Water Absorbency and Mechanical Properties of Kenaf Paper Blended via a Disintegration Technique

Nurul Izzati Mohd Zawawi, a Ainun Zuriyati Mohamed Asa’ri, a,* Luqman Chuah Abdullah, a Hazwani Husna Abdullah, a Jalaluddin Harun, b and Mohammad Jawaid a

In this study, blended paper was prepared by blending synthetic polyethylene (PE) via a disintegration technique. The produced paper was targeted to resist water or moisture. Unbleached kenaf whole stem pulp was used as the main source of fibre in making the paper. The pulp was blended with two types of PE: low-branched (LB) and high-branched (HB) polymers. To study the effect of PE addition to the paper, the water absorbency and mechanical properties were characterized. The pulp to PE mixtures were prepared at ratios of 9:1, 8:2, 7:3, 6:4, and 5:5. Scanning electron microscopy (SEM) showed that the PE was melted between the fibre linkages. The Cobb test determined that the blended paper absorbed less than 20 g/m² of water within 60 s. The best water contact angle successfully achieved was at 84°, which is almost hydrophobic. The mechanical properties, such as tensile strength and tear strength, were in the range of accepted standard requirements. The obtained results indicated that blending via a disintegration technique can be applied in the process of making water-resistant paper. The produced paper is suitable for the manufacturing of water-resistant corrugated packaging materials.

Keywords: Disintegration; Kenaf; Blending; Papermaking; Water-resistant paper; Polyethylene

Contact information:  a: Laboratory of Biopolymer and Derivatives, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor; b: Malaysian Timber Industry Board, Level 13-17 Menara PGRM, No. 8, Jalan Pudu Ulu, Cheras 56100 Kuala Lumpur, Malaysia; *Corresponding author: ainun.introp@gmail.com

INTRODUCTION

Papermaking is ordinarily carried out using natural fibres, which can be derived from woody, non-woody, or agro-based materials. These are biodegradable, recoverable, renewable and low cost resources, so that they can be regarded as well-liked material for papermaking. Due to the presence of hydrophilic groups such as hydroxyl, carboxyl, or sulfonic groups in the paper matrixes, cellulosic paper is able to absorb water or moisture from the surroundings (Jacob and Anandjiwala 2007). This phenomenon may negatively affect paper quality due to the swelled fibres, which contributes to loss of strength under conditions of high humidity or exposure to moisture. Thus, unless appropriate treatments are carried out, natural cellulosic fibers are not, by themselves, ideal for various long-term applications of paper products. Therefore, techniques are found in order to provide hydrophobicity or water repellence properties to the paper surface. Paper has a high level of porosity from 50% to 95% texture, which gives a bulky sheet (Pereira et al. 1999). The porous constructed from the interlocked fibres provide an interconnected network of...
pores opened to the exterior. These pores may be treated in order to block the movement of water.

Water-resistant paper is a kind of paper that is intended to resist water exposure without having major physical changes. If the droplets are placed on the paper surface, a contact angle reading below 90° is considered as less hydrophobic, more than 90° is hydrophobic, and a droplet showing a contact angle over 150° indicates that the surface is superhydrophobic (Yang and Deng 2008; Hu et al. 2009). Paper is commonly and very importantly intended to be used in packaging objects that are susceptible to water. In addition, hydrophobicity is also beneficial for outdoor usage of paper such as maps, guidebooks, and labels that will be exposed to weather. The information contained in the papers may be destroyed or unreadable if the paper changes its form by absorbing water. Various approaches can be used in the making of highly water-resistant papers. One well-used method is referred to as a coating technique, where synthetic or natural substances are used to laminate the paper substrate surface. Another method is the impregnation via an immersion technique. This technique involves the immersion of paper in solutions or dispersions of polymers or formulation substances prior to the drying process. Both techniques involve the preparation or ready-made paper before coating or impregnation takes place. In papermaking practices, internal sizing, surface sizing, and surface coating are the techniques that may produce water resistance properties. However, the levels of water resistance obtained via internal or surface sizing generally are not enough to meet the requirements for high value end-products (Shen and Qian 2012) such as packaging materials for the shipping and handling process. The cited authors reported that conventional barrier coating has been found to be a less economical technique due to thick coating layers and poor recyclability. As such, in a coating method, the paper surface must be coated and layered by >50 µm of coating formulations in order to achieve the desired water resistant levels. On the other hand, impregnation via immersion technique may cause cracking and loss of coating (Van der Reyden et al. 1993). Therefore, the dimensions and mechanical properties may be greatly affected.

Soo et al. (2012) dipped their secondary pulp handsheet into the dissolved cellulose acetate which provide better resistance to water wettability in producing Braille papers. Previously, another interesting study, carried out by Larontoda et al. (2003) immersed their kraft paper under vacuum and atmospheric condition in producing waterproof paper. Their cassava-starch acetate covered the paper surfaces, which led to the decrement of water absorption and water vapour permeability. Both Soo et al. (2012) and Larontoda et al. (2003) immersed their papers in cellulose acetate or cassava-starch acetate solutions before the heating. Hazwani et al. (2013) applied a coating method in producing water-resistant paper. The water contact angle of the coated samples was almost superhydrophobic, which means the paper has very high repellence to water. Medina (2008) blended kenaf and jute fibres with acrylic acid resin in order to develop an even distribution of matrix over and around the fibres. By applying the resin in such a manner, the manufactured composites have higher strength and rigidity as targeted after pressing process. Istek et al. (2010) prepared deco paper using an immersion technique in producing laminated particle board.

Polyethylene (PE) is one of the strongest and lightest material for fibres in the world. It can be provided in the form of a synthetic wood pulp, which is created by polymerization of ethylene, containing carbon and hydrogen of ethylene monomer. It is designed to be used on conventional papermaking equipment (Kindler 1974). Typically
its melting point is between 120 and 140 °C. Its mechanical properties depend significantly on variables such as the extent and type of branching, the crystal structure, and the molecular weight (Vasile and Pascu 2005). With regard to sold volumes, the most important polyethylene grades are high density polyethylene, linear low density polyethylene, and low density polyethylene. The melting point for low density PE is 105 to 115 °C. These fibres may be mixed with natural cellulosic fibre for the intended property. Teruo and Masahiro (1998) reported that heat treatment of synthetic pulp made from PE resulted in paper that exhibited desired properties. The PE functions as a heat sealable fibre that can melt and seal the voids within fibres (Heinrich 1992).

Kenaf is a versatile plant with promising potential for pulp and paper industry. It is a fibrous plant of Malvaceae family. It needs less than 6 months to obtain a suitable size for industry application (Abdul Khalil et al. 2010). It consists of two distinct fibres, which are inner core fibre (60 to 75%) and outer bast fibre (25 to 40%). Inner core fibre has shorter fibre length as compared to outer bast fibre. This fibre gives smoother sheets surface (Villar et al. 2009). Outer bast fibre produces high quality pulp comparable to those of softwood fibres due to its high slenderness ratio (fibre length/diameter), which ensures achievement of stronger paper (Villar et al. 2009). Kenaf bast pulp can provide paper with high strength properties exceeding paper from conifer fibres as a consequence from its high fibre length. In papermaking, the combination of core and bast kenaf fibres will produce better quality of paper in terms of physical appearance and mechanical strength (Mahmudin et al. 2012). Due to its fast growth and production of a good quality of fibre, kenaf has attracted increasing interest as an alternative fibre source for the pulp and paper industry.

The main objective of this study was to develop water-resistant paper via a simple method. Johansson et al. (2012) investigated that ease of processing is one of the factors identified as a fundamental issue for sustainable utilization of renewable material. With regard to this factor, blending via a disintegration technique is suggested to meet the requirements. To the best of our knowledge, water-resistant paper prepared via this technique has not yet been reported. As such, the early phase of this study involved commercial conventional polymer to be blended during papermaking of whole stem kenaf fibres.

**EXPERIMENTAL**

**Materials**

Kenaf stalks variety V36 at 4 months old were obtained from National Kenaf and Tobacco Board (NKTB) kenaf plantation at Bachok, Kelantan, Malaysia. Two types of synthetic wood pulps, polyethylene (PE) namely as low (LB) and high branched (HB) polymer were purchased from Schwarzwälder Textil-Werke (STW) Company, Germany. The LB has 1.35 to 1.80 mm fibre length while HB has 0.75 to 1.05 mm fibre length. Both polyethylenes were in powder form, white in colour with a melting point at 135 °C.

**Methods**

*Preparation of unbleached pulp*

The kenaf stalks were chipped to 2 cm width and air-dried until the 10% moisture content for storage purpose. The kenaf chips of 1 kg oven-dried were pulped via kraft
pulping: 17% active alkali, 25% sulphidity. The wood:water ratio was 1:7, the time to reach 170 °C was 90 min, the time at 170 °C was 120 min, and the cooking time was 210 minutes. The unbleached kenaf pulp was produced after completing the pulping with yield 46% and Kappa no.13. Prior to papermaking process, the pulp were beaten at 500 revolutions using PFI Mill Beater in order to obtain better paper formation.

**Blending via a disintegration technique in the papermaking process**

The unbleached kenaf pulp slurry was disintegrated and blended with PE in a British disintegrator for 25 min at 10,000 rpm. A kenaf to PE mixture was prepared at ratios of 9:1, 8:2, 7:3, 6:4, and 5:5. The blended pulps were then used in the papermaking process. The papermaking was carried out according to TAPPI Standard T205. The wet handsheets were oven-dried at 140 °C for 30 min. The papers were codified as KP (kenaf paper, which contained 100% kenaf whole stem fibres, non-blended), K1 (9:1), K2 (8:2), K3 (7:3), K4 (6:4), and K5 (5:5). These samples were prepared according to whether LB- or HB-branched PE was being used.

**Specific surface area and pore volume distribution**

Nitrogen adsorption experiments were conducted to determine the pore volume distribution and specific surface area of three selected samples, KP, K1, and K5, representing the accumulation of PE added during the disintegration stage. The adsorption analysis was performed using Quantachrome Instruments, Model AS1Win™. The specific area was evaluated using the Brunauer-Emmet-Teller (BET) method, while pore volume was measured using the BJH (Barret-Joyner-Halenda) method.

**Morphology observation using scanning electron microscopy (SEM)**

The morphology of the samples was observed using a Carl Zeiss Model 1450VP variable pressure scanning electron microscope. Prior to scanning, the samples were coated with a fine gold layer. The paper surface was studied to observe the surface structure differences between a series of non-blended and blended papers.

**Water absorption**

The methods used to examine the water absorption for the samples were the water contact angle measurement and the Cobb test. These tests were done according to TAPPI Standard T535 um-91 and TAPPI Standard T441, respectively. The water contact angle of the paper surface was measured using a FECA Contact-Angle Meter. The Cobb test is a gravimetical analysis where 100 x 100 mm samples are weighed before and after their immersion in distilled water for 60 s.

**Mechanical testing**

Prior to mechanical testing, the samples of blended paper were conditioned at 23.0±1 °C and 50.0±2% relative humidity based on TAPPI Standard T402 sp-08. The conditioning of paper samples was performed for 24 h.

Tensile and tear strength tests were carried out according to TAPPI Standard T494 om-01 and TAPPI Standard T414 om-88, respectively. These tests were carried out using a Büchel-Van Der Korput horizontal tensile tester and an Elmendorf tear tester. The values of both tensile and tear strength were determined by indexing each strength with the paper grammage. Eight replicates were conducted for each test.
RESULTS AND DISCUSSION

Specific Surface Area, Pore Volume Distribution, and Morphology Observation Using Scanning Electron Microscopy (SEM)

Specific surface area (SSA) is a property of a solid material that describes its total surface area per unit of mass. The SSA will increase with the decrement and increment of the size and number of particles, respectively. Pore volume distribution is defined as the sum of the volumes of all pores in one gram of the adsorbent.

The SSAs and the pore volume distributions of samples with different contents of PE are shown in Table 1. The BET specific surface area of blended paper samples K1 and K5 were 0.197 m²/g and 1.845 m²/g, respectively. However, these values are lower than those of non-blended paper (2.787 m²/g). This shows that the addition of PE reduced the SSA value. The PE is believed to coat the surfaces of the fibres, which reduces the total surface area. This phenomenon was most pronounced in K1, as shown in Fig. 1. The results obtained were not similar to those of Annergen et al. (1996). They found that the specific area for synthetic fibres which were impregnated via the immersion technique with an aluminium silicate complex became higher than the control. This means that a higher content of PE present in the fibre linkages promoted an increase in SSA compared to the non-blended paper.

Results for the pore volume distribution exhibited a decreasing trend with the increasing addition of PE. The KP, K1, and K5 samples represented pore volumes of 0.007, 0.005, and 0.003 cc/g, respectively. Logically, KP, the non-blended sample, contained a higher pore volume than K1 and K5. Due to the addition of polymer, the pore volume distribution values decreased, as shown in Table 1.

The SEM micrographs of the non-blended and blended samples of kenaf paper are shown in Fig. 1a, b, and c. These micrographs provide clear support to the results of SSA and pore volume distribution (Table 1). Figure 1a shows the pores or voids among and between the fibres linkages. The morphology of samples K1 and K5 showed the melted location of PE on the fibres and pores as well. It is obvious that PE formed a layer on the paper surface. The PE filled the superficial pores, as shown in Fig. 1b and c. The hygroscopic properties of the blended paper were obtained as a consequence of these fillings. Larontoda et al. (2003) obtained similar results, but the layer observed via SEM in their study was cassava-starch acetate. Eichler et al. (1997) proved that the filling process can be promoted by solvent evaporation and consequent substitution by air. However, there are still pores observed on the surface of the paper, as shown in Fig. 1b and c. The PE was distributed in the fibre linkages instead of covering the surface of the paper. PE was present in the fibres in a different manner compared to the immersion technique. Schematic illustrations showing the differences between the paper structures prepared via the immersion and disintegration techniques are shown in Fig. 2. A higher content of PE decreased the pore volumes in the tested samples. Superior efficiency is achieved using the immersion technique rather than the disintegration technique. However, both paper surfaces still resisted water. Unlike the findings of Lainio (2010), the synthetic fibres were observed via SEM as having a straight, un fibrillated, unchanged shape and did not bond well with cellulose fibres. She introduced synthetic fibres such as PE and polypropylene (PP) using a calendering approach.
Table 1. Results of Surface Area and Pore Volume for Three Types of Samples: KP (Kenaf Paper, Which Contained 100% Kenaf Whole Stem Fibres, Non-Blended), K1 (9:1), and K5 (5:5)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Surface area, m²/g</th>
<th>Pore volume, cc/g</th>
</tr>
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<tbody>
<tr>
<td>KP</td>
<td>2.787</td>
<td>0.007</td>
</tr>
<tr>
<td>K1</td>
<td>0.197</td>
<td>0.005</td>
</tr>
<tr>
<td>K5</td>
<td>1.845</td>
<td>0.003</td>
</tr>
</tbody>
</table>

**Fig. 1.** SEM micrographs showing the voids and melted areas that occurred in samples (a) KP, (b) K1, and (c) K5

**Fig. 2.** Schematic illustrations showing the fibre network of paper prepared via the (a) immersion and (b) disintegration techniques
Water Absorption Properties

The results of the Cobb and water contact angle (WCA) tests are illustrated in Fig. 3. The presented values are the averages of the values obtained in the assays, which were carried out in triplicate. It is interesting to observe that the Cobb test and water contact angle showed the same trend for the blended samples. The lower value of the Cobb test and the higher value of the water contact angle represent superior water repellence. The Cobb value indicates the paper’s ability to absorb water. The smaller the Cobb value is, the better the water resistance of paper (Hu et al. 2009). In other words, a lower value means the paper has a higher resistance to water. The non-blended sample (KP) could not present any Cobb value due to its high water penetration. Therefore, it is not recorded in the figure. However, the value of K1 could be measured, although it was not within the acceptable standard range. Generally, the addition of more than 10% PE was found to increase water repellence, as represented by K2, K3, K4, and K5. These papers exceeded the minimum requirement in the water absorption test. The hydrophobicity obtained was due to the production of crystalline properties from the PE (Hayato 1975). A comparison is also made between LB and HB PE. The HB PE represented an extreme decrease in the Cobb value with the addition of 20% PE. The water absorption was observed to have less of a decrease with the addition of 30 to 50% of both LB- and HB PE, as shown by K3, K4, and K5.

Fig. 3. The water absorption test comprises the Cobb test and water contact angle measurement for blended samples using low- and high-branched polyethylene

Water resistance can be observed through the contact angles (Thawornwiriyanan et al. 2008). No reading could be captured for non-blended paper due to its fast water absorption. As reported by Yang and Deng (2008), the water droplet is quickly absorbed by untreated paper. The LB PE displayed a slightly higher degree of WCA compared to the HB PE. This indicates that HB PE promoted a greater penetration into the pores and increased the porosity compared to the LB PE. It is also clear that more than 40% of the PE did not make any significant changes to the degree of water contact angle for either LB or HB PE. This indicates that the PE ratio may influence the efficiency of the polymer for coating and entering the fibre layer and fibre pores, respectively. The highest
degree of water contact angle achieved for both series of blended samples was 84°, as shown in Fig. 4. The blended papers prepared via the disintegration technique exhibited a high potential for paper products to be upgraded as hydrophobic and superhydrophobic paper (Fig. 5).

**Fig. 4.** A water droplet on the blended paper showing the water contact angle at 84°

![Water droplet on paper](image)

**Fig. 5.** Schematic illustrations of the definition of surface water contact angles

<table>
<thead>
<tr>
<th>Angle</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>&lt; 90°</td>
<td>Less hydrophobic</td>
</tr>
<tr>
<td>90°</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>&gt; 150°</td>
<td>Superhydrophobic</td>
</tr>
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</table>

**Mechanical Properties**

The mechanical properties of the samples were analysed by measuring the tensile and tear strengths. The experimental values are given in Fig. 6. As predicted, both strengths of the blended samples decreased with the incorporation of PE. Fundamentally, any presence of filler or organic material, such as PE in this case, may decrease the paper strength. This is due to the interruption of fibre bonding between the fibres with the presence of a synthetic pulp such as PE. The obtained results show that the blending promoted significant modifications in the mechanical properties. Once the PE was added to the pulp mixture, the mechanical strength was tremendously affected. It was expected that the PE would not improve the paper mechanical strength due to its unique properties in relation to binding the fibres. This result is parallel to the findings by Lainio (2010), who applied PE to papermaking aided with a calendering approach (temperature at 100 °C) and infra-red drying of the paper surface.

For instance, the samples blended with 10% LB and HB PE have tensile strengths decreased by about 17.4% and 12.4%, respectively, compared to KP. The following blendings of 20 to 50% PE reduced the tensile and tear strengths, but the values are still above the minimum standard requirement. Overdosing of PE directly leads to an over-use
of resources, unlike coating or impregnation via immersion, which led to papers prepared with the desired strengths.

![Fig. 6. Effect of blending with two types of PE on the mechanical properties of the kenaf paper: (a) tensile index and (b) tear index](image)

High-branched PE is observed to be less harmful to the paper strength than low-branched PE. A branched polymer is a polymer with a chemical side chain extending from the main backbone. A higher branched polymer may enhance the strength of materials. As reported by Hult et al. (1999), hyper-branched polymers are different from linear polymers. Hyper-branched polymers have fewer entanglements than linear polymers. In comparison, HB PE showed better tensile and tearing indices than LB PE. This may be due to fewer entanglements with HBPE, which provides more spaces for better polymer distribution in the fibre network. Increased possibilities for the polymer to cover a greater area during the melting process and the locked linkages of fibres resulted in more work required to pull out the fibres during the mechanical tests. Higa et al. (2005) also proved that the branched chain length is one of the factors which increase the tensile strength of the solid polymer electrolyte.

**CONCLUSIONS**

1. The blending via disintegration technique for kenaf fibres with PE can be an alternative technique for producing water-resistant paper.

2. The HB PE seemed to be less detrimental than the LB PE in terms of mechanical aspects. However, LB PE showed superior water resistance via both the Cobb and water contact angle tests. Therefore, the addition of at least 20% PE is suggested to meet the needs of such paper for both water absorption and mechanical strength using the disintegration and blending techniques.
ACKNOWLEDGEMENTS

The authors would like to thank the Economic Planning Unit (EPU) of the Prime Minister’s Department of Malaysia for financing the study and the Institute of Tropical Forestry and Forest Products (INTROP) and the Faculty of Forestry, Universiti Putra Malaysia, for providing the facilities.

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Article submitted: July 8, 2013; Peer review completed: August 14, 2013; Revised version received and accepted: September 11, 2013; Published: September 16, 2013.