler composition with the usage of the UPR matrix indicating that the addition of filler can increase material stiffness. This was due to the increase of matrix bond strength and the filler in the interface section. Raju et al. [8] concluded that the young modulus increased along with the addition of fillers. At the composition of 7.5% of young modulus the composite decreased from the 5% composition, this was because the increasing number of fillers and the decreasing matrix caused the fibers to not spread evenly, thus reducing the value of young modulus. Meanwhile, the modulus value increased as the fiber size decreased. This was due to the more reactive nature which caused higher mobility of the polymer chain molecule than the plasticity such that the stiffness level decreased.

3.2 Energy impact

Figure 4 shows the effect of the filler composition with compatibilizer addition on the energy impact of UPR filled with cellulose from peanut shells. The energy impact was to measure how much energy a material can absorb before it fractures. Figure 4 showed that the addition of the filler amounts from 2.5% to 5% with a 4% compatibilizer could increase the value of the composite energy impact. The energy impact increased linearly with the addition of cellulose up to 5% composition. The impact energy value and the width of the test composite surface affected the energy impact value. Increasing the number of fibers caused an increase in composite resistance to pendulum shock load. This was following the composite basic principle that the fiber acted as a reinforcer [9].

![Figure 4](image_url)

Figure 4. The effect of the filler composition with compatibilizer addition on the energy impact of UPR filled with cellulose from peanut shells.

Another thing was also influenced by proper interface network flexibility between the matrix and filler so that with the increase of filler material content, the composite material will absorb the high impact energy [10]. The decrease in composite strength occurred in the matrix and filler ratio from 7.5% to 12.5% and 6% and 8% MA. This was due to the increasing number of fillers and the smaller number of matrixes prevented the matrix from moistening the entire section, in other words, saturated and uneven distribution of the filler as well as an occurrence of agglomeration. Similar results were reported by Srinivasababu [11] that composite energy impact increased when the fiber content was high and then decreased due to the excessive amount of fiber that reduced the adhesiveness of the matrix.
3.3 Water absorption
Figure 5 shows the effect of the filler composition on water absorption of UPR composites filled with 4% compatibilizer addition.

![Figure 5](image)

**Figure 5.** The effect of the filler composition on water absorption of UPR composites filled with 4% compatibilizer addition.

This property indicates whether a composite can incur damage when used in the submerged condition. When the composite is immersed in water, the water diffuses into the composite. This should be avoided because water can damage the composite structure from the inside, therefore reduces the mechanical properties of the composite. Figure 5 showed a significant increase in water absorption of the composite, especially in the first 24 hours. At the initial immersion (24 hours), the ability of the filler to absorb water was still very high and caused more water to penetrate the composite, resulting in a significant increase in water absorption value at the beginning of immersion. After that, the absorption of water in the composite material was no longer significant. This was because the ability of the composite in absorbing water has decreased until it finally reaches the saturation point of water absorption (stop absorbing water). The connection between the number of fillers and water absorption can also be observed in that the increasing number of fillers increases composite water absorption. This is because the moisture content in the fiber was affected by various hemicellulose and lignin. If the hemicellulose and lignin content decreased then the moisture absorption of natural fiber also decreased [12].

3.4 FTIR (Fourier Transform Infrared)
Figure 6 shows the FTIR characteristics of UPR composites contained 5% of Filler with and without the addition of MA.
Figure 6. The FTIR characteristics of UPR composites contained 5% of filler with and without the addition of MA.

FTIR analysis aimed at determining the formation of functional clusters of cellulose filler UPR and MA compatibilizer. From Figure 6, it can be observed that there was a decrease in the absorption peak of the wavenumber at 3363.8 cm\(^{-1}\) which was the strain of alcohol (OH) indicating that the addition of MA compatibilizer modifies/bound the peanut shell filler that contained cellulose, and the UPR matrix. The fracture of the carbon group of the UPR at the wave number 2924.09 cm\(^{-1}\) showed the alkane group on the UPR which acted as a matrix. The emergence of wave numbers at 752.2 cm\(^{-1}\) and 1623.40 cm\(^{-1}\) which are aromatic and alkene groups derived from the molecular structure of MA where the pentagonal group C aromatic ring which bound the double bond with the group O that formed alkene group. At 1269.12 cm\(^{-1}\) was an ether group (C-O) where the MA content was observed in the mixture of the cellulose with the UPR so that the interface strength increased and multiplied the hardness of the composite product. At 580.2 cm\(^{-1}\) and 512.2 cm\(^{-1}\) waves indicated chloride group in which the peanut shell cellulose filler was cleaned by hydrolyzing it using a hydrochloric acid solution (HCl) to formed cellulose which could bind properly with a UPR matrix. After the addition of MA as a compatibilizer of UPR matrix and cellulose filler, there was a noticeable change in the FTIR graph between the two curves at the waves of 752.2 cm\(^{-1}\) and 1269.12 cm\(^{-1}\). The wavelength was included in the range of the ether group (C-O) and the aromatic group. The C-O group was obtained from cellulose groups derived from peanut shell powder in which the carbon group of the original cellulose bound with the O group of MA. On the other hand, the aromatic group derived from MA which would subsequently be bound with a UPR matrix so that the MA in this study served as compatibilizer/connecting matrix and fillers can result in strong interface bonding.

3.5 SEM (Scanning Electron Microscope)
Figure 7 shows the morphology of the composites with different filler content.
The morphology of UPR composite with 4% MA Contained (a) 5% of filler and (b) 7.5% of filler.

The purpose of the SEM analysis was to determine the void fraction in the composite. Figure 7(a) showed the result of SEM composite analysis by the addition of peanut shell cellulose filler and MA compatibilizer. Figure 7(a) showed the fracture of the composite which had a dense morphology. This was caused by tensile forces experienced by the composite during the tensile strength test. The pull given to the composite agitated the composite bond which was indicated by the formation of laxity or uneven surface and it can be observed that the filler sufficiently filled the entire surface of the matrix.

Figure 7(b) showed the result of SEM analysis of product composite at 7.5% composition on the fractured section with 500 times magnification. Figure 7(b) showed a composite surface where the peanut shell powder cellulose with compatibilizer (MA) that served only as a matrix strengthener. The filler was not enough to fill all the matrix. But, the cellulose fillers were not well dispersed.

4. Conclusion

The addition of peanut shell powder filler in the composite can increase the tensile properties of the composite. The addition of 4% of MA and 5% of filler is the optimum limit to produce the highest tensile properties and energy impact. It is around 26.041 MPa for tensile strength, 7.5% for young modulus and 100 J/mm² for energy impact. Meanwhile, the effect of fillers addition will be increasing water absorption’s value. It can be concluded from the FTIR results that the matrix and a filler will make a strong interface bonding. It can be observed at 5% of filler, the filler sufficiently filled the entire surface of the matrix, but, at 7.5% of filler addition, the fillers were not well dispersed.

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