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The behavior of compatibility of Ap-g-PHMA to impact polypropylene/kenaf fibres composites

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Abstract. In this research, the behavior of poly(hexyl methacrylate (PHMA) grafted to Amylopectin (Ap-g-PHMA) as a compatibilizer on isotactic polypropylene (iPP)/kenaf fibres composites was studied. In order to improve interfacial interaction between hydrophilic kenaf fibre and hydrophobic matrix polypropylene (PP), Ap-g-PHMA is used as a compatibilizer. Field Emission Scanning Electron Microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FTIR), and mechanical testing were used for the composite characterization. The properties of binary and ternary systems have been analysed as a function of both fibre and compatibilizer content. All compatibilizer systems showed enhanced fibre dispersion and interfacial adhesion. It was found that using Ap-g-PHMA has a significant effect on composite properties. Fibre loading at 40% ratio showed very good effect regarding mechanical properties with 1% compatible agent. It is concluded, that incorporation of coupling agent had shown a better result than that of without it at a certain level of fibre loading.

Keywords: Compatibilizer, Ap-g-PHMA, Polypropylene/Kenaf fibre, morphology, mechanical and thermal properties.

1. Introduction

Polymer composites-based on natural fibres are currently of concern in the innovation of materials for various applications, such as automotive, building, appliance, packaging materials as well as biomaterials. The main advantages of natural fibres are biodegradable, renewable, low cost, low density, and high toughness. Unfortunately, their compatibility between fibre and the polymer matrix is very weak, has low fibre dispersion, such as too low moisture barriers, thereby decreasing material performance. Moreover, polymer composites -based on natural fibres will give great impact on the composite nature, which is related to particle size, dispersion, and geometry of the filler in the matrix. In order to improve the interaction between fibres and polymers, surface modification of fibres and polymer functional is needed, as well as the necessary addition of compatibilizer [1].



To improve interfacial adhesion in composites with natural fibres can be treated by physical/chemical fibre interface or using specific compatibilizer. Chemical modification using compatible agent reactive group, such as using the hydroxyl functional groups of the fibre surface, while the other side is left to copolymerize with the matrix, is a very interesting way to allow the formation of covalent bonds between fibres and matrix, so as to improve mechanical properties [2]. More than forty substances as compatible agents have been used in production and research areas. Among these materials, one of the most popular is the maleated polypropylene (MAPP). With MAPP, it is found that the interfacial bonding strength, flexural modulus, and other mechanical properties increased with 3% concentration. Imre and Pukánszky [3] reported that the silane-modified polymer increased the interfacial adhesion between fibre and matrix, and this effect is better than that obtained for the composite MAPP. Handayani *et al.* [4] has developed poly(methyl methacrylate) (PMMA) grafted to Amylopectin (Amylopectin-g-PMMA) as well as poly(hexyl methacrylate) (PHMA) (Amylopectin-g-PHMA) copolymers for compatibilizer agent. The performance of Ap-g-PHMA copolymers has been studied in composite PP/CFF, and it was showed that compatibility of PP/CFF composites increased with the addition of Ap-g-PHMA, as well as dispersion, interfacial adhesion, and tensile strength properties.

A lignocellulose natural fibre such as sisal, coir, jute, hemp, pineapple leaves, and kenaf are potential as composites reinforcement. These fibres have many interesting specific properties, such as high stiffness, impact resistance, flexible, and flexural modulus. In addition, fibre is available in large quantities, it is renewable and biodegradable. Other desirable characteristics include low cost and low density. Hydrophilic of the natural fibres produces, high water absorption and weak adhesion to the hydrophobic matrix [5]. Natural fibres can be treated to improve the adhesion between natural fibres hydrophilic and hydrophobic polymer matrix, such as by alkali treatment, acetylation, maleic anhydride treatment, etc [6]. Cellulose has a great potential as polymer reinforcement since it is not easy to disperse in the polymer, because it is high polarity. That is one of the major challenges to overcome.

The homogeneousness of particle size will facilitate dispersion in the polymers, because of high energy surface will enhance the surface dispersion. Cellulose must be altered from hydrophilic to more hydrophobic, the hydrophilic behaviour of cellulose associated with the hydroxyl group in the fibre surface. Different chemical modifications have been used in previous studies to enhance the hydrophobicity of fibres [7]. Acetylation is chemical modification where the chemical compound reacts with a hydroxyl group on the cellulose so that the hydrophilic surface modification cellulose became more hydrophobic. Acetylation of cellulose depends on the accessibility and liability of OH-groups in the amorphous and crystalline regions in the cellulosic polymer chain [6].

The purpose of this research is to study the performance of biocomposites iPP/Kenaf due to the effect of Ap-g-PHMA addition as a compatible agent. iPP can't mix with Kenaf due to differences in their nature; hydrophilic and hydrophobic, respectively, without addition of compatible agent. On the other side, with Ap-g-PHMA addition as a compatible agent, the iPP and Kenaf can mix together because its hybrid nature which can bond with hydrophobic and hydrophilic site. Moreover, resulted biocomposite is expected to have good characteristic, for example good tensile strength.

2. Material and Method

2.1. Materials

2,2'-Bipyridine (bipy) (99%) and DMSO-d (99.9%) were purchased from Sigma-Aldrich. Ethyl α -bromoisobutyrate, EBiB (99%), amylopectin (α -1,4-glucan with α -1,6-cross-linking; one terminal group per 25 glucose units) and Hexyl methacrylate (HMA) were purchased from Sigma-Aldrich. CuCl (I) and CuCl (II) with purity 99.9% were purchased from Merck. DMF (99.9%), THF (99.9%) and DMSO (99.9%) as a solvent were purchased from Merck. Isotactic Polypropylene (iPP) with MFR 10 g/10 min was supplied from Candra Asri Petrochemical (CPAC-Indonesia), Kenaf fibres were supplied by Department of Metallurgy and Materials (Universitas Indonesia), and the fibres were ground in a Polymer laboratory (Institut Teknologi Indonesia) up to 300 μ m and the treated by caustic soda to remove impurities. MAPP was supplied from PPK-LIPI (Bandung).

2.2. Chemical Modification and Compatibilizer

2.2.1. Synthesis of Amylopectin macro-initiator (Ap-EBiB). Amylopectin macro-initiator (Ap-EBiB) was obtained by reacting amylopectin with EBiB as described previously [4].

2.2.2. Synthesis of Compatibilizer amylopectin-graft-PHMA (Ap-g-PHMA). Copolymerization of Ap-g-PHMA was obtained by reacting Ap-EBiB with (HMA) and (BPy/CuCl+CuCl₂) ATRP catalyst system in mixed media reaction (DMF:H₂O) as previously described [4].

2.2.3. Acetylation of Kenaf Fibre. Kenaf was extracted with mixed of acetone and methanol (2:1 v/v) in a soxhlet extractor for 6 hours before acetylation. The extracted fibre was dried in the oven at 100°C for overnight and then it was cooled in a desiccator. 10 g fibre was placed in an oven-dried of 500 mL round-bottom flask and was filled with a sufficient amount of acetic anhydride and 5% by weight of pyridine to ensure that the fibres were completely covered with the reagent. To avoid thermal degradation of fibre, the flask was heated at 100°C under reflux at atmospheric pressure. The reaction was conducted for 4 hours, and at the end of the reaction, the treated fibre was extracted using acetone and methanol (2:1 by volume) in a Soxhlet extractor for 6 hours to remove unreacted acetic anhydride and acetic acid by-product. Acetate fibres were dried in an oven at 100°C for overnight, then it was placed in a desiccator and held at room temperature [7].

2.3. Mixing Procedure

Kenaf fibre is dried at 80°C until its moisture content reached below 5%. The fibres were compounded into a polypropylene impact in the Minilab II Haake™ Rheomix CTW 5 conical twin-screw extruder (Thermo Scientific Haake GmbH, Karlsruhe, Germany), that provide with a barrel temperature of 160°C ± 20°C from the feeding zone to the dead zone, respectively. Fibres dried in an oven at 105°C for 24 hours before compounding to achieve a moisture content of less than 5%. 2 levels of load prepared for all composites. Fibre contents entered for kenaf fibre composite with a weight ratio of 40 (by weight) and concentration of compatible agent are 1,2 and 3% (by weight). Samples were compounded arranged in test specimens by injection moulded using a 20-ton Battlefield BA 200CD Plus machine, with a UNILOG 4000 control system (closed-loop control). A mould from Master mold Inc, having cavities for tensile specimens according to ASTM D638 Type 1 and rectangular bar, 125 mm x 12.5 mm x 3.13 mm, was used to produce test specimens.

2.4. Characterization

Tensile tests were carried out using an Instrons machine with a load cell of 5 kN. Tests were performed as specified in ASTM D 638-Type I: a Test method for tensile properties of plastic. The gauge length was 50 mm and the crosshead speed of testing was 50 mm/min. Five specimens were tested for each batch. Tensile modulus (TM) and tensile strength (TS) were taken for analysis.

Scanning Electron Microscopy (SEM) micrograph were taken to examine on the surfaces of bulk samples and films, Freeze-Fractured in liquid nitrogen; the samples were sputter-coated with a fine layer of gold in an Edward sputter coater and analysed with a QUANTA 200 FEG scanning electron microscope (FE-SEM).

The Fourier transforms infrared (FTIR) analyses of IPP/CFF/PP-g-MA, IPP/CFF/Ap-g-PHMA and IPP/CFF were performed using a Perkin-Elmer FTIR spectrometer (Spectrum 2000 series, resolution 2.0 cm⁻¹, 100 scans) having diamond Attenuated Total Reflection (ATR) device between 4000-500 cm⁻¹.

3. Result and Discussion

Compatibilizer performance was studied in composite iPP/Kenaf fibres, the addition of the coupling agent will improve the characteristics of composites [3]. The optimal condition processes of Ap-g-PHMA synthesis and kenaf fibre preparation have been established previously [4, 7, 8]. FTIR spectroscopy is used to identify chemical characteristics of the fibre before (b) and after acetylation (a), Ap-g-PHMA compatibilizer and PP/KF composites with Ap-g-PHMA compatible agents, respectively. Fig. 1 shows the FTIR spectra that indicates the functional group changes occur with the addition of a

compatible agent at the wavenumber region of 800-1800 cm^{-1} [1]. Significant peak number of the Ap-g-PHMA carbonyl stretching band ($\text{C}=\text{O}$) at about 1721 cm^{-1} (c) was shifted to 1745-1746 cm^{-1} for (d,e,f) were recorded, as well as the changes of hydroxyl group ($\text{C}-\text{OH}$), hydrocarbon groups ($\text{C}-\text{H}$) and relevant ether band ($\text{C}-\text{OC}$) stretching in the spectra of cellulose at 1464, 1377, 1176, 1017, 1113, and 1000 cm^{-1} respectively. These findings supported the formation of stable Esther on PP/Kenaf fibre interface [9]. It is known from the literature that after acetylation in FTIR spectra should show an intensive peak near 1234 cm^{-1} , which would be assigned to ester and $\text{C}-\text{O}$ bond [10].

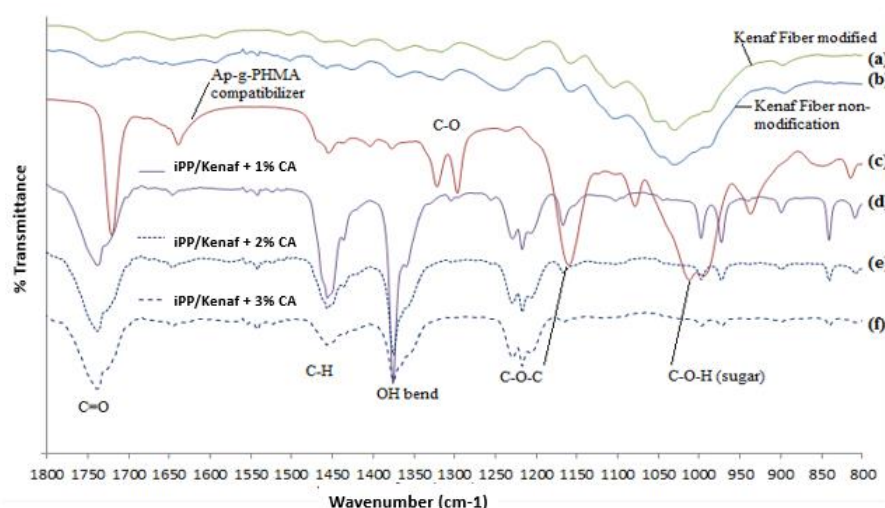


Figure 1. FT-IR spectra of acetylated Kenaf Fibre (line a), Kenaf fibre (line b), and iPP/Kenaf with 1%, 2% and 3% Ap-g-PHMA compatibilizer, respectively (line c-e).

The correlation of chemical structure-properties of PP/Kenaf composites with acetylated cellulose fibres and Ap-g-PHMA will enhance interfacial adhesion and compatibility of the materials. This discussion focused on the effect of compatibilizer on to composite surfaces such as morphology, thermal behavior, mechanical properties and the interaction of fibre/matrix in the systems.

FE-SEM micrographs of the fracture surface of iPP/Kenaf non-acetylated, iPP/Kenaf acetylated, iPP/Kenaf/MAPP, and iPP/Kenaf/Ap-g-PHMA at 160°C composites are presented in Fig. 2. Fig. 2a and 2b explain the difference between fracture of iPP/Kenaf non-acetylated and iPP/KF acetylated, which indicates that Fig. 2b. for iPP/Kenaf acetylated shows a surface fracture with better interfacial adhesion indicated by the surface of fibre moistened with a polymer layer. This is indicated that improved compatibility of treated kenaf to acetic anhydride. But there are still some holes in some spots on the surface that indicated no adhesion between fibre/matrix.

Fig. 2c shows a PP/KF/MAPP composites after the pull, which reflects the drawdown is still strongly bound to the matrix, which shows the interaction between fibre and matrix, there is a failure of interaction between fibres with a matrix that shows the holes where they are left by fibre due to pull. This is due to the MAPP coupling agent which causes strong bonding between matrix and fibre so that the compatibility between materials increases [10]. Composite PP/KF/Ap-g-PHMA at 160 ± 20°C, after pulled shown in Fig. 2d. It is seen that there are holes left by fibres due to pull because of the lack of adhesion between fibre/matrix. On the other hand, there is a pull-out indicating a strong interaction between fibre and matrix. This is caused by the Ap-g-PHMA coupling agent performance to improve mixed compatibility after pulled [11].

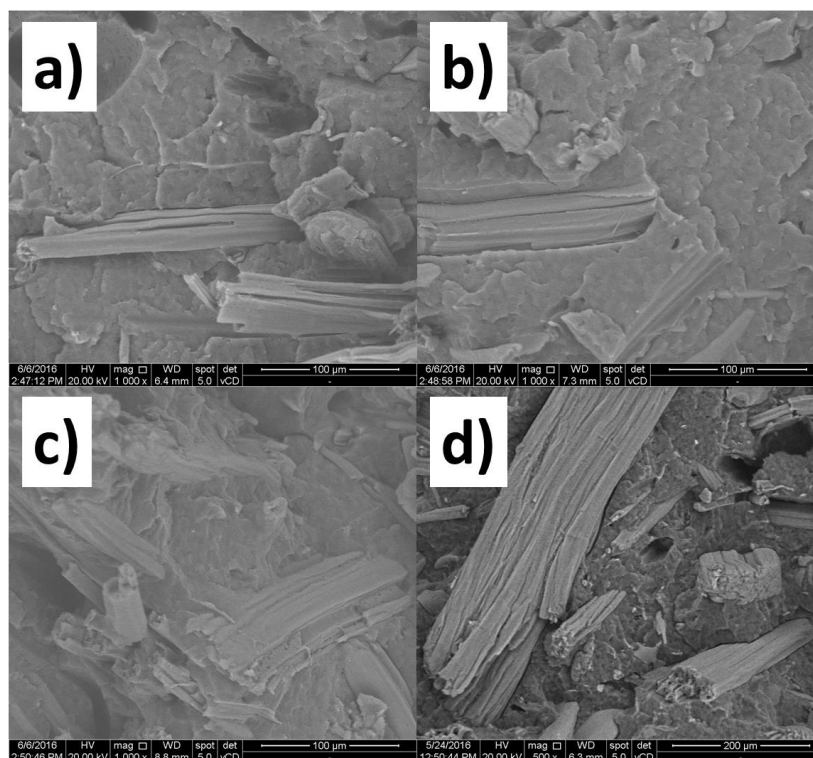


Figure 2. FE-SEM micrographs of a) PP/Kenaf non-Acetylated, b) PP/Kenaf Acetylated, c) PP/Kenaf compatibilized with MAPP, and d) PP/Kenaf Modified compatibilized with 3% Ap-g-PHMA.

The mechanical properties of polymer corresponding composites were identified as a function of fibres and compatibilizer content as shown in Fig. 3. Incorporation of kenaf fibres and Ap-g-PHMA to iPP caused a significant increase of the tensile strength of the composites with 40% fibres compared to iPP/KF un-compatibilized up to 1% compatibilizer after that declined with the addition of Ap-g-PHMA 2-3% [1]. iPP/Kenaf composites with 30% fibres show that the greater content of Ap-g-PHMA indicates that the mechanical properties decreased in this case of tensile strength. This is caused by the low interfacial interaction between iPP/Kenaf composites may result in incompatibilities that affect the decrease in mechanical properties [3].

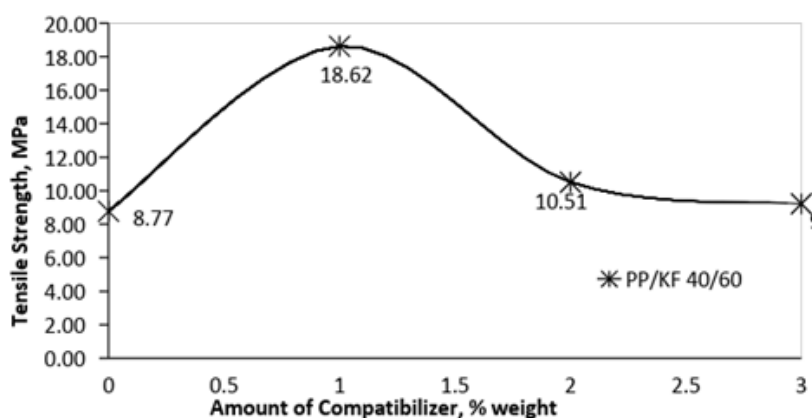


Figure 3. Effect compatibilizer content on Tensile Strength Properties of PP/Kenaf composites.

4. Conclusions

The performance of Ap-g-PHMA as a coupling agent (1-3%) to the PP/Kenaf composites 60/40 showed an increase in mechanical properties with the addition of 1% Ap-g-PHMA. The performances of PP/Kenaf/Ap-g-PHMA 60/40 has Tg 100.57°C and Tm 166.57°C with a tensile strength of 16.33±0.88 MPa. The addition of 1% Ap-g-PHMA improved the tensile strength of about 58% compared to the composites without compatible agents. This value is higher than the PP/Kenaf which is a composite with MAPP compatible agent.

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