Hygrothermal Aging and Tensile Behavior of Injection-Molded Rice Husk-Filled Polypropylene Composites

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ABSTRACT: The effect of the filler volume fraction on the tensile behavior of injection-molded rice husk-filled polypropylene (RH–PP) composites was studied. Hygrothermal aging behavior was also investigated by immersing the specimens in distilled water at 30 and 90°C. The kinetics of moisture absorption was studied from the amount of water uptake by specimens at regular interval times. It was found that the diffusion coefficient and the maximum moisture content are dependent on the filler volume fraction and the immersion temperatures. Incorporation of RH into the PP matrix has led to a significant improvement in the tensile modulus and a moderate improvement in the tensile strength. Elongation at break and energy at break, on the other hand, decreased drastically with the incorporation of the RH filler. The extent of deterioration incurred by hygrothermal aging was dependent on the immersion temperature. Both the tensile strength and tensile modulus deteriorated as a result of the combined effect of thermal aging and moisture attack. Furthermore, the tensile properties were not recovered upon redrying of the specimens. Scanning electron microscopy was used to investigate the mode of failure of the RH–PP composites. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 742–753, 2001

Key words: polypropylene; rice husk; hygrothermal aging; composites; water absorption; tensile properties

INTRODUCTION

Among the commodity thermoplastics, polypropylene (PP) has been one of the most popular candidates as a matrix material due to its versatility to accept numerous types of fillers and reinforcements. Typical fillers and reinforcements for PP are glass fibers, glass sphere, talc, asbestos, mica, wollastonite, calcium carbonate, and silica.[1] It has been widely reported that the incorporation of particulate fillers into thermoplastic matrices induces substantial changes in terms of their physicochemical and mechanical properties. At present, for instance, different types of fillers are incorporated in order to gain enhancement in one or more mechanical properties such as stiffness and strength. The other obvious reason of incorporating fillers into polymer matrices is to reduce the cost.[2]

Recently, researchers have had a great interest in utilizing natural-occurring fiberous materials such as wood flour, oil palm fruit bunch, sisal, and coconut shell as fillers for PP.[3] The fillers were incorporated into the PP matrix by various compounding techniques such as a two-roll mill or through either a single-screw or twin-screw extruder. The use of these natural fillers in polymer matrices has resulted in a significant enhancement in the tensile modulus or flexural modulus of the resulting composites. However, due to the

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geometrical nature of the fillers, that is, its irregular shape with a low aspect ratio (length-to-diameter ratio), the improvement in the tensile strength and impact strength are rather limited compared to synthetic fibers such as glass, carbon, or kevlar. Further improvements in the strength properties of filled composites were achieved via chemical treatment of the fillers using either compatibilizers and/or coupling agents.[4]

In this present study, a relatively new type of lignocellulose filler was investigated. The origin of the filler is from the husk of the rice grain—hence, the term rice husk (RH) filler. So far, extensive R&D efforts have been devoted to investigating the potential of rice husk ashes (RHA) as fillers for PP. As the name implies, RHA are derived from the burning of RH in the open air outside the rice mills. According to Ahmad Fuad et al.,[5] the two types of RHA, that is, white RHA and black RHA, have a good potential to serve as fillers for PP, especially in applications demanding high stiffness, excellent dimensional stability, and moderate tensile strength.

As far as RH is concerned, there are only a limited number of research works that have been published on RH-filled PP. In countries that produce rice, the disposal of RH waste poses a growing problem, due to the low bulk-density nature of the husks. In Malaysia, for instance, the annual production of rice is estimated to be some 2 million tonnes and generates about 400 tonnes of waste husks.[6] Thus, finding useful applications of RHs will certainly help to alleviate problems related to the disposal of the waste husks. The second driving factor is the economic advantage: RH is readily available at extremely low cost as an unwanted by-product of a rice mill. Of course, additional cost is involved for further processing such as grinding and sieving, if necessary, but the cost is not high.

Like other lignocellulosic-based fillers, cellulose, hemicellulose, and lignin form the major components of the RH filler. Due to the high cellulosic composition, the main drawback of RH is its high tendency to absorb moisture from the environment. Therefore, this article reports on the hygrothermal aging (refers to the aging process which involves the combination of water and temperature) behavior of the RH–PP composites at different filler loading. The effect of filler loading and hygrothermal aging on the tensile properties of the composites are reported. A fractography study by scanning electron microscopy (SEM) was also used to investigate the mode of fracture.

EXPERIMENTAL

Materials

The PP used was from The Polyolefine Co. Pte. Ltd. (Singapore), with the trade name Cosmoplene, its density and melt flow index specified as 0.91 g/cm^3 and 6.1 g/10 min (220°C/2.16 kg), respectively. RH, comprising about 40% cellulose, 30% hemicellulose, and 30% lignin, was supplied by BERNAS, Alor Setar (Malaysia). The filler particle size was sieved using the mesh size of 35–60 (175–246 μm). RH was oven-dried at 90°C for 24 h prior to compounding and processing to obtain a moisture content of less than 0.2% and to avoid formation of voids in the injection-molded specimens.

Compounding and Molding

PP granules and various RH filler loading (10, 20, 30, and 40 wt %) were compounded in a HAAKE intermeshing counterrotating twin-screw extruder (Rheomex CRW 100) having a barrel temperature profile ranging from 170 to 195°C from the feeding zone to the die zone at a screw speed of 25 rpm. The extrudate was subsequently cooled and pelletized. The pellets were then injection-molded into a tensile test specimen in accordance with ASTM D639 Type I on a Battenfeld BA 350CD Plus with a Unilog control system. Specimens were prepared using a 120 bar injection pressure and barrel temperature profile ranging from 170 to 185°C. Pellets were oven-dried at 90°C for 24 h prior to injection molding.

Sample Characterization

Density Determination

The density, ρ, of the test specimens was determined according to the ASTM D792 water-displacement method (Method A) using the equation

$$\rho = W_1/(W_1 - W_2) \tag{1}$$

where W_1 and W_2 are sample weights in air and water, respectively.

Determination of Filler Volume Fraction

Determination of the filler volume fraction, V_f, of the test specimens with different filler loading was carried out using the following equation:

Table I   Various Conditions of the Specimens Tested

Condition	Remark	Filler Volume Fraction (V_f)
Unaged	Dry, as-received (AR)	0.00, 0.06, 0.13, 0.18, 0.26
Aged	Wet, HA at 30 and 90°C	0.26
	RD after being HA at 90°C	0.26

$$\rho_c = \rho_f V_f + \rho_m (1 - V_f) \qquad (2)$$

where ρ_c, ρ_f, and ρ_m are the density of the composite, filler, and polymer matrix, respectively. The densities of the RH, ρ_f, and PP matrix, ρ_m, used in the equation are 1.49 (ref. 6) and 0.91 g/cm^3, respectively. The assumption that there are no voids in the test specimen had been taken into account.

Kinetics of Moisture Absorption

The kinetics of the moisture-absorption study was carried out by direct immersion of PP and RH–PP (10, 20, 30, and 40 wt % filler loading) test specimens in distilled water at 30 and 90°C. The weight of the specimens were measured at regular intervals and the moisture content at time t, M_t, was calculated by

$$M_t = (W_t - W_d)/W_d \qquad (3)$$

where W_t and W_d are, respectively, the weight after the exposure time t and the dry weight.

Tensile Test

The tensile properties were determined with an M500 Tensometric AZ testing machine, using a test speed of 5 mm/min in accordance with ASTM D-638. The test was performed at 28°C and on specimens with the conditions stated in Table I. Five specimens were tested for each case.

Scanning Electron Microscope (SEM)

The mode of fracture was studied by analyzing the fracture surface. This was carried out using the SEM machine Model Leica Cambridge S-360 where the fracture surface of the test specimens was coated with a thin gold layer to avoid electrical charging during the examination.

RESULTS AND DISCUSSION

Sample Characterization

Density Determination

Table II shows the theoretical and experimental density values for PP composites. It is noted that the densities of the composites show an increment with the filler loading. This is attributed to the higher density of RH than that of the PP matrix. Therefore, incorporation of RHs into PP increases the densities of the composites. These data were then used to determine the filler volume fraction, V_f, of the composite using eq. (2). From the table, it can be seen that there is no significant difference between the theoretical and experimental values.

This indicates that compounding using a twin-screw extruder was efficient because there was very little filler lost during the compounding. A similar result was also obtained by Ahmad Fuad et al.[5] for white rice husk ash (WRHA)- and black rice husk ash (BRHA)-filled PP.

Filler Volume Fraction Determination

Both theoretical and experimental V_f values for the composites calculated using eq. (2) are shown in Table III. It can be seen that V_f increases steadily with the incorporation of RH. Again, no significant difference was observed between the experimental and theoretical values. This is fur-

Table II   Experimental and Theoretical Density Values for PP Composites

Filler Loading (wt %)	Experimental	Theoretical
10	0.94	0.95
20	0.98	0.99
30	1.01	1.03
40	1.06	1.08

Table III Experimental and Theoretical Values for Filler Volume Fraction (V_f) of RH–PP Composites

Filler Loading (wt %)	Filler Volume Fraction (V_f)	
	Experimental	Theoretical
10	0.06	0.06
20	0.13	0.13
30	0.18	0.20
40	0.26	0.29

ther indication of the efficiency of a twin-screw extruder in compounding the RH–PP composites.

Kinetics of Water Absorption

Figure 1 shows the water-absorption curves of PP and RH–PP composites at a water-immersion temperature of 90°C. It can be seen that the kinetics of water absorption for the PP composites conforms to Fick's Law behavior, that is, the initial moisture absorption follows a linear relationship between M_t and $t^{1/2}$, followed by saturation with the immersion time.

The weight gain resulting from moisture absorption can be expressed in terms of two param-

eters: the diffusion coefficient or diffusivity, D, and the equilibrium moisture content, M_m, as[7]

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{D_t}{h^2}\right)\pi^2\right] \quad (4)$$

where h is the thickness of the sample. From the experimental curve of the moisture content, M_t versus the square root of the exposure time, $t^{1/2}$, the diffusion coefficient, D, can be calculated from the initial portion of the curve using the following equation:

$$D = \frac{\pi\, h^2(M_2 - M_1)^2}{16 M_m^2 (t_2^{1/2} - t_1^{1/2})^2} \quad (5)$$

where h, M_1, and M_2 are the sample thickness and moisture content (percent weight) at times t_1 and t_2, respectively, while M_m is the maximum moisture content.

The values of the apparent diffusion coefficient, D, and the maximum moisture content, M_m, as derived from the absorption curves are tabulated in Table IV. It can be seen that the diffusion coefficient, D, increases with the filler content. Neat PP is almost inert to moisture as evident from its moisture-uptake curve shown in Figure
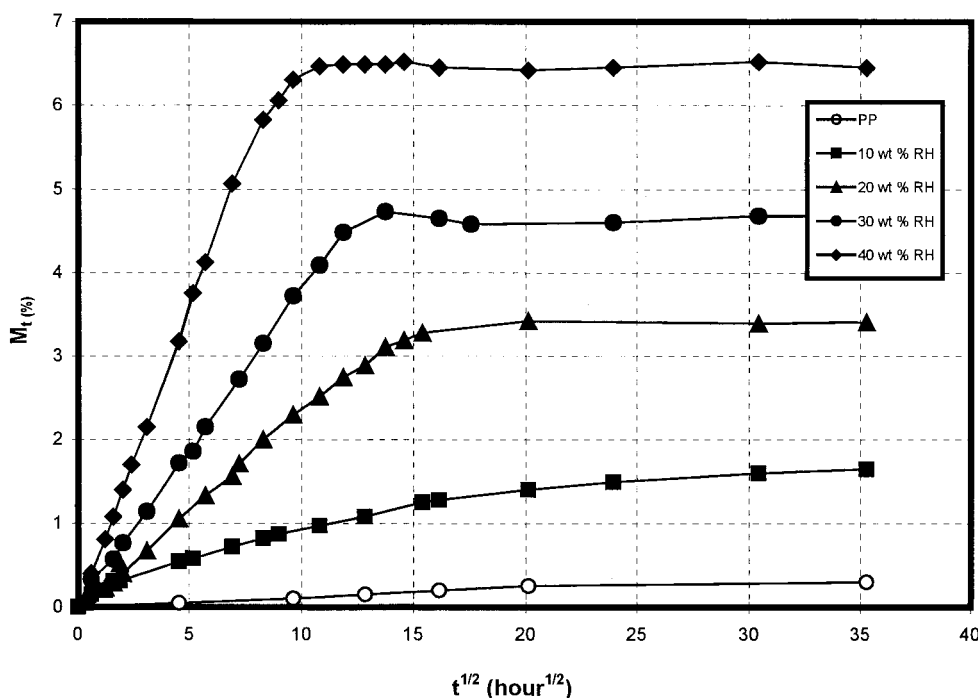

Figure 1 Water uptake, M_t, as a function of time, $t^{1/2}$, of PP and RH–PP composites at 90°C.

Table IV   Moisture Content (M_m) and Diffusion Coefficient (D) of PP and RH–PP Composites

Filler Loading (wt %)	30°C		90°C	
	M_m (%)	D ($\times 10^{-15}$ m^2/s)	M_m (%)	D ($\times 10^{-15}$ m^2/s)
0	0.16	—	0.32	—
10	0.52	2.19	1.65	20.53
20	1.18	8.17	3.19	121.39
30	1.87	15.94	4.58	203.97
40	4.16	88.33	6.25	588.89

1. PP has a moisture content of only 0.01% after 1245 h immersion in water at 90°C. Therefore, it can be concluded that the water-absorption behavior of the RH–PP composites is affected mainly by the RH content in the composites. D increases with the filler content as the hygroscopic hydroxyl groups, —OH of cellulose, hemicellulose, and lignin in the cell wall of the RH increased. These —OH groups have a strong tendency to hydrogen-bond with the water molecule.[3] A recent study by Bledzki and Gassan[4] reported that the presence of jute fiber in epoxy resin has a strong influence on the moisture-absorption property of the composites. The absorption of water by capillary action via the fiber–matrix interface has also been identified. In the present study, determination of the exact mechanisms of water absorption into RH–PP composites was not possible due to the complex geometrical nature of the RH particles.

The values of D obtained in the present study are not in agreement with the range of values reported by Loos and Springer.[7] According to these workers, the values of the diffusion coefficients, D, for most polymers and their composites fall in the range of 10^{-11} to 10^{-12} m^2/s. The present observation is also contrary to the report by Mohd. Ishak and Berry[8] on the short carbon fiber-reinforced nylon 6,6 system and Mohd. Ishak et al. on short glass- and short carbon fiber-reinforced polyarylamide[9] and short glass fiber-reinforced poly(butylene terphthalate).[10] The values of D for those composites were reported to be in the range of values reported by Loos and Springer. This peculiar observation may be attributed to the fact that, in the present study, the water molecules were being absorbed by the dispersed phase, that is, by the RH fillers and not by the continuous PP matrix. As PP is known for its good resistance against moisture absorption, it will hinder direct diffusion of water molecules into the RH fillers. Thus, it is not surprising that it took about 100 h for the 40 wt % RH to reach the steady maximum moisture content (Fig. 1) as compared to only about 50 h for polyarylamide with 40 wt % short glass fiber[9] at the same immersion temperature. The faster diffusion rate in the latter is due simply to the hygroscopic nature of polyarylamide matrix that formed the continuous phase. Thus, a similar explanation could also be offered for other hygroscopic polymer matrices such as polyamides and thermoplastic polyesters and their related composites.

As can be seen from Table IV, D is also a function of the immersion temperature. The data show that the increase of temperature has increased the D values significantly at any filler content. The water-absorption behavior of the composites is a controlled diffusion or permeation process.[11] The water-diffusion mechanism is controlled by the activity of the water molecules which is affected by the temperature.[12] Therefore, a sharp increase of D at 90°C from 30°C can be attributed to the higher activity of the water molecules at 90°C. Thus, it becomes obvious that a much longer period of time is needed to reach the equilibrium moisture content values at 30°C as compared to those of 90°C. Similar observations have been reported by several workers on other thermoplastic and thermoset-based composites.[11] From the table, it should be noted that the maximum moisture content, M_m, increased with increasing of the filler content. This may again be attributed to the increase in the hygroscopic hydroxyl groups (—OH) in RH as the filler content increases. A similar trend was recently reported by Rozman et al.[13] on oil palm empty fruit bunch (EFB)-filled PP composites. In an earlier study, Klason et al.[14] demonstrated that in the case of other lignocellulosic thermoplastic composites the water absorption is proportional to the filler loading, as the sorption by the thermoplastic matrix,
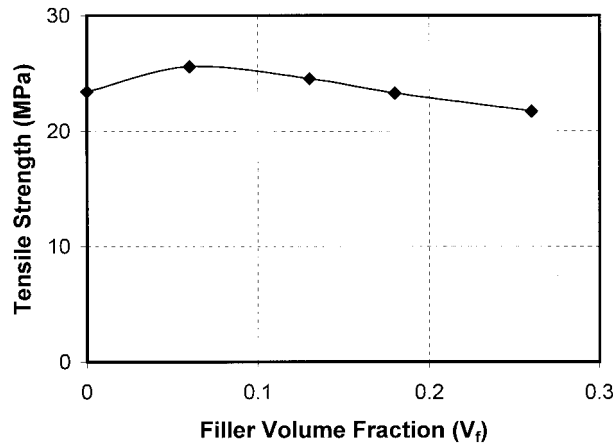
Figure 2 Variation of tensile strength with filler loading for RH–PP composites.

such as PE and PP, could be neglected. Another recent study by Mohd. Ishak et al.[15] revealed that the water resistance of EFB–HDPE composites was improved by chemical treatment of the composites. The incorporation of a coupling agent, 3-aminopropyltriethoxysilane (3-APE), was found to reduce the amount of water uptake by the composites. This was attributed to the ability of the chemical to form a protective layer at the interfacial zone, which, consequently, prevents direct diffusion of the water molecules into the EFB filler.

Tensile Properties

Effect of Filler Loading

Figure 2 shows the effect of RH loading on the tensile strength of the RH–PP composites. It can be seen that the tensile strength of the RH–PP composites remains more or less the same with increasing filler loading. A slight drop in the tensile strength is observed when V_f is higher than 0.18, that is, after 30 wt % filler. Incorporation of a filler into a polymer may increase or decrease the tensile strength of the resulting composites.[16,17] The slight improvement in the tensile strength of the PP composites with V_f lower than 0.18 may be attributed to good filler–matrix adhesion and uniform dispersion of RH in the PP matrix. This is evident from the SEM study (Fig. 8) that will be discussed in detail later. However, the decrease of tensile strength was observed when the V_f increases from 0.18. This shows that the enhancement in tensile strength is rather limited at a much higher filler content. This may be

attributed to the geometrical nature of the RH fillers. Unlike synthetic fibers such as glass and carbon fibers that have a uniform cross-sectional area and relatively high aspect ratio, that is, the length-to-diameter ratio, l/d, for irregular-shaped fillers, like RH, their capability to support stress transmitted from the polymer matrix is rather poor. A similar observation was reported by Ahmad Fuad et al.[16] for RHA-filled PP composites. Apart from having a similar geometrical factor to that of RH, RHA has a strong tendency to form agglomerates that result in poor adhesion of the filler to the PP matrix.

The effect of RH loading on the tensile modulus of the PP composites is shown in Figure 3. The original purpose of the incorporation of fillers, especially the particulate filler, into the polymer matrix is to improve the modulus of the resulting composites. As expected, the tensile modulus, which indicates the material stiffness, increases steadily with the filler content. An enhancement of 194% in stiffness was observed for the RH–PP composite with a filler loading of 40 wt % (V_f = 0.26). Similar results were reported by Ahmad Fuad et al.[5] for the RHA–PP system. This suggests that incorporation of RH has suppressed the flexibility of the PP matrix. An extensive research by Riley et al.[18] on various mineral-filled PP found that the modulus of the composites are affected by the filler modulus, filler loading, and filler aspect ratio. High stiffness-filled composites require particulate fillers of a high modulus and a high aspect ratio and, preferably, at high filler loading.

Figure 4 shows the effect of the filler volume fraction on the elongation at break (EB) of the
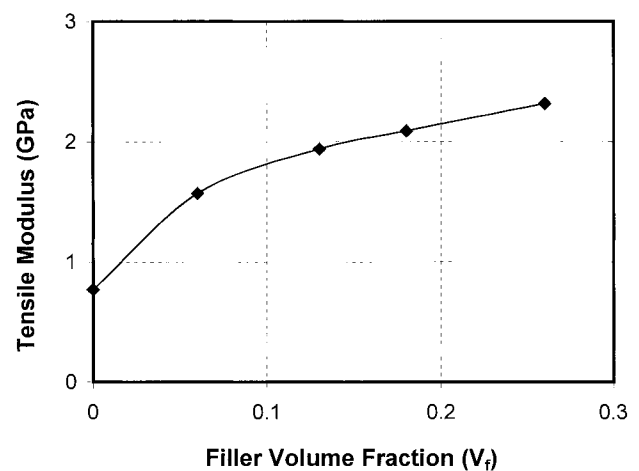

Figure 3 Tensile modulus as a function of filler loading for RH–PP composites.
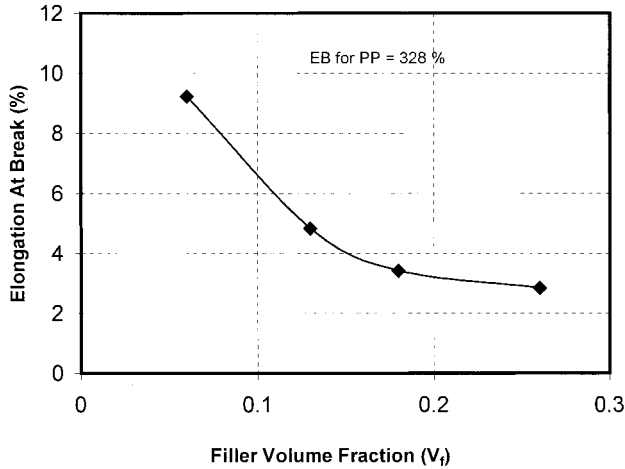
Figure 4   Effect of filler loading on the EB of RH–PP composites.

composites. It can been seen that incorporation of RH even as low as 10 wt % into PP resulted in a drastic drop of the EB, that is, about 97%. It appears that the failure mode of the PP matrix has shifted from ductile to brittle with the incorporation of RH. This can be attributed to the presence of RH which suppressed the ability of the PP matrix to undergo a plastic-deformation process. Therefore, the composites fracture at a lower EB. Similar observations have been reported by several workers for other lignocellulosic thermoplastic composites such as EFB-filled high-density polyethylene (HDPE) and PP composites.[3] However, a further reduction in EB is expected with the chemical treatment of the filler.

Similar results were reported by several workers on filled PP and HDPE composites treated with various types of compatibilizers such as maleic anhydride-grafted PP (MAH-g-PP), poly(propylene acrylic acid)s, and coupling agents such as 3-(trimethoxysilyl)propyl methacrylate and 3-aminopropyltriethoxysilane.[3]

Figure 5 shows the effect of RH loading on the energy at break of the RH–PP composites. The trend agrees very well with the data observed in the variation of the EB with the incorporation of RH. The energy at break characterized the toughness of the composites, which represents the ability of the composites to resist the propagation of cracks. The decrease of the energy at break with the filler content is also associated with the weak interfacial bonding formed between RH and the PP matrix. As the weak regions increases, the cracks can travel more easily and lead to fracture; the energy to break is therefore reduced. It appears that the incorporation of RH has suppressed the composites' ability to absorb energy. Similar observations were reported by Rozman et al.[19] and Ahmad Fuad et al.[5] for EFB-filled HDPE and RHA-filled PP composites, respectively.

Effect of Hygrothermal Aging

The study of the hygrothermal aging effect was carried out on the RH–PP composite ($V_f = 0.26$) that was immersed in distilled water at 30 and 90°C. The properties of the hygrothermally aged (HA) and redried (RD) specimens after hygrothermal aging were further characterized by tensile
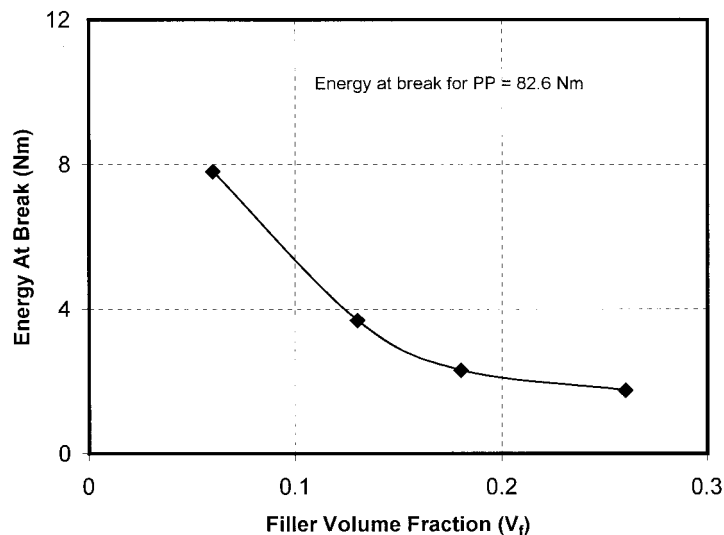

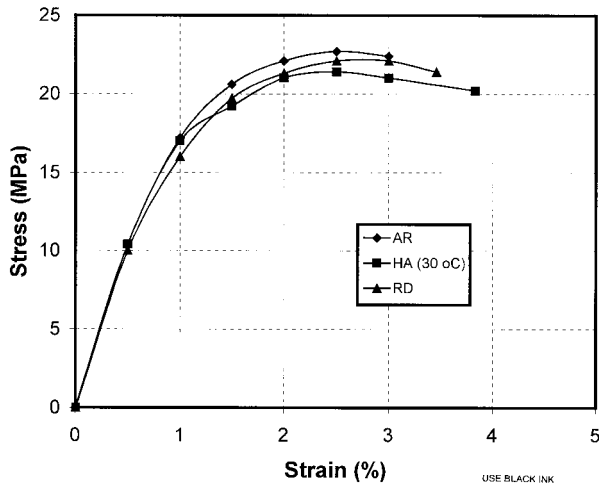**Figure 5**   Variation of energy at break with filler loading for RH–PP composites.

Figure 6 Stress–strain plot for RH–PP composites in AR, HA at 30°C, and RD states.

test in order to investigate the extent of the deterioration that incurred by hygrothermal aging. Figures 6 and 7 show the tensile stress–strain curves for RH–PP composites in as-received (AR), HA, and RD states.

It can be seen that the change in the stress–strain curves for the RH–PP composites immersed at 30°C (Fig. 6) is relatively small compared to that at 90°C (Fig. 7). In the latter, the presence of water has lowered the stress level at any given strain. This implies that the efficiency of the stress transfer from PP to the RH filler

deteriorated after the composites were subjected to hygrothermal aging at high temperature. It seems that the weakening of the filler–matrix adhesion resulted in a slight increase in the EB of the RH–PP composites, but at the expense of tensile strength and modulus as highlighted below.

The extent of deterioration in the tensile properties caused by hygrothermal aging is illustrated in Table V. It is evident that the deterioration effect in the tensile properties became more severe as the immersion temperature was increased to 90°C. As can be seen from the table, the retentionability of the tensile strength in the water-immersion temperature of 30 and 90°C is 96.6 and 85.4%, respectively. The decrease of tensile strength can be attributed to the deterioration at the interfacial bonding between the PP matrix and the RH which subsequently reduced the efficiency of the load transfer. A reduction in the tensile modulus is also observed for HA RH–PP composites. Again, the reduction of the property is higher for the RH–PP composites which were HA at 90°C than for those at 30°C. The degradation of the interfacial regions is obviously related to the water-immersion temperatures. At an immersion temperature of 30°C, the PP matrix is basically still intact and thus able to provide some protection against the direct interaction of water molecules with the RH fillers. In addition, at ambient, the moisture attack at the filler–matrix interface is not that severe. Thus, the PP matrix
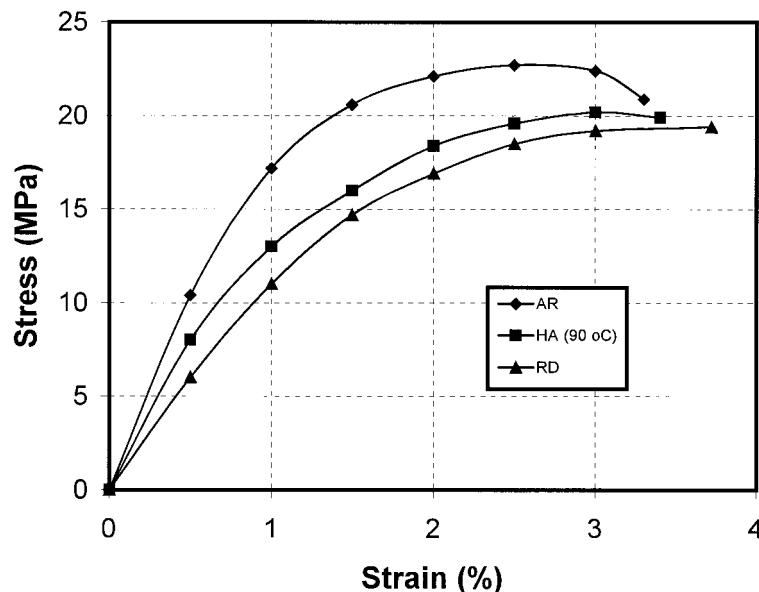

Figure 7 Stress–strain plot for RH–PP composites in AR, HA at 90°C, and RD states.

Table V   Tensile Properties for RH–PP Composite (V_f = 0.26) in AR, HA, and RD States

Tensile Properties	AR	30°C		90°C	
		HA	RD	HA	RD
Tensile Strength (MPa)	21.7	20.9 (96.3)	20.0 [92.2]	18.5 (85.3)	18.0 [82.9]
Tensile Modulus (GPa)	2.3	2.1 (91.3)	2.1 [91.3]	1.6 (69.6)	1.3 [56.5]
EB (%)	2.8	3.9 (139.3)	3.2 [114.3]	3.4 (121.4)	3.7 [132.1]

( ) Percentage retention; [ ] percentage recovery.

is still capable of transmitting the stress to the RH filler. However, at a water-immersion temperature of 90°C, the rigorous interaction between the water molecules at the interface as well as the RH fillers is unavoidable. This will obviously affect the efficiency of the stress transfer from the PP matrix to the RH fillers and, consequently, deteriorate the tensile properties of the RH–PP composites. Furthermore, there is also a possibility that the absorbed water reduced the stiffness of the filler through the plasticization effect.

In another study, Mohd. Ishak et al.[20] reported that there is some qualitative evidence from the fractography study using SEM which revealed that the water uptake has to some extent damaged the interface and changed the dimension of the cell walls of the EFB fillers. In a related study on wood flour-filled PP, Ballentinez and Park[21] reported that the nature of interaction between the water molecules and the lignocellulosic filler is strongly dependent on the water temperature and the immersion period. At a high water temperature, the possibility of the hydrolysis process to take place becomes more prominent. The intramolecular hydrogen bonding that existed in the lignocellulosic materials will be replaced by the hydrogen bonding forming between the materials and the water molecules.

From Table V, it is interesting to note that the deterioration in the tensile modulus caused by hygrothermal aging at 90°C is more severe than that of the tensile strength. A similar trend was also observed for the short carbon fiber-reinforced nylon 6,6 system.[8] From the data shown in Table V, the percent recovery of both the tensile strength and the tensile modulus for the RH–PP composites aged at 90°C is lower than that at 30°C. This is also evident from the stress–strain curves shown in Figures 6 and 7. Upon redrying, the stress–strain properties of the RH–PP composites HA at 30°C are almost fully recovered but it is contrary for the RH–PP composites HA at

90°C. Surprisingly, the tensile properties, especially the tensile modulus, of the redried specimens is slightly lower than that of the wet specimens. This is contrary to the trend observed in commercial short glass and/or carbon fiber-reinforced thermoplastics.

Recent hygrothermal aging studies by Mohd. Ishak and Berry[8] and Mohd. Ishak et al.[9] on short carbon fiber-reinforced polyamide 6.6 (PA66) and short glass fiber-reinforced polyarylamide (PAR), respectively, revealed that the water absorption and desorption in both composites is a reversible physical process even when an immersion temperature as high as 100°C was used. The mechanical properties of the composites were almost fully restored by drying since the effect of water is merely as a plasticizer. Thus, the mechanical properties of the redried composites is far superior compared to those of the wet samples. Similar observations were also reported in the case of poly(butylene terephthalate) (PBT) and rubber-toughened PBT composites,[22] albeit the percentage recovery of the residual properties was not as good as for the PA66 or PAR composites. Even though PBT has a strong tendency to undergo hydrolysis under hot and humid environments due to the presence of ester groups, upon redrying, the residual mechanical properties are still superior compared to that of the HA specimens.

Based on those observations and taking into account that the PP matrix is basically inert to water, the possible explanation for the opposite trend observed in the present study may be obtained by considering the differences in the chemical nature between RH and that of carbon and glass fibers. RH, like other lignocellulosic fibers, is very sensitive to moisture. There is a possibility that some kind of microstructural changes might have taken place in the RH as a result of the exposure to hot water and subsequently redrying it. Bledzki and Gassan[4] proposed that the geometrical changes are due to the moisture sorption

Figure 8 SEM micrograph of RH–PP composites in AR state.

Figure 9 SEM micrograph of showing the presence of fiber bundles in RH–PP composite in AR states.

and swelling in the wood-filled composites. As in the case of other lignocellulosic fibers, there are two types of swelling upon immersion in water, followed by redrying, that is, reversible and irreversible swelling. The former would result in the composite reverting to its original dimensions, while the latter would end up with some degree of degradation.[23] Thus, it is believed that the latter would adversely affect the interfacial bonding between RH and PP and, consequently, would lead to inferior mechanical properties of the composites. This subject will be dealt with in more detail in a forthcoming investigation.

Modes of Failure

The microstructure of the composites such as the filler dispersion in the polymer matrix and the filler–matrix interfacial bonding are known to play a significant role in determining the mechanical properties of filled composites. Figure 8 shows an SEM micrograph of RH–PP composites (40 wt %) tested in the AR state. It can be seen that RHs of different shapes and sizes were unevenly distributed throughout the PP matrix. At a higher magnification, filler bundles can be observed on the crack plane, as shown in Figure 9. The strong tendency to agglomerate among themselves may be attributed to the presence of hydrogen bonding. Thus, it can be expected that these filler bundles will resist dispersion of the individual fibers as filler loading increases and will obviously reduce the efficiency of stress transfer from the matrix to the fillers. This will then result in a detrimental effect to the ultimate performance, namely, the tensile strength of the RH–PP composites. There is also an indication of a small-scale plastic deformation process in the form of
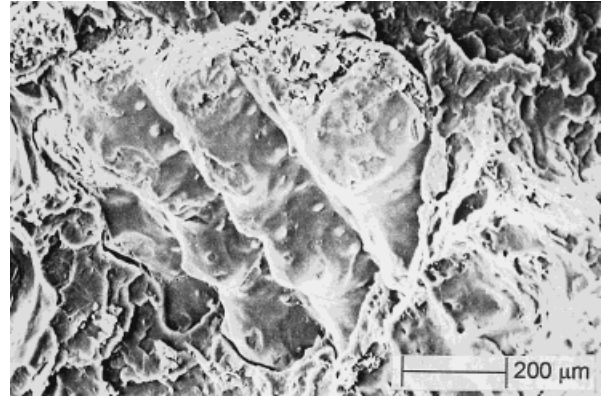
matrix tearing and shear yielding of the PP matrix. However, judging from the steady reduction in the EB (Fig. 3) and the energy at break (Fig. 4) with increasing RH loading suggests that such a matrix-related toughening mechanism failed to retain the ductility of the RH–PP composites.

As mentioned earlier, one of the main problems associated with lignocellulosic thermoplastic composites is the poor compatibility between the constituent phases. The polar nature of RH is obviously not capable of forming a good interfacial bonding with the nonpolar PP. Thus, some evidence of filler-bundle debonding (as indicated by the arrow) could also be observed from the SEM micrograph illustrated in Figure 9. The existence of extensive filler bundle pullout on the fracture plane of EFB–HDPE composites was reported earlier.[19]

Figure 10 depicts the fracture surface of the RH–PP composite that was subjected to HA at

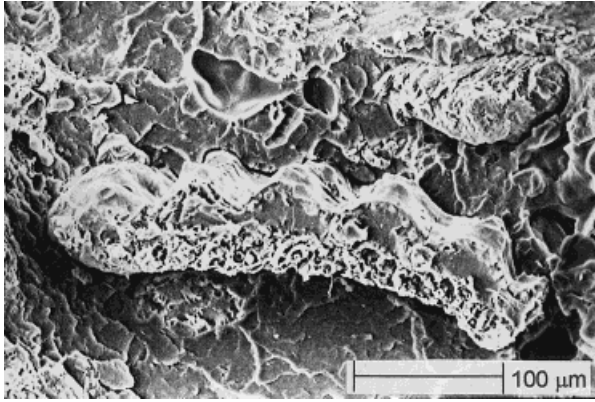**Figure 10** SEM micrograph of RH–PP composites after subjected to being HA at 90°C.

Figure 11   SEM micrograph of RH–PP composites in RD state.

90°C for 1245 h. It can be seen that filler-bundle debonding is evident on the crack plane. Mohd. Ishak et al.[20] reported that immersion of the composites in hot water does, to a certain extent, change the microstructure of the EFB. A fractograph study using SEM revealed crack formation on the filler bundle surface. The nature of that the cracks run parallel to the length of the fiber suggests that the cracks are formed perpendicular to the plane of the cell wall. Although such an observation is not prevalent in the present RH–PP composites, the significant reduction in both the tensile strength and the tensile modulus of the composites are believed to be related to weak regions formed at the filler–matrix interfacial as a result of a moisture attack at high immersion temperatures.

The appearance of the fracture surface of redried RH–PP composites is shown in Figure 11. It can be seen that there is a close resemblance to the wet specimens (Fig. 10). The filler seems to be detached from the surrounding matrix. During the redrying process, the cell wall shrinks and reverts back to it original dimension. According to Rozman et al.,[24] the internal stress produced during the swelling and shrinking processes is known to give rise to permanent damage to the fiber and subsequently causes interfacial degradation. Some evidence of the plastic deformation process of the PP matrix can also be observed in the redried composites. However, judging from the relatively low EB and energy-to-break values of the composites (as indicated in Figs. 3 and 4), it becomes clear that the contribution of the matrix-related toughening mechanisms is rather small. Thus, a combination of factors may adversely affect the mechanical properties of the EFB–PP composites.

CONCLUSIONS

The conclusions based on this study are as follows:

1. The kinetics of water absorption of RH–PP composites are observed to conform to Fick's Law behavior. It was also found that the diffusion coefficient, D, and the maximum moisture content, M_m, are dependent on the filler volume fraction and the immersion temperatures.
2. The incorporation of RH into the PP matrix resulted in a significant enhancement in the tensile modulus of the composites. However, this is at the expense of the reduction in the ultimate properties, namely, the tensile strength, EB, and energy to break. Qualitative evidence derived from the SEM observations indicate that the poor ultimate performance can be attributed to the poor filler–matrix interfacial bonding, to the size irregularity of the RH, and also to the nature of RH fillers, which has a strong tendency to exist in the form of bundles.
3. Immersion of the RH–PP composites in water resulted in a reduction of the tensile properties, the extent of which was found to be dependent on the water-immersion temperature. This was attributed to the interfacial degradation and also to the microstructural changes in the RH. The latter, which is associated with the structural breakdown of the cell wall, is believed to result in permanent damage to RH and, consequently, reduced its efficiency in acting as a reinforcement. Thus, the mechanical properties of the composites were not fully recovered even after redrying of the composites.

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