



Direct Usage of Products of Poly(ethylene terephthalate) Glycolysis for Manufacturing of Rice Husk/Unsaturated Polyester Composite

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Received 10 July 2006; accepted 30 April 2007

ABSTRACT

Unsaturated polyester resin, synthesized from glycolyzed product of poly (ethylene terephthalate) (PET) waste was combined with rice husks to form rice husk (RH)/polyester composites. PET from post-consumer soft drink bottles was recycled through glycolysis, followed by polyesterified with maleic anhydride and then cross-linked with styrene to produce a formulation for the resin. Characterizations of the synthesized resin were performed by hydroxyl and acid values determinations and Fourier transform infra red (FTIR) technique. The FTIR result for the prepared resin showed that cross-linking between polyester chain and styrene as cross-linkable monomer occurred at their unsaturated active sites. The effects of filler loading and surface modification of rice husks on the mechanical properties and water absorption of the composites were also investigated. It has been observed that the increasing filler loading resulted in reduction of tensile strength, elongation-at-break and impact energy but increased tensile modulus, hardness and water absorption. At similar filler loading, alkalized filler composite has higher mechanical properties. This observation was well supported by the SEM investigations of the fracture surfaces.

Key Words:

unsaturated polyester resin;
glycolysis;
recycled PET;
rice husk;
mechanical properties.

INTRODUCTION

PET is extensively used in the manufacture of soft drink bottles. Due to its subsequent percentage volume in the main stream waste and its high resistance to atmospheric and biological agents, a growing number of research works has been carried out by means of conversion of plastic waste to a value added product thus, to

reclaim new applications for polymer wastes. The use of PET wastes is inexpensive and effective because the PET consumption waste collection has recorded the fastest growth rate in global plastic market due to ongoing expansion of PET bottle usage. The worldwide production of PET is above 13 million tons/year and is increas-

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ing annually by 15 to 20% [1]. With such a large consumption, the effective utilization of PET wastes is of considerable commercial and technological significance.

PET waste may be converted into extruder or moulded articles after repelletizing, or it may be depolymerized to yield raw materials for resin synthesis. Another possibility is the recycling of segregated wastes by blending with small quantities of virgin monomer, bis(hydroxyethyl) terephthalate. However this work often lowers the quality of the final product [2]. It is more economical to convert PET into low molecular weight oligomers by glycolysis, in the presence of a transesterification catalyst [3]. When glycolysis is carried out using ethylene glycol (EG) or propylene glycol (PG) the oligomers obtained may be used in the synthesis of unsaturated polyesters (UP) by reaction with maleic anhydride [4]. This process has two distinct advantages of the process. The first one is that the PET waste is converted into a commercial value-added product, and the second one is the production of terephthalic acid (TPA)-based UP resins without the processing difficulties encountered by the use of plain TPA. The final product produced by glycolysis process has also higher modulus and strength than the product prepared by mechanical recycling.

Although a small number of studies have been carried out to utilize the glycolyzed product of PET into fibre reinforced composites using glass fibres [5] any report is not found on using natural fibre or filler. Hence, this study is an attempt of using natural fibre as reinforcing filler, replacing synthetic fibre which is more common, using the prepared resin as the matrix. Rice husk is chosen as the natural cellulose filler as it is one of the biomass materials abundantly available in Malaysia. However, in producing a good lignocellulosic composite, the main obstacle to be resolved is the compatibility between the filler and the matrix. Lignocellulosic materials present high moisture sorption and low microbial resistance which are disadvantages that need to be challenged and improved as far as possible. Previous studies have also shown that the waxy substances are the cause of poor fibres wettability and adhesion characteristics but they can be eliminated by extraction with organic solvents [6]. Various methods such as using sodium hydroxide [7,8] or coupling agents [9,10] have been used to modify the sur-

faces of natural fibres. Preliminary tests have proven that a simple and cheap method such as alkalization is most effective for the UP matrix [11].

The aim of this work is to investigate the possibility of using the glycolyzed product of PET waste as a matrix when rice husk (RH) is used in producing natural filler reinforced thermosets. The effects of filler loading and alkali treatment have been also investigated.

EXPERIMENTAL

Materials

Chemical Recycling of PET

The preparation of unsaturated polyester resin is based on the esterified glycolyzed product of PET with maleic anhydride and ethylene glycol [11]. The resin was first prepared by reacting the post-consumer PET soft drink bottles (washed, dried, and grinded) and ethylene glycol through glycolysis in a four-necked round bottom flask of 1 L capacity in the presence of zinc acetate (0.5 wt% of PET) as catalyst under refluxing at 180°C for 7 h. This was followed by a polyesterification step between the glycolyzed product and maleic anhydride. Later, hydroquinone in was added to an amount of 0.45 wt% of PET to prevent pre-mature curing before intermixed with 35% (w/w) styrene. Chemicals and solvents are of Analar grade and are used without further purification.

Rice husk

Rice husk (RH) supplied by Bernas Sdn. Bhd. was ground and sieved into sizes of 120-200 μm and used without any surface treatment. RH was dried in an oven at 70°C for an overnight before being treated with NaOH. The dried RH was immersed in 5 wt% NaOH solution for 1 h at 30°C then washed thoroughly with deionized water and air dried to produce 5 wt% alkali treated fillers.

Fabrication Method

RH/Polyester composites containing raw untreated and treated RH were fabricated using a simple hand lay up technique. The working surface is polished and a mould-releasing agent is applied on the surface. The prepared resin was mixed with cobalt octoate (accelerator) and methyl ethyl ketone peroxide (MEKP) as

a catalyst at a ratio of resin/MEKP/cobalt octoate of 100: 1.5:0.5 for curing. Other samples were prepared from 10% to 40% RH as filler (v/v). All samples were cured at room temperature for 20 h and post cured at 80°C for further 2 h.

Characterization of the Resin

The acid value was monitored during the reaction and determined by titrating the solution of weighed resin in acetone, with 0.2 N standard alcoholic KOH solution using phenolphthalein as indicator. The infrared Fourier transform spectrometer quenched with diffuse reflectance unit (DRIFT, Perkin Elmer 2000) was used to characterize the resin before and after curing.

Mechanical Testing

Tensile testings of the specimens have been carried out using an Instron 5567 as per ASTM D 638-91 at a cross-head speed of 5 mm min⁻¹ and a gripping length of 100 mm. Specimens were 100 × 15 × 3 mm in size. Impact energy was measured with a digital universal fractoscope (Ceast 6546/000) according to ASTM D 256. The hardness measurements were taken according to ASTM D 2240-91 using Shore scale D Durometer.

Water Absorption

The test was conducted according to ASTM D 471. Composite samples were first dried by heating in an oven at 70°C for about 24 h weighed and then soaked in a bath of deionized water at room temperature. After 24 h, the composite samples were removed from water, wiped with tissue paper, and weighed again. The percentage mass swell was then calculated as follows:

$$\text{Water absorption (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Where, W_1 and W_2 are the weights of the sample before and after immersion, respectively.

Morphological Study

A study on the morphology of the tensile fracture surfaces of the composite was carried out using a Philips SEM XL 30 scanning electron microscope. The fractured surface was spun coated with a thin layer of gold before characterization was done.

RESULTS AND DISCUSSION

Characterization of the Unsaturated Polyester Resin

The UPR prepared was a green colour liquid as a result of the pigments present in the PET bottles. At room temperature, the liquid turns to a semi-solid material therefore, preheating (e.g., in a water bath) was needed before using it. The hydroxyl value, acid number, and average of molecular weight of the resin were 26 mg KOH/g, 22 mg KOH/g, and 2328 g/mol, respectively. The FTIR spectrum of the resin is shown in Figure 1 and the corresponding peak assignments are included in Table 1.

FTIR was also used to observe the cross-linking during the curing process of the resin. The FTIR spectra of the prepared resin after curing (Figure 1) showed that the result of heating (during curing process) has diminished the bands at 912 cm⁻¹ characteristics of C=C vinyl (in styrene), 981 cm⁻¹ characteristics of C-H out-of-plane bending in CHR=CHR (in polyester) and 1641 cm⁻¹ indicative to the C=C in polyester. Thus, it suggests that cross-linking has occurred between polyester chains and styrene as cross-linkable monomer at their unsaturated active sites.

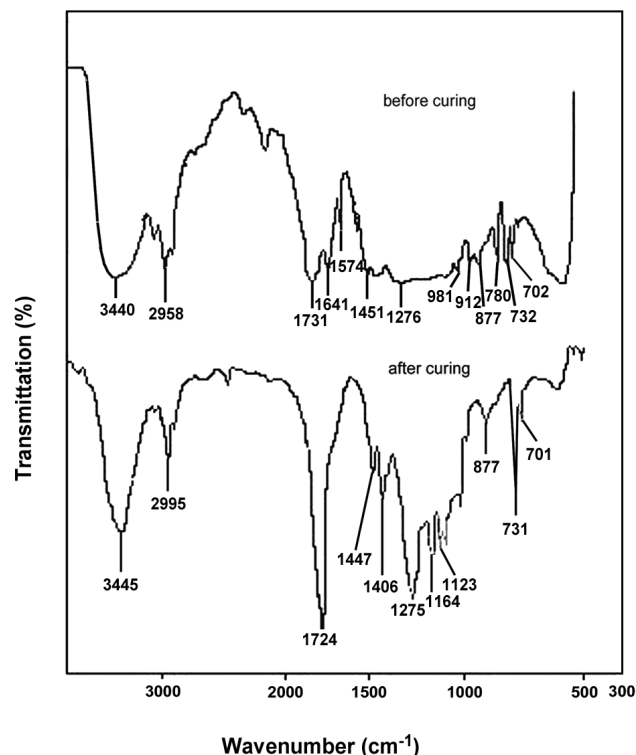


Figure 1. FTIR Spectrum of the prepared UPR.

Table 1. Band assignments of the FTIR absorptions of the prepared resin.

Band position (cm ⁻¹)	Assignments
3440	$\nu(\text{OH})$
2958	$\nu_{\text{as}}(\text{CH}_2)$
1731	$\nu_{\text{s}}(\text{C}=\text{O})$
1641	$\nu_{\text{s}}(\text{C}=\text{C})$
1574	$\nu_{\text{s}}(\text{C}=\text{C}) \phi$
1451	$\delta_{\text{as}}(\text{CH}_3)$
1276	$\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$
981	$\delta(\text{C}-\text{H})$
912	$\nu_{\text{s}}(\text{C}=\text{C})$ vinyl
871, 780, 732	$\delta(\text{C}-\text{H}) \phi$

(ν): stretching, (δ): bending, (s): symmetrical, (as): asymmetrical, and (ϕ): aromatic.

Characterization of the Composites

Mechanical Test

Figure 2 shows the variation of tensile strength with filler loading for treated and untreated RH. It can be seen that both systems show a decreasing trend as the filler loading increases. Other researchers [13] have observed a similar trend in other lignocellulosic-filled composites. Unlike fibres that have a uniform cross section and relatively high aspect ratio, the irregular-shaped fillers, such as RH, are rather poor at their capability to support stress-transmission in form of the matrix. Thus, the strength enhancement in the filled composite is in general, much lower than that of the fibre-reinforced composites. Nielsen [14] has reported that in the particulate filled composites due

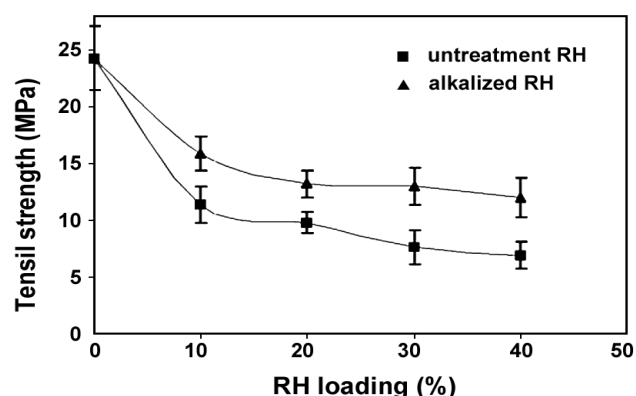


Figure 2. Effects of RH loadings on tensile strength of RH/UPS composites.

to poor stress-transfer at the filled-polymer interphases, discontinuities are created which generates weak structure. Agglomeration of the filler particles and dewetting of the polymer at the interphases aggravate the situations by creating stress concentration points which are accounted for the weakness in the composite.

It can also be seen in Figure 2 that at a similar RH loading, tensile strength of alkali treated RH is higher than the untreated RH. The result indicates that alkali treatment results in an improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking, hence promoting more resin-filler interpenetration at the interface. The alkali treatment improves the surface adhesive characteristics by removing the natural and artificial impurities such as lignin, wax, and pectin, thereby producing rough surface topography. The alkali treatment also helps to improve the dispersion of filler in the matrix, led in reducing the agglomeration of the filler [15].

The effects of treated and untreated RHs on tensile modulus of RH/polyester composites are shown in Figure 3. The increase in modulus with RH loading in both systems indicates the ability of RH to impart greater stiffness to the matrix. A similar observation can be seen in Figure 4 for hardness test results. For irregularly shaped fillers, the strength of the composites decreases due to the inability of the filler to support stress-transferred from the polymer to the matrix. On the other hand, poor interfacial-interfacial bondings between filler and matrix cause partially separated microspaces which can obstruct stress propagation when load is applied and enhance the stiffness of the composites. It increases brittleness and leads to

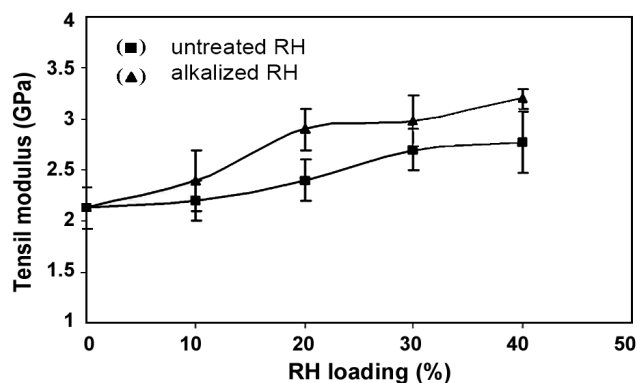


Figure 3. Effects of RH loading on tensile modulus of RH/UPS composites.

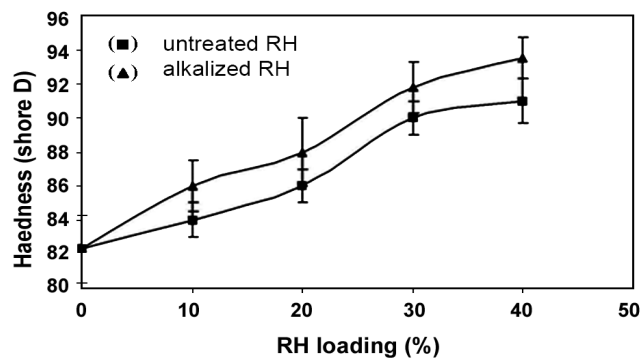


Figure 4. Effects of RH loading on hardness of RH/UPS composites.

increase in the modulus [16]. However, at similar filler loading, polyester matrix with treated RH exhibit higher tensile modulus and hardness than the similar systems without alkali treatment. As discussed earlier, this may be attributed to the improvement in the filler-matrix bonding, which leads to an increase in the efficiency of stress-transfer from the matrix to the filler phases.

Figure 5 shows the effect of filler loading on elongation-at-break of RH/polyester composites with and without alkali treatment on RH. Elongation-at-break showed a significant decrease by increasing filler loading which indicates hindrance of RH to molecular mobility or deformability of polyester matrix. It is known that fillers with higher stiffness than the matrix can increase the modulus of composites, but generally cause a dramatic decrease in the elongation-at-break. If the adhesion is poor, the elongation-at-break may decrease even more [17]. However, the treated RH has reduced this phenomenon where the RH/polyester composite exhibits higher elongation-at-break

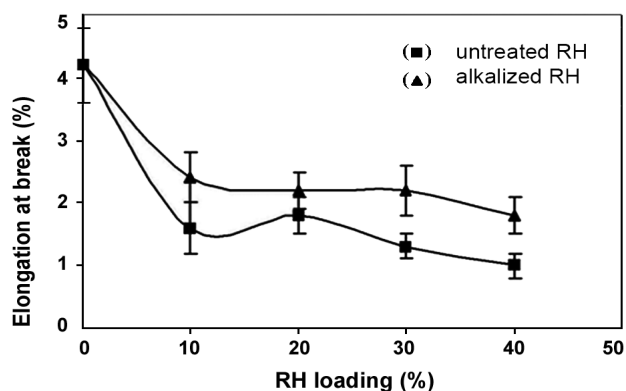


Figure 5. Effects of RH loading on elongation-at-break of RH/UPS composites.

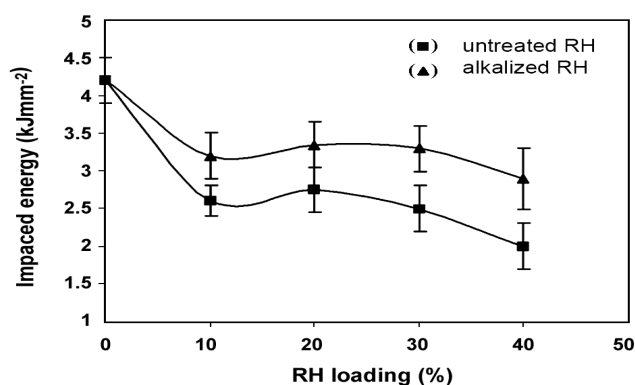


Figure 6. Effects of RH loading on impact energy of RH/UPS composites.

than the similar composite without fibre surface treatment. Alkali treatment onto fillers surface improves dispersion of the particles, reducing agglomeration by reducing the hydrogen bonding that holds them together [18].

The effect of filler loading on the impact energy of RH/polyester with and without alkali treatment of RH is shown in Figure 6. It can be observed that by introducing RH, the impact energy decreases rapidly and then becomes stable after 10 wt% of filler loading. Impact energy is an indication of tolerability for sudden force where the composite is subjected to rapid crack propagation through the material. The crack propagation is usually initiated through RH particles in the filled composite. Filler can absorb the energy to stop the crack propagation if the filler-matrix interaction is strong enough. The result therefore indicates that the filler-matrix is weak especially for the RH without alkali treatment.

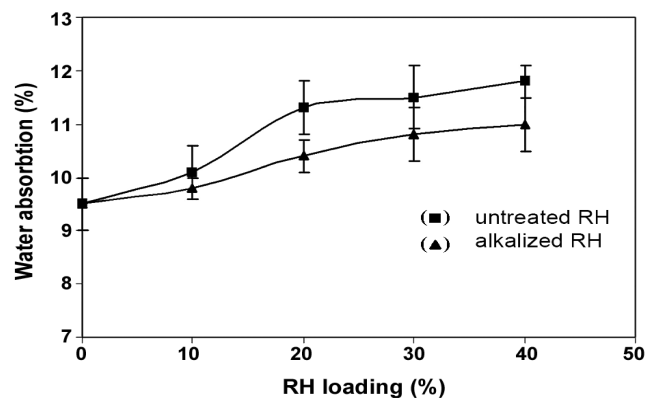


Figure 7. Effects of RH loading on water absorption of RH/UPS composites.

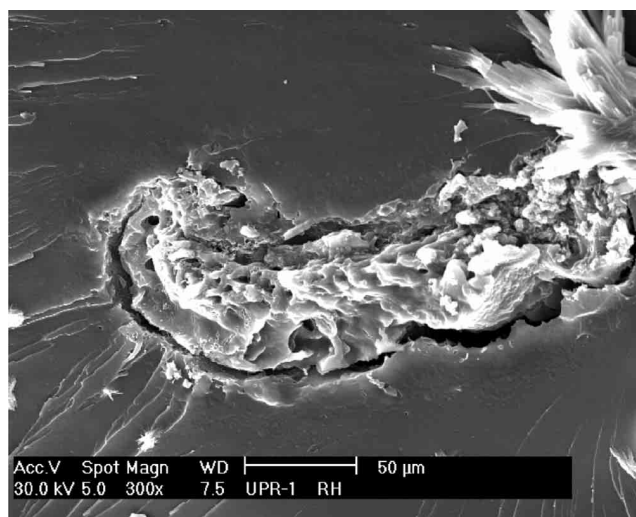


Figure 8. SEM of the fracture surface of untreated RH/UPS composites (300x).

Water Absorption

Figure 7 shows variation of water absorption versus RH loading in RH/polyester composites. RH is lignocellulose fillers and therefore hydrophilic in nature. The composites made from this filler showed higher water uptake. However, alkalinized filler shows lower water absorption properties than that of untreated filler. With the alkali treatment, more interfacial regions are expected to be formed between the filler and the polymer matrix. Thus, this matter would render the region stiffer and subsequently reduces the penetration of water. Mishra et al. [19] obtained similar effects of sodium hydroxide when used for sisal fibres. They reported that alkali treatment resulted in lower water absorption as compared with the untreated fibres composites. It could be due to the greater adhesion between the fibre and matrix.

SEM Analyses

Figures 8 and 9 show the SEM micrographs of fracture surfaces of RH/polyester composites without and with alkali treatment of RH, respectively. Tensile fracture surfaces in both figures clearly show that the size of RH without treatment (Figure 8) is bigger than the size of RH after surface treatment (Figure 9) indicating the cell wall thickening and shrinkage of fillers during the alkali treatment. It is believed that the reduction of filler particle sizes led to increase of the fillers' contact with the matrix. Prasad et al. have reported that the fatty acids which form the waxy cuti-

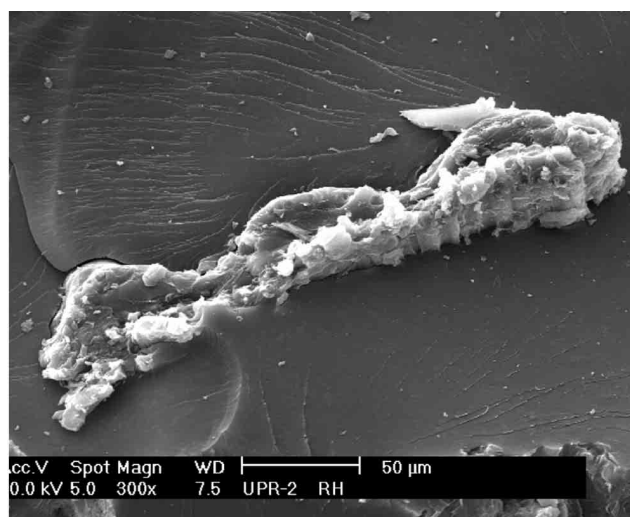


Figure 9. SEM of the fracture surface of alkalinized RH/UPS composites (300x).

cle layer on the natural fibres are removed by alkali treatment [20]. The bigger size of RH could also be due to the agglomeration and poor dispersion of filler in the matrix [21]. Figure 9 also shows that the interaction of filler-matrix is improved without crack propagation occurring at the filler-matrix interfaces. Whereas, for untreated filler, there are some parts in the matrix where fillers are not completely distributed (Figure 8). These observations show that the alkali treatment increases the interfacial adhesion between the fillers and the matrix. The results therefore indicate that the morphological studies agree considerably with the improvement of mechanical properties of the treated RH/polyester composites.

CONCLUSION

Recycling of PET waste through glycolysis was successfully performed to obtain unsaturated polyester resin. This resin offered a function as matrix for natural filler in a RH reinforced thermoset, thus it may act as a beneficial means for a new product of recycled PET. The incorporation of RH into polyester matrix increases the tensile modulus, hardness, and water absorption but decreases the tensile strength and elongation-at-break. Poor filler-matrix interactions and filler dispersions are believed to be responsible for the poor ultimate properties. However, with the alkali surface treatment, the properties of RH filled polyester, synthesized from glycolized product of

poly (ethylene terephthalate) (PET) waste were improved significantly.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Higher Education of Malaysia for providing financial assistance through research grant UKM-ST-01-FRGS0007-2006.

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