

Characterization of Polypropylene Composite Reinforced with Wood Flour or Cellulose Fiber

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Abstract. The use of lignocellulosic materials as reinforced polymer composite has been in great demand during the last decade due to some of its advantages. The lignocellulosic material may be in the form of wood flour or cellulose fiber, both of which have different properties and structures due to effects of the resulting composite product. This study aims was to compare lignocellulosic materials as reinforcing agent in polypropylene composite, i.e in the form of wood flour or cellulose fibers. The characterization conducted were the physical and mechanical properties of the composite. The characteristics of lignocellulose materials were investigated using FTIR and XRD analysis. Cellulose fibers were obtained by pulping with an alkaline solution, followed by bleaching treatment. The results showed that the chemical treatments could increased the crystallinity of the fibers, therefore resulted in an increase of physical and mechanical properties of polypropylene composites.

1. Introduction

The use of natural fibers in the plastic composite products is in great demand now days. Natural fiber has several advantages, such as low cost, easy processing and biodegradable [1,2]. The problem in making plastic composites so far is the compatibility between hydrophilic cellulose and the hydrophobic polymer matrix. The content of wood materials, consisting of cellulose (40-50%), hemicellulose (20-30%), lignin (20-30%) and small amounts of inorganic and extractive materials [1,3]. Wood has hygroscopic properties (can absorb and release water from the surrounding environment) due to the presence of hydroxyl groups in the wood component. Therefore wood has hydrophilic properties (strong water absorbing ability), rigidity and can be biologically degraded. This property causes cause wood is not easy to be combined with non-organic materials such as hydrophobic (water-resistant) plastics. Combination of these two different properties materials will result in weak bond between fiber and matrix, and make it incompatible with a hydrophobic plastic matrix, due to the low wettability and weakness of the interface [4, 5, 6]. A weak bond between a hydrophilic fiber and a hydrophobic matrix can affect the physical and mechanical properties of the composite product. Faruk *et.al* [7] explains that in order to increase the interfacial adhesion between fibers and matrices, modifications must be made to one of the components. Modification of fibers can be done by physical and chemical methods. Corona / plasma and mercerisation are used to influence mechanical bonding with the polymer matrix. While the chemical fiber modification is used to form reaction of the hydroxyl group on the fiber with the appropriate reactive compound to form a covalent bond. The newly formed group will act as an interface between the fibers and matrix resulted in better



properties composites. Another chemical modification is the use of additional component to matrix and fiber known as compatibilizer or coupling agents. The coupling agent serves to modify one or both composite components in order to improve the adhesion [8]. In this study, plastic composites were made using fillers of wood powder and purified fibers (cellulose fibers), then evaluate the characteristics of the plastic composite.

2. Materials and methods

The material used in this research was *Eucalyptus pellita* wood fiber obtained from PT. TPL sector AekNauli. Polypropylene impact copolymer (block copolymer) BI9.0GA was obtained from PT. Chandra Asri Petrochemical, Cilegon. The most important characteristic of the BI9.0GA impact copolymer (block copolymer) is the impact resistance(not easily broken), low temperature resistance (reaching -30°C), melt flow rate (MFR) 9.0 g / 10 min and density 0.9 g / cm^3 . The coupling agent used was Licocene PPMA 6452 TP (Clariant Chemical, Ltd. German). Characteristics of Licocene PPMA 6452 TP are acid number: 41 mg KOH / g, softening point: 143°C , density: 0.93 g / cm^3 and 7% grafting rate of maleic anhydride. Chemicals used in this study (pro analysis grade) include sulfuric acid (95%), ethanol, benzene, sodium chlorite (NaClO_2), acetic acid, sodium hydroxide, distilled water and hydrochloric acid.

Fibers were produced by pulping process using 25% NaOH solution at $160\text{--}170^{\circ}\text{C}$, 8 atm. Then the fibers were washed with water until neutral pH. The bleaching process conducted with hypochlorite solution in 4 cycles.

2.1. Composite Manufacture

Preparation of composites was carried out through the following stages: the blending of wood flour/cellulose fibers, polypropylene (PP) matrix and maleated polypropylene (MAPP) coupling agent using HaakePolydrive lab plastomill at 175°C , 60 rpm for 20 min. Three different compositions (percentage) between fiber / PP / MAPP of the material used were 30/65/5, 40/55/5 and 50/45/5. Furthermore, the mixture was formed into a pellet, then made into a sheet/composite size 11 x 11 cm by using hot presses at a temperature of 180°C for 20 min. After that it was cooled for 10 minutes. Furthermore, the resulting composite was conditioned at room temperature.

2.2. Fiber and Composite Characterization

Determination of the degree of crystallinity was conducted by measuring the structure and Miller index of fiber using X-Ray Diffraction at 40kV and 30 mA, an angle of $10^{\circ}\text{--}40^{\circ}$ with $\text{CuK}\alpha$ radiation Ni filter ($\lambda = 1.54060 \text{ \AA}$) as well as JCPDS analysis. The molecular functional group bonding analysis and the absorption band change were performed using ABB MB 3000 (Reliable FTIR Laboratory Analyzer, Canada) at wave numbers $4450\text{--}500 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The sample analysis was performed by placing 2 mg of sample in KBr powder (0.4 g) to obtain KBr-IR pellet. The entire spectra will be recorded at room temperature condition. In particular this procedure produced spectral data of the relationship between absorbance and wave number.

Physical properties of composite films analysis including water absorption and thickness swelling used sample size of 2x2 cm. Before the testings were conducted, the weight and thickness of each sample were measured. Subsequently the sample was immersed in aquades at room temperature for two days. After two days each sample was wiped with tissue paper to remove residual water and then weighed and measured its thickness. The mechanical properties testing include tensile strength, modulus young and break elongation of composite film were conducted based on ASTM D882-75b (Standard Test Method for Tensile Properties of Thin Plastic Sheeting) at 50 mm / min crosshead speed.

3. Results and Discussion

3.1 X-ray Diffraction Analysis

X-ray diffraction patterns of the lignocellulose materials showed improvement of cellulose structure after bleaching treatment. Bleached pulp showed the highest crystallinity value of 61.16% followed by

pulp (50.49%) and wood flour (31.31%) as shown in **Figure 1**. Fiber composition was modified by removing the amorphous portion of the fiber increased the crystallinity of the fiber.

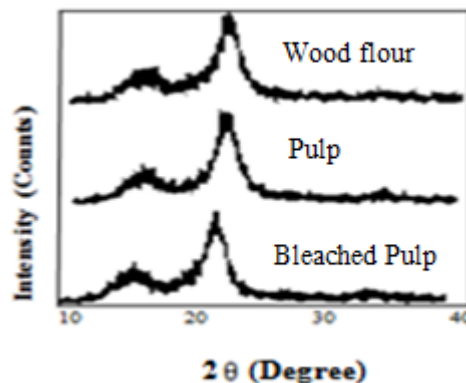


Figure 1. Diffraction Results of X-ray Wood Flour and Fibers

3.2 FTIR analysis

FTIR spectra indicated the formation of new chemical functional groups after pulping and bleaching treatment. In general, the entire sample spectrum confirmed the presence of absorption bands of xylan, glucomannan and cellulose as pulp-making chemical components. The presence of glucomannan was indicated by peak in an area of $800\text{--}900\text{ cm}^{-1}$. The presence of absorption at peak 1700 , 1600 and 1200 cm^{-1} showed the presence of xylan. The presence of cellulose was indicated by peak 1100 , 1300 and 1400 cm^{-1} as well as changes in CH and OH waves in regions 2900 and 3300 cm^{-1} . The entire infrared spectrum of the sample still showed the presence of lignin in the uptake range of 1500 cm^{-1} [9,10, 11, 12].

In peak 952 cm^{-1} (**Figure 2**) there was a peak change between fiber without treatment and fiber with pulping and bleaching treatment. Absorbance of clusters ($\text{C}=\text{O}$) at peak 952 cm^{-1} were 0.65, 0.68 and 0.60. These changes occurred due to the degradation of lignin, cellulose and hemicellulose content in the composites with each treatment.

Before the pulping and bleaching treatment, the absorbance of carbon group (C-H) at the point 2788 cm^{-1} was 0.12 and after the pulping process were 0.30 and 0.29. The addition of carbon clusters showed that composite films were degraded due to the influence of pulping and bleaching processes. The change of every 2788 cm^{-1} peak was influenced by changes that occur in the content of lignin, cellulose and hemicellulose. As stated by [13,14] that peak changes in each fiber treatment are due to stretching of cellulose, hemicellulose and lignin vibrations and the occurrence of C-H deformation of cellulose and lignin.

OH group with absorbance 0.31 was found in composite film at point 3456 cm^{-1} . This is due to the matrix and the wood powder separation created a cavity that allows the presence of OH groups attached to the composite film. After pulping and purifying process, the absorbance of OH groups were 0.41 and 0.31. This was possible at the time of pulping due to the presence of water bound to OH. The absorbance decreased in the bleaching process because of the bond between the fibers and the matrix is better. The process of crystallinity of fiber composite film can occur by estimating the strain ratio. A decrease in the strain ratio will cause a decrease in crystallinity. According to FTIR, pulp bleaching results had a higher crystallinity value than those of all treatments [13,15,16]. The higher the crystallinity value means the better the physical and mechanical properties of the composite.

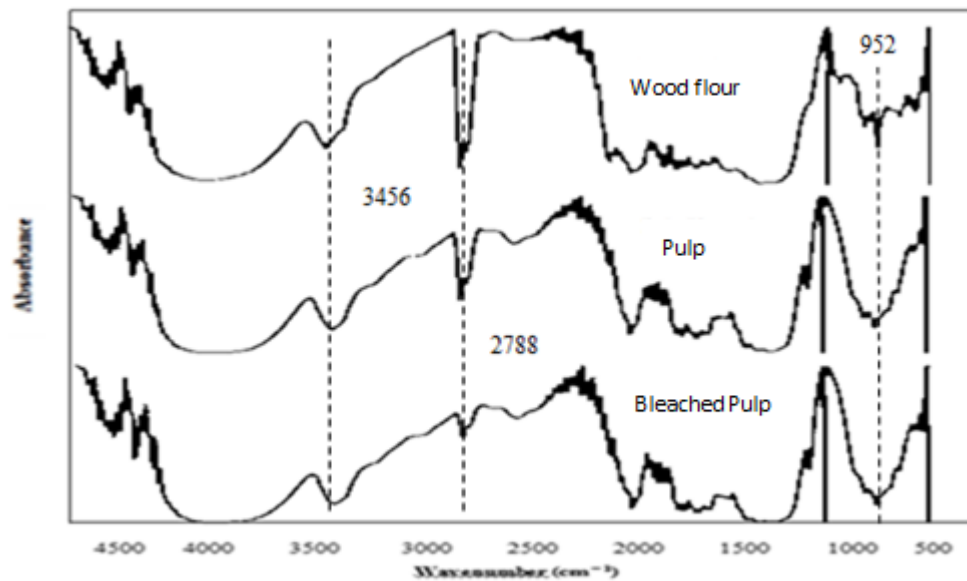


Figure 2. Characteristics of Infrared Fibers Spectra

3.3 Physical and Mechanical Characteristics of Plastic Composites

Figure 3 shows the composite film density values in the range 0.40 - 0.83 g / cm³. Density is one of the physical properties that is very influential on the quality of composite film. A relatively high density indicates that the resilience of the composite film is high [17]. This is in accordance with the statement of [17] that basically, composites can be made from various cellulose fibers and the higher the density, the higher the mechanical properties.

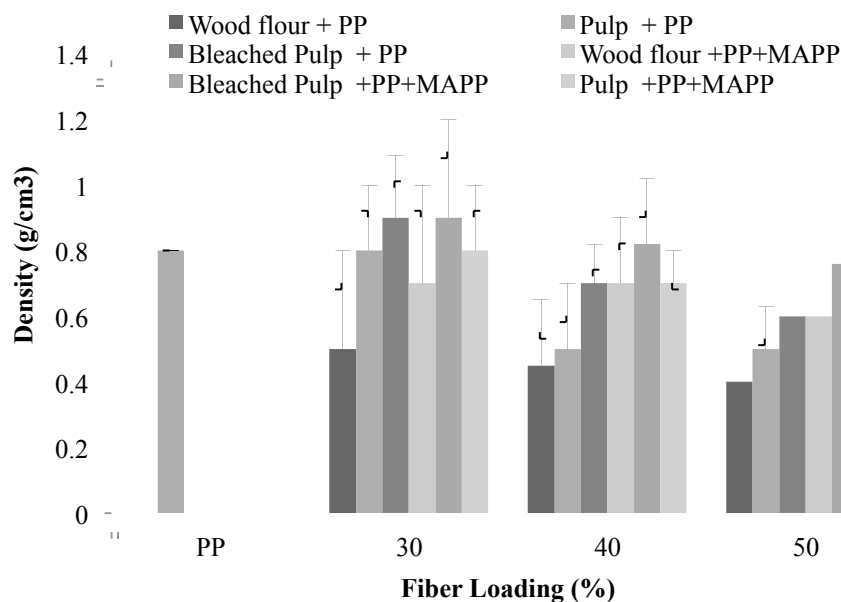


Figure 3. Density of plastic composite

Figure 4 shows the average water absorption rate of a composite film immersed for 24 hours. The water absorption of film composite soaked for 24 hours ranged from 2% - 10%. Although the PP used as an adhesive is a hydrophobic material, but due to different fiber and

matrix compositions, it was likely that not all fibers were covered by adhesives. Thus the water can still enter either through the film cavities or the pores of the fibers. According to [1], although the general perception states that wood fibers in wood plastic products (WPC) are encased by resin plastics, but in fact the water absorption still occurs in commercial WPC products. Water absorption occurs on wood particles for example, on the part near the surface of the film rather than the plastic phase.

The water absorption of composite film without MAPP tended to be higher than of the composite film with MAPP. This was happening because when the composite was soaked, the compatibilizer successfully glue the dust matrix well so that the water absorption becomes low.

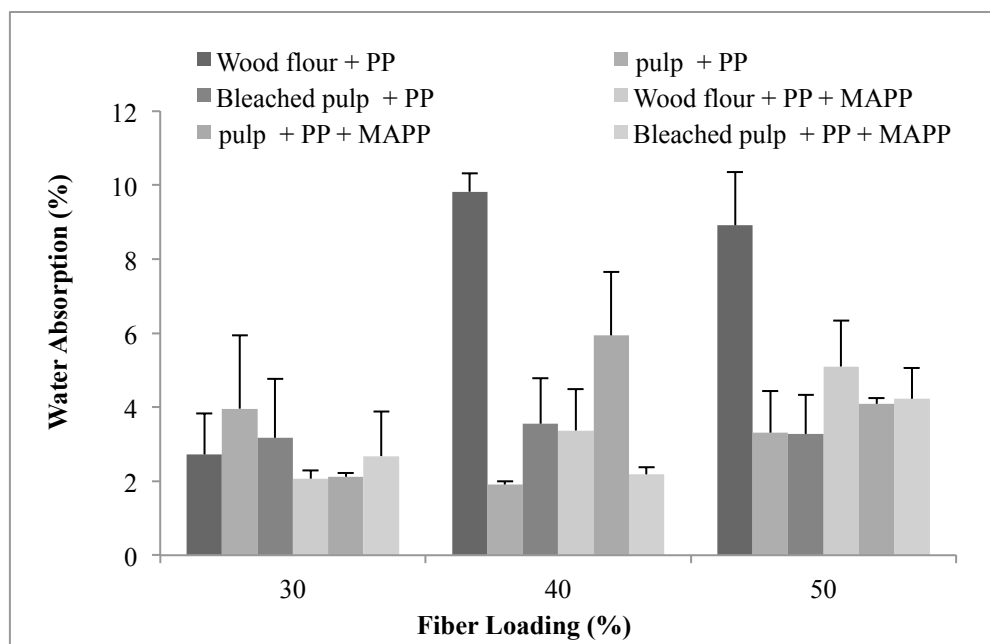


Figure 4. Water Absorption of the plastic composite

Averagely, film thickness was swelling after soaking for 24 hours in water. The increment of composite film thickness after 24 hours varied between 7% - 30% (**Figure 5**). The high value of the composite film thickness was in line with Manning, et.al [12], the varies fibers and matix composition of fibers and matrix varies so that the fibers are not completely covered by matrix, compatibilizer and showed high water absorption.

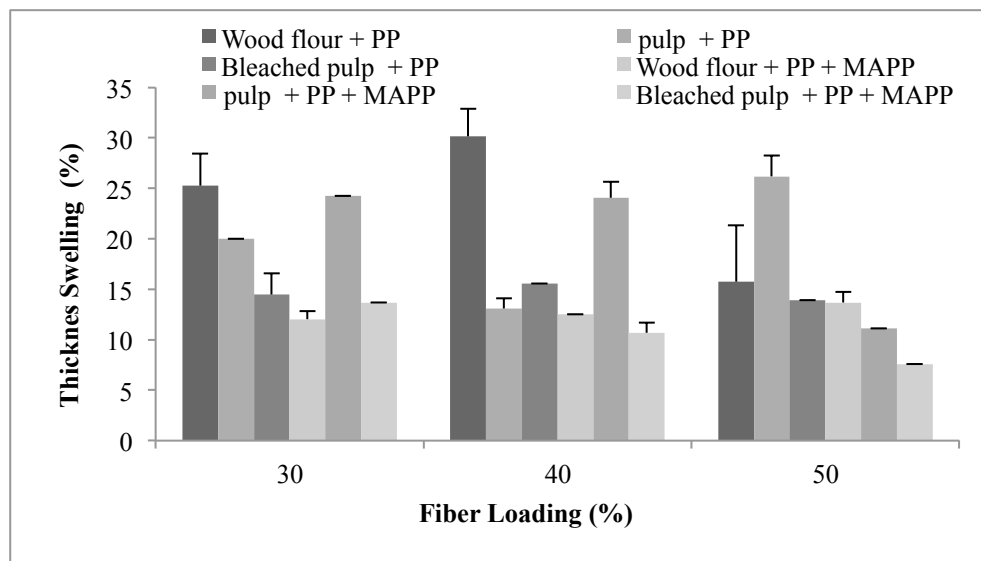


Figure 5. Thickness Swelling of Plastic Composites

The tensile strength values of the composite film tend to decrease with the reduced number of matrices. The low matrix composition resulted in low cohesiveness and interface interaction with fiber as a consequence reduced material capacity to withstand loads. Tensile strength values for composite films of wood powder and control pulps ranged from 13 to 36 MPa. While the tensile strength value for the composite film of the bleached pulp were between 17 - 35 MPa (**Figure 6**). The results showed that the composite film of bleached pulp had a greater range of tensile strength values compared to the composite film of the wood flour and the control pulp. This was due to the variation in fiber and matrix composition and the compatibilizer causing reaction between MAPP additive and matrix was well. Besides, purification process of cellulose fibers which removes amorphous portion causes the fibers to be more stable as shown by increasing crystallinity values. The increase of crystallinity value has an impact on the increase of compatibility between fiber and matrix. Furthermore, the adhesion between matrix and fiber increased, resulting in the compatibility of composite film.

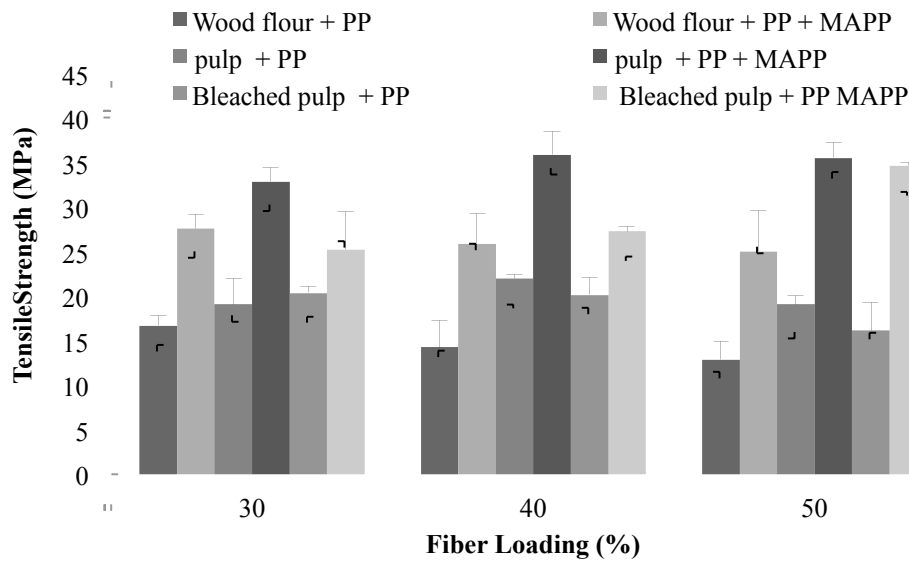


Figure 6. Tensile Strength of Plastic Composites

The modulus young values for composite film of wood flour and pulp ranged from 1 - 2.2 GPa. While the modulus young values for the composite film of the bleached pulp were between 1.5 - 3.3 GPa. The result showed that the composite film of the bleached pulp had a larger range of modulus young values compared to the composite film reinforced with wood flour and the pulp (**Figure 7**). This is because the fibers and matrix are mixed evenly and well bonded by MAPP so that the compatibility of the resulting composite film was achieved.

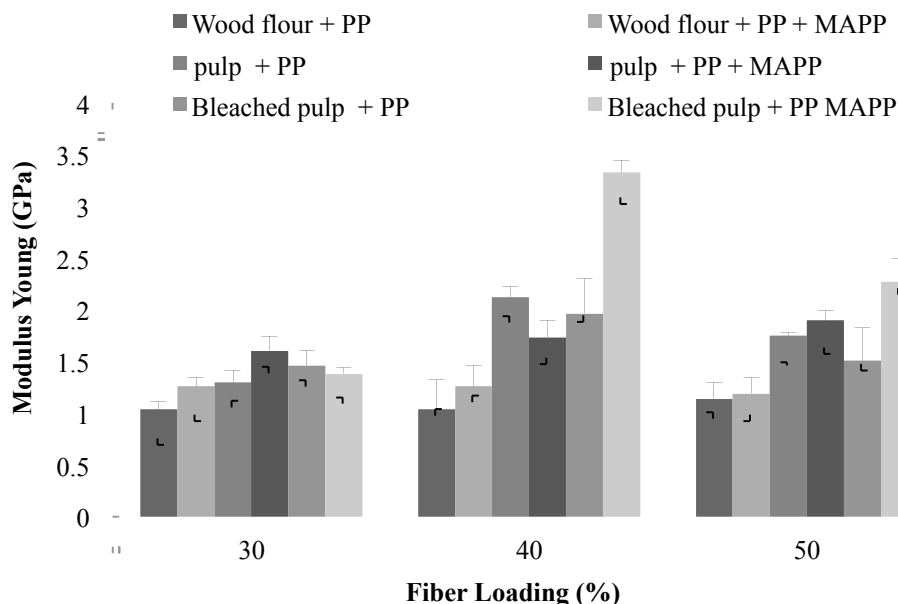


Figure 7. Modulus Young of Plastic Composites

The values of break elongation for film composite of wood powder and control pulps ranged from 3.3 to 5.1 (%). While the value of fracture element for the composite film of the bleaching pulp ranged from 2.8 to 4.5 (%). The result shows that the composite film of the

bleaching pulp has a smaller fault elongation range compared to the composite film of the wood powder and the control pulp (**Figure 8**). The higher the number of fibers so that the value of fission breakdown will decrease. The highest elongation value is in the number of 70% matrix. It is assumed that smaller fiber size increases the surface area of the filler while the number of matrices remains, so that there may be some uncoated filler by the PP matrix optimally.

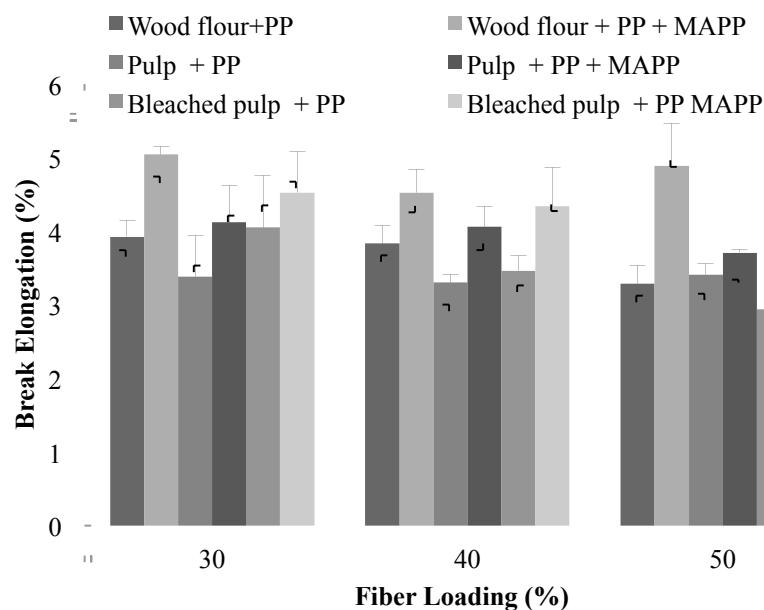


Figure 8. Break Elongation of Plastic Composite

4. Conclusions

Chemical treatment increased the fiber crystallinity value from 31.31% to 61.16%. The increase of crystallinity value has an effect on the increase of physical and mechanical properties. The optimum physical and mechanical properties of plastic composites are shown by the plastic composites reinforced cellulose fiber with the addition of MAPP. This is due to removal of the amorphous region (hemicellulose) at purification process, so that the fibers are more stable, and the addition of MAPP further improves its interfaces.

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5. Reference

- [1] Ndiaye D and Tidjani A 2012 Effects of coupling agents on thermal behavior and mechanical properties of wood flour/polypropylene composites *Journal of Composite Materials* **46(24)** 3067–3075
- [2] Lu T, Jiang M, Jiang Z, Hui D, Wang Z and Zou Z 2013 Effect of Surface Modification of Bamboo Cellulose Fibers on Mechanical Properties of Cellulose/Epoxy Composite *Composites: Part B* **51** 28-34

- [3] Ye X, Wang H, Zheng K, Wu Z, Zhou H, Tian K, Su Z and Tian X 2016 The interface designing and reinforced features of wood fiber/polypropylene composites: Wood fiber adopting nano-zinc-oxidecoating via ion assembly *Composites Science and Technology* **124** 1-9
- [4] Li Z, Zhou X and Pei C 2011 Research Article Effect of Sisal Fiber Surface Treatment on Properties of Sisal Fiber Reinforced Polylactide Composites *International Journal of Polymer Science* DOI 10.1155/2011/803428
- [5] Lima PRL, Santos RJ, Ferreira SR and Filho RDT 2014 Characterization And Treatment Of Sisal Fiber Residues For Cement-Based Composite Application *Eng. Agric., Jaboticabal.* **34(5)** 812-825
- [6] Taramian A, Doosthoseini K, Mirshokraii SA and Faezipour M 2007 Particleboard manufacturing: an innovative way to recycle paper sludge *Waste management* **27(12)** 1739-1746 DOI 10.1016/j.wasman.2006.09.009
- [7] Faruk O, Bledzki AK, Fink HP and Sain M 2012 Biocomposites reinforced with natural fibers: 2000–2010. *Prog. Polym. Sci.* **37(11)** 1552-1596 DOI 10.1016/j.progpolymsci.2012.04.003
- [8] Lu JZ, Wu Q, Harold S and McNabb J 2000 Chemical Coupling in Wood Fiber and Polymer Composites: A Review of Coupling Agents and Treatments *Wood Fiber Sci.* **32(1)** 88-104
- [9] Bivi RM, Siti NFMD, Khairulmazmi A, Idris A, Ahmed OH, Zamri R and Sariah M 2012 *In vitro* effects of salicylic acid, calcium, and copper ions on growth and sporulation of *Ganoderma boninense* *Afr. J. Biotechnol.* **11(70)** 13477- 13489
- [10] Arbelaiz A, Fernandez B and Cantero G 2005 Mechanical properties of flax fiber/polypropylene composites. Influence of fiber/matrix modification and glass fiber hybridization *Composites Part A: Applied Science and Manufacturing* **36** 1637-1644
- [11] Casey M 1980 Effect of Fiber Pretreatment Conditioning on Interfacial Strength and Mechanical Properties of Wood Fiber/PP Composites *Journal of Applied Polymer Science* **41** 1245-1252
- [12] Manning MJ, Ascherl FM and Mankowski ME 2006 Wood-plastic composite durability and the compelling case for field testing In: *Yusoff MNM et al.* editor. *Advance and Challenges in Biocomposites Symposium. Proceedings of the 8th Pacific Rim Bio-Based Composites*; Kuala Lumpur **92** 19-27
- [13] Fahma F, Iwamoto S, Hori N, Iwata T and Takemura A 2010 Isolation, Preparation, and Characterization of nanofibers from oil palm-empty-fruti-bunch (OPEFB) *Cellulose* **17** 977-985
- [14] Popescu CM, Popescu MC, Singurel G, Vasile C, Argyropoulos DS and Willfor S 2007 Spectral Characterization of Eucalyptus Wood *Applied Spectroscopy* **61(11)** 1168-1177
- [15] Chen Z, Hu TQ, Jang HF and Grant E 2016 Multivariate Analysis of Hemicelluloses in Bleached Kraft Pulp Using Infrared Spectroscopy *Applied Spectroscopy* **70(12)** 1981-1993
- [16] Rosa MF, Medeiros ES, Malmonge JA, Gregorski KS, Wood DF, Mattoso LHC, Glenn G, Orts WJ and Imam SH 2010 Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior *Carbohydr. Polym.* **81** 83–92
- [17] Bjarnestad S and Dahlman O 2002 Chemical compositions of hardwood and softwood pulps employing photoacoustic fourier transform infrared spectroscopy in combination with partial least-squares analysis *Analytical Chemistry* **74(22)** 5851-5858