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APPLICATION OF RICE HUSK ASH AS FILLERS IN POLYPROPYLENE: EFFECT OF TITANATE, ZIRCONATE AND SILANE COUPLING AGENTS

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Abstract—The effects of applying titanate (LICA 38), zirconate (NZ 44) and silanes (PROSIL 2020 and PROSIL 9234) coupling agents to rice husk ash (RHA) in polypropylene composites are described. RHA consists predominantly of silica. Polypropylene composites of 10–40 wt% filler loadings were compounded using a Brabender twin screw extruder. The melt flow index decreased with filler content but for the composite treated with the built-in peroxide generator (PROSIL 2020), the reverse was true. For most of the composites, the flexural modulus increased with filler content while tensile strength, elongation at break and Izod impact strength showed a decrease. PROSIL 2020 coupling agent improved the tensile strength of the composites most, while the impact properties were enhanced by the LICA 38 and the PROSIL 9234 coupling agents. None of the coupling agents increased the stiffness of the composites except for NZ 44 at maximum filler loading. The mechanical properties of the RHA composites were compared to polypropylene composites filled with commercial fumed silica and talc.

INTRODUCTION

The application of rice husk ash (RHA) as a filler in polypropylene has been reported in our earlier publications and the effects of some coupling agents were also described [1, 2]. In this paper the studies of RHA-filled polypropylene are extended to include four different types of coupling agents, a titanate (LICA 38), a zirconate (NZ 44) and silanes (PROSIL 2020 and PROSIL 9234). The objective is to investigate the effect of these coupling agents on the mechanical properties of the polypropylene composites. The properties of these RHA composites were compared to those of polypropylene filled with commercial fumed silica and talc.

As the name implies, the rice husk ashes (RHA) used in this experimental work are derived from rice husks, which is usually regarded as agricultural waste and an environmental hazard. Rice husk when burnt in open air outside the rice mill yields white ash that consists predominantly of silica and has a good potential to serve as filler in thermoplastics.

Reports on the application of RHA as a filler material in thermoplastics is believed to be quite limited. Perhaps, the earliest work on such an application was that of Lathrop [3], who incorporated up to 60% of rice husk flour in a phenol-formaldehyde resin. Later, Mehta and Pitt [4] described the use of RHA as a reinforcing agent for synthetic and natural rubbers and for the manufacturing of hydraulic cement. Investigation of RHA's potential application as a replacement to carbon black in epoxidized natural rubber was also proposed recently [5, 6].

On the other hand, the use of RHA on non-polymeric products had been extensively reported by Beagle [7] and Houston [8]. Examples of other applications include synthesis of zeolite [9, 10], and as filler materials in the building industry [11, 12]. Nakata *et al.* [13] described details of silica preparation from rice husk and the properties of the ash obtained by combustion at temperatures between 400–1500°C.

Coupling agents have been commonly applied for improvement of properties in fibre or particulate-filled composites [14–20]. The most common type of coupling agent presently used are organofunctionalsilanes and organotitanates. The other coupling agent that is less readily available due to a higher production cost is the organozirconate group [21]. All the coupling agents above may be simplified to the general formula of $R{-}M{-}X_3$ where R is the organofunctional group, M is the tetravalent base metal (Ti, Zr and Si) and X is a hydrolysable group (e.g. ethoxy for the silane-based coupling agent). Each coupling agent has its own virtues and limitations. For instance when coupling to silica, the Si—O—Si bond from the silane-based coupling agent being stronger than the Ti—O—Ti bond is likely to impart better mechanical properties to the resultant composites than the titanate-based system. Titanium tends to scavenge free radicals and thus affects cure efficiency while Zr^{4+} being a peroxide activator accelerates the curing process [21].

Application of another type of ash, i.e. pulverized fuel ash (PFA) as a filler in polypropylene has been reported by Davies *et al.* [22, 23] where silane treatment improved the tensile strength and modulus, but slightly reduced the impact property of their PFA composites. Anzai *et al.* [24] patented the use of

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spherical fused silica as the major filler in various resins where the use of a silane coupling agent was preferred. Silicas have been commonly used as fillers but the application are mainly limited to rubber compounding [25–27]. Interesting accounts of silica were described by Wagner [28] and Sekutowski [29].

EXPERIMENTAL

Materials

RHA was obtained from a rice mill in Bagan Serai, North Malaysia. The polypropylene used was Propelinas 600G (homopolymer) from Polypropylene (M) Sdn Bhd with density and melt index specified as 0.9 g/cm^3 and 12 g/10 min respectively. The coupling agents chosen were LICA 38 [neopentyl(diallyl)oxy, tri(dioctyl)pyro-phosphato titanate], and NZ 44 [neopentyl(diallyl)oxy, tri(N-ethylenediamino) ethyl zirconate] supplied by Kenrich Inc.; PROSIL 9234 (n-octyltriethoxysilane) and PROSIL 2020 [a proprietary silane containing the peroxide bis(t-butyl peroxy)di-sio-propyl benzene] were acquired from Prosil Inc. for comparison purposes, AEROSIL 380 fumed silica purchased from Degussa AG was incorporated into the polypropylene. Readily available commercial talc filled polypropylene compounds at 20% (Sumitomo BWH52) and 40% filler contents (Nagase Calp 4600G) were subjected to the same specimen preparation techniques and mechanical testings.

RHA used in this study has been analysed to have about 95% silica content. Details of the chemical and physical properties of the RHA filler particles used have been discussed previously [2].

An application technique of the coupling agent was carried out as advised by the manufacturer of the respective coupling agents. For the titanate and zirconate coupling agents, it was the polypropylene resin itself that was treated rather than the filler. This is contrary to that of the silane coupling agents where the RHA filler itself underwent coupling agent treatment prior to compounding.

The dosage of the LICA 38 was 0.2 wt% of polypropylene plus 0.5 wt% of RHA. The coupling agent was diluted in n-pentane to make up a 5% solution which was sprayed onto the polypropylene as the latter was rotated in a table-top tumbler mixer. The dosage for the zirconate coupling agent is somewhat different. At lower filler loading, 0.2 wt% of polypropylene was used; at higher loadings (30 and 40% filler content), 0.5 wt% of RHA was applied. This dosage is in line with the recommendation of the manufacturer, i.e. 0.2 wt% of polypropylene or 0.5 wt% of RHA. The coupling agent was diluted in propanol to assist distribution of the coupling agent on the polypropylene resin subsequent to compounding.

For the silane coupling agents, the treatment levels used were 0.5 and 1.5 wt% of filler for the PROSIL 9234 and PROSIL 2020 respectively. The former was diluted in ethanol to make up a 10% solution. The RHA filler was charged into a bench top tumbler mixer and the PROSIL solution was added slowly over a period of 15 min to ensure uniform distribution of the coupling agent. After completion of the silane addition, the filler was continuously mixed for 30 min. The treated filler was then dried at 100°C for at least 2 hr.

Compounding

The untreated and treated RHA were compounded into polypropylene by means of a Brabender DSK 42/7 twin screw compounder with a temperature profile of 190, 200 and 210°C (from feeding to die zone). The compounds were extruded through a twin 4 mm rod die to a water bath, pulled and pelletized. Filler loadings of 10, 20, 30 and 40 wt%, were compounded. Owing to a processing difficulty, the 40% loading could not be compounded for the fumed silica/polypropylene composites.

The compounded samples were prepared into test specimens using a 20 tonne Battenfeld BA 200 CD Plus machine. A test specimen mould from Mastermould Inc. was employed for production of test specimens.

Studies on the morphology of the composites' tensile fracture surfaces were carried out using a scanning electron

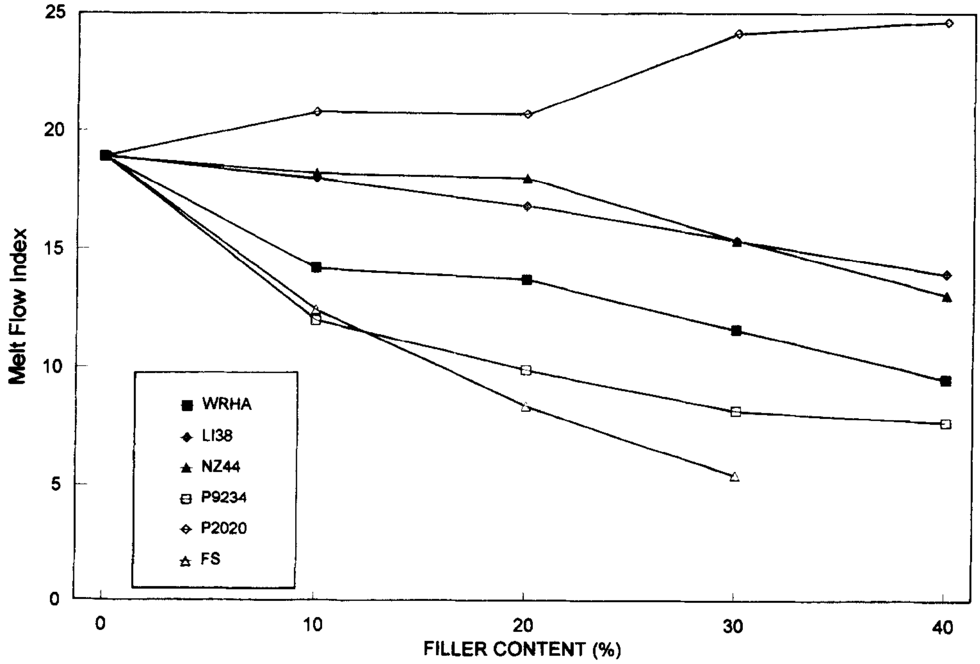

Fig. 1. Effect of filler loading and coupling agents on the flow behaviour of RHA composites. WRHA represents uncoupled RHA, the coupled composites are denoted by the respective numbers and FS stands for fumed silica composites.

microscope (SEM), model Phillips XL-40. Samples were coated in platinum using a Hitachi E102 ion sputter.

Mechanical tests

A flexural test was carried out according to ASTM D790 at a test speed of 2 mm/min on a Lloyd L1000S tensile/compression machine. Tensile tests were carried out using an IR non-contacting extensometer for elongation determination. The gauge length was 65 mm and the speed of testing was 5 mm/min. An Izod impact test was performed using a 2 J hammer (Ceast equipment) based on ASTM D256-88. Impact specimens were notched (45°C) using a Davenport notch cutting apparatus.

All mechanical tests were carried out at standard laboratory conditions of 27°C and 65% r.h. in accordance to the ISA 291 standard on conditioning and testing atmospheres for tropical countries.

RESULTS AND DISCUSSION

Melt flow index

As filler content increases, the MFI value decreases for all composites with the exception of the PROSIL 2020 treated composite. This is shown in Fig. 1. This is an expected result as addition of fillers to the polypropylene restricts molecular motion, imposing extra resistance to flow. The titanate and zirconate treatments result in a smaller degree of MFI reduction when compared to that of silane PROSIL 9234.

Addition of PROSIL 2020 coupling agent, however, caused a marked increase in melt flow index of the RHA composite. In fact the presence of PROSIL 2020 seems to cause a significant change in the rheology of the melt since the usual trend of decreasing melt index values to filler content is reversed; the melt index actually increases with filler contents. A higher MFI value indicates easier flow of material. The increase in MFI values indicates a decrease in the molecular weight of the polypropylene matrix. Probably this is caused by molecular chain scission initiated by the actions of the free radicals generated by the peroxide in the coupling agent. The degradation results in lowering of the molecular weights of the polypropylene matrix and consequently easing the flow of the melt Tzoganakis *et al.* [30] produced nine different molecular weight polypropylenes through controlled peroxide degradation and showed similar effects of decreasing shear stress with lowering of molecular weight.

The fumed silica-filled composites experience the greatest fall in MFI values confirming the processing difficulty experienced during compounding of the samples. This may be attributed to the extreme fine particle size (0.4 μm) of the fume silica as compared to that of RHA particles (5 μm).

Mechanical properties

The mechanical properties of the RHA composites are as shown in Table 1.

Flexural modulus

As expected the modulus, which indicates material stiffness, increases steadily with increasing filler content for all the RHA composites as shown in Fig. 2. None of the coupling agents increased the flexural modulus of the composites (with the exception of the NZ44 at the maximum loading of 40%). The coupling agents appear to allow easier movement of the RHA particles within the polypropylene matrix resulting in more flexible composites. Overall, the modulus of the fumed silica-filled composite is greater, probably due to its finer particles size. Again the comparison would be fairer if the particle size of the fumed silica is of the same order as the RHA particles. The moduli of the RHA composites are also lower than the moduli of the commercial talc composites. The treated RHA composites did maintain the general trend of increasing modulus with higher filler loading but the stiffness improvements were

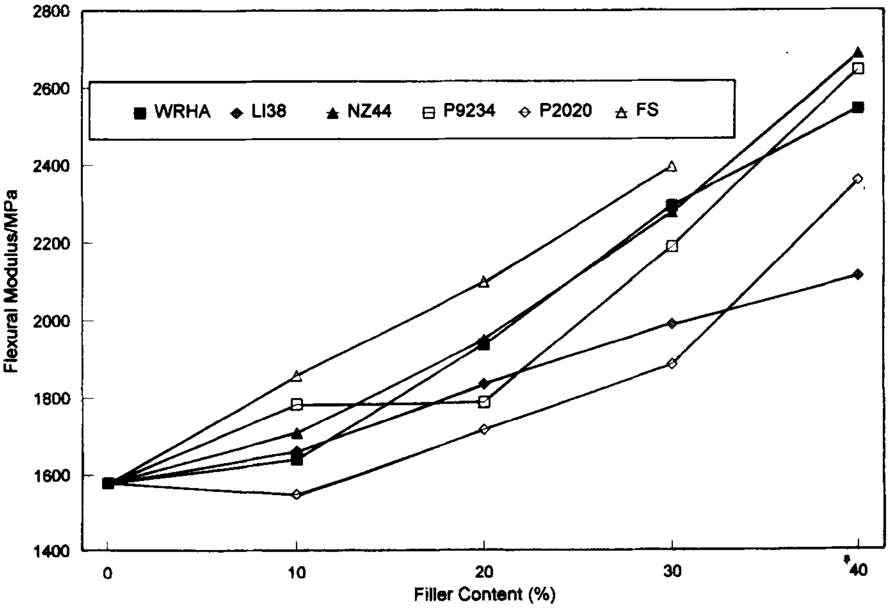

Fig. 2. Effect of filler loading and coupling agents on the flexural modulus of RHA composites. Legends are as explained in Fig. 1.

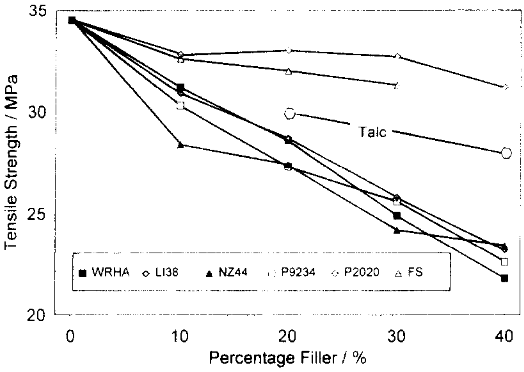

Fig. 3. Effect of filler loading and coupling agents on the tensile strength of RHA composites. Legends are as explained in Fig. 1.

somewhat less than those of the uncoupled composites.

The modulus of composites has been represented by a number of equations, the first and simplest being from Einstein [31]

$$E_R = 1 + 2.5\phi \qquad (1)$$

where E_R is relative modulus (of composite to polymer) and ϕ is volume fraction of filler. This equation is, however, applicable only to materials filled with low concentrations of non-interactive spheres. For low aspect ratio fillers such as the RHA, the equation from Lewis and Nielsen [17]

$$E_C/E_P = (1 + \eta\xi\phi)/(1 - \eta\Psi\phi) \qquad (2)$$

is more applicable. η is a constant related to the Einstein coefficient, ξ is related to relative moduli of fuller and polymer and $\psi\Phi$ is a parameter dependent on the maximum packing fraction of the system. Theoretical calculation for modulus is not possible at this moment because the modulus of the RHA filler (which determines the value of parameter ξ) is not available yet.

Tensile properties

Applications of LICA 38 and PROSIL 9234 did result in some improvement of the tensile strength but the changes were not much (Fig. 3). On the other hand, a negative effect on the tensile strength was observed for the composites with the zirconate-

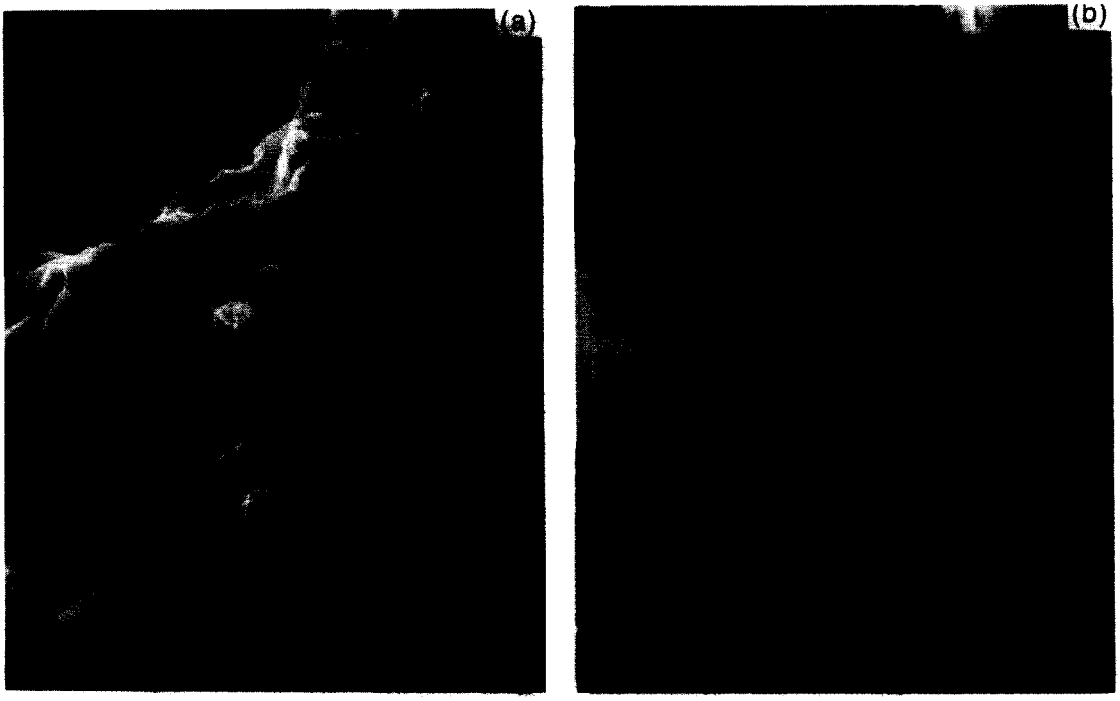

Fig. 4. SEM micrographs of (a) PROSIL 2020 composite and (b) uncoupled WRHA composite after tensile fracture (×2000). Extensive surface modification in the former may be observed due to the improved filler to matrix adhesion by the action of the coupling agent. Note the brittle mode of failure as compared to the ductile mode in the uncoupled system.

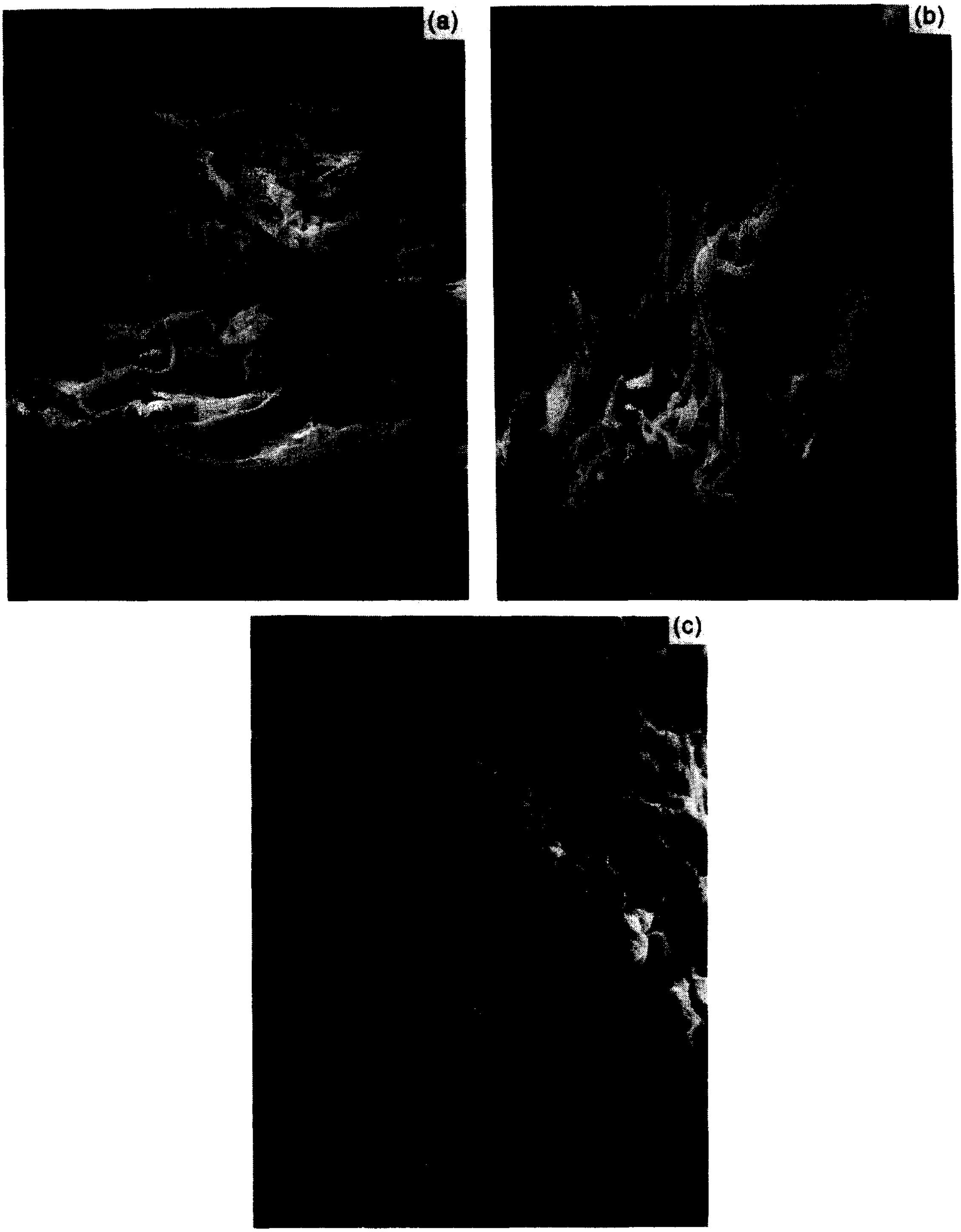

Fig. 5. SEM micrographs of RHA composites treated with (a) LICA 38; (b) NZ 44; and (c) PROSIL 9234 coupling agents after tensile fracture (× 2000). Only slight surface modification may be observed. Note the ductile failures in (a) and (b) and brittle failure for (c).

coupling agent particularly at low filler loading. Of all the coupling agents, PROSIL 2020 seems to give the greatest enhancement to the tensile strength of the composites, particularly at higher filler loading (where the improvement was as much as 31 and 43% for the 30 and 40% filler contents respectively). This seems to agree with the manufacturer's study that the PROSIL 2020 gave the best tensile strength in the mica/polypropylene system when compared to seven other coupling agents under investigation [32]. This improvement may be attributed to an improvement in the filler–matrix adhesion. Treatment of fillers by the coupling agent modifies the nature of the interface as described previously. SEM micrograph in Fig. 4(a)

Fig. 6. SEM micrograph of fumed silica composite after tensile fracture (× 2000).

shows pronounced modification of the PROSIL 2020 treated composite's interface when compared to the uncoupled RHA composite (Fig. 4(b)). The composites filled with fumed silica displayed the higher tensile strength relative to the other composites. Again the extreme fine particles size may account for these differences.

Izod impact resistance

The impact property of the RHA composites, as expected, decreases with increasing filler content (Fig. 7). At a filler loading of 20% and greater, all the four coupling agents do improve the impact strength of the composites. LICA 38 and PROSIL 9234 brought greater improvement compared to those of NZ 44 and PROSIL 2020. It appears that improved filler–matrix adhesion did favour the impact property of the RHA-polypropylene composites. As for the LICA 38 and NZ 44 coupling agents, the fall in impact strength was only at 10% loading after which the impact strength stabilized and did not change significantly with higher filler loading. Compared to the commercial polypropylene-talc composites, at 20% filler content level, the impact strength of the polypropylene-talc is still superior than all the RHA composites. However, at 40% filler content, the strengths of all the treated RHA composites are equal or better than the former. Overall the RHA composites also have better impact strength than the fumed silica-filled composite. It is also worth noting that the present Izod impact strength values revised the former values reported in our earlier papers [1, 2].

Without any coupling agent to modify the RHA surface characteristics, poor wetting of the particles by the polypropylene matrix is expected. This gives rise to poor interfacial adhesion between the filler and the polymer matrix resulting in weak interfacial regions. During the impact test, a crack travels through both the polymer as well as along the weaker interfacial regions. The latter cannot resist crack propagation as effectively as the polymer region hence reducing the impact strength [33]. Increasing the filler content merely increases the interfacial regions that exaggerate the weakening of the composites to crack propagation.

Morphological aspects

SEM micrographs of the tensile fracture surfaces of the RHA composites are shown in Figs 4(a, b), 5(a–c) and 6. The effectiveness of PROSIL 2020 as the coupling agent for improving the filler–matrix adhesion may be observed in Fig. 4(a) when compared to the uncoupled polypropylene/RHA composite's surface in Fig. 4(b). In the latter SEM, the discrete RHA particles or agglomerates are clearly visible, evidently without any adhesion to the polypropylene matrix. Figure 5(a–c) shows the surfaces of the RHA composites with the titanate LICA 38, zirconate NZ 44 and the silane PROSIL 9234 coupling agents. Some amount of surface modification may be observed but at a much lower degree when compared to

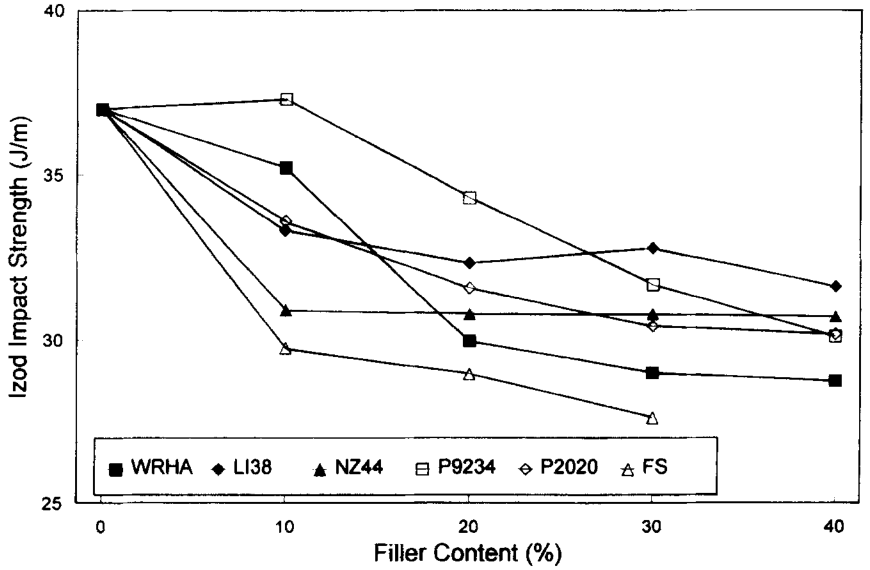

Fig. 7. Effect of filler loading and coupling agents on the Izod impact strength of RHA composites. Legends are as explained in Fig. 1.

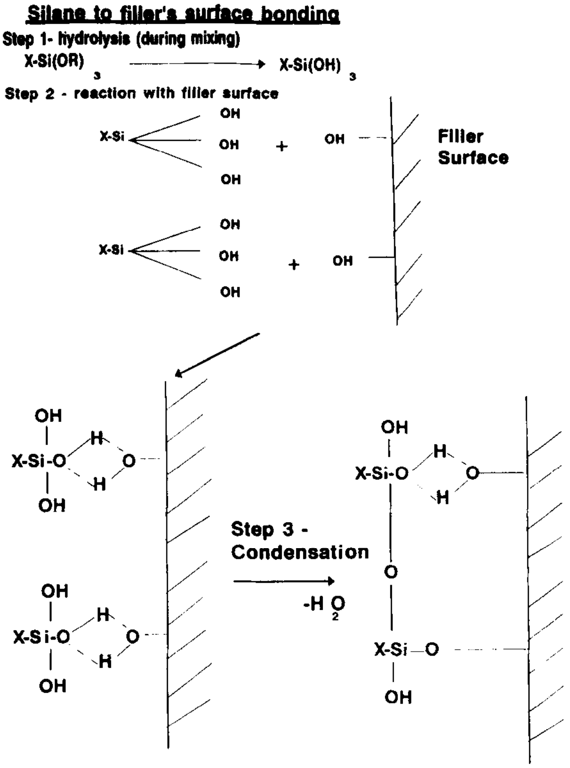

Fig. 8. Bonding mechanism of silane coupling agent to RHA filler's surface.

that observed in Fig. 4(a). These observations give an indication as to the degree of coupling achieved by the various coupling agents and are reflected by the amount of tensile strength enhancement shown earlier in Fig. 3. The PROSIL 2020 coupling agent, with the inbuilt peroxide, bis(t-butyl peroxy)di-isopropyl benzene, that resulted in the best filler–matrix adhesion, gives the greatest enhancement to the tensile strength of the RHA composites. On the other hand, the three coupling agents caused only a small improvement to the tensile strength of the composites.

The SEM micrographs also indicate the mode of failures of the RHA composites. The uncoupled composite [Fig. 4(b)] and those treated with the titanate and zirconate coupling agents [Figs 5(a and b)] experienced ductile failures. It appears that the incorporation of the RHA does not alter the ductile mode of failure of the original polypropylene matrix. On the other hand, the SEM micrograph in Fig. 4(a) shows that addition of the PROSIL 2020 coupling agent results in a marked transition of the failure mode (to brittle fracture), hence the drastic reduction in elongation. Even 10% incorporation of the PROSIL 2020 treated filler causes a sudden reduction of elongation, e.g. from excess of 600% for neat polypropylene down to 15.4% and eventually to 3.1% at maximum loading. It seems that the higher degree of coupling between the filler to matrix interface allows less molecular reorientation when subjected to a stretching force. The SEM micrograph of PROSIL 9234 composite [Fig. 5(c)] also indicates a brittle mode of failure although no significant enhancement in the tensile strength was observed. A small degree of filler wetting may be observed in the middle region of the micrograph Figure 6 shows the brittle failure in the fumed silica composite. It appears that the extremely fine silica particles get into the polypropylene molecular chains arrangement, disrupting and hampering mobility of the chains. Upon application of tensile stress, the material breaks abruptly, hence the brittle fracture.

Mechanism of coupling agent

The reaction mechanism of the tetrafunctional organo-metallic compounds based on silicon and titanium is believed to occur in three steps as shown by the simplified illustration in Fig. 8. First the alkoxy group in the coupling agent undergoes a hydrolysis process. Water for the hydrolysis may come from the surface humidity of the filler (in the case of the silane treatment), and from the surface or in the polypropylene resin in the case of the titanate treatment. Next the group reacts with the hydroxyl of the filler surface by hydrogen bond formation. Then, Si—O or Ti—O cross links are formed between the filler surface and the adjacent functional groups in a condensation reaction with the elimination of water. The zirconate coupling agent is also believed to function under a similar mechanism.

The nature of interactions on the polymer-coupling agent interface is more complex. For matrix polymer containing reactive groups, there is a possibility of covalent bond formation between the group and the organofunctional group of the coupling agent. Polypropylene being a non-polar has very little intrinsic reactivity and hence simple coupling as described above may not take place. Some additive such as peroxide may be introduced to attack the polypropylene molecular chains creating reactive sites for the bonding process [34]. Prosil 2020 is a proprietary silane coupling agent containing a peroxide that acts as free radical generator. A thermal effect during the compounding process results in the peroxide disintegration and releases free radicals. The radicals in turn attacked polypropylene molecules abstracting hydrogen thus creating radical sites on the polypropylene matrix. Silane groups that are already attached to the filler surface may graft to these radical sites to finalize the polypropylene-filler bonds. PROSIL 9234, LICA 38 and NZ 44 on the other hand do not create chemical bonds but probably improve the filler-matrix adhesion by assisting wetting of the filler's surface.

Economic and ecological advantages

The RHA fillers claim two distinct advantages over the other commercial fillers. Firstly, because of the economic factor; having the origin of an unwanted by-product of a rice mill, the RHA is readily available at extremely low cost, typically at a low price of US$ 100 per tonne. Of course a further cost is involved for further processing (e.g. grinding to size) but the cost is not high. Usually the RHA is obtained from open field burning sites burners and may be ground directly. Overall, the processed RHA filler should command a considerable price advantage over other commercial fillers particularly commercial silica.

Secondly, in the current world's ever-increasing sensitivity to the environmental issue, disposal of rice husks waste poses a rapidly growing problem, in part due to the low bulk density of the husks. The annual production of rice in Malaysia is estimated to be some 1.7 million tonnes and generates approx. 340 tonnes of waste husk [35]. At present, the common method of disposal is dumping the RHA (which has been burnt at mill sites) on a waste land, consequently creating environmental, pollution and land dereliction problems. Hence, finding useful applications of the RHA would help to alleviate problems related to the disposal of the waste husks.

CONCLUSIONS

The four coupling agents used in this study brought various changes to the mechanical properties of the composites. PROSIL 2020 notably improved the tensile strength while PROSIL 9234 and LICA 38 improved the impact property. The zirconate coupling agent brought marginal improvement to the stiffness of the composites. In contrast to the composite filled with commercial fumed silica, most of the RHA composites have better impact properties but lower tensile and flexural strengths.

Of all the coupling agents used in this study, the peroxide-containing PROSIL 2020 seems to produce the most impressive set of properties. It results in the greatest enhancement to the tensile strength to the RHA composites, even better than the commercial grade polypropylene/talc composite and polypropylene filled with commercial silica. The impact strength is improved though marginally. Unfortunately there is a tradeoff—some of the modulus increase has been sacrificed. It is worth noting too that even in the absence of any coupling agent treatment, the uncoupled RHA composites still exhibit reasonable properties over the neat polypropylene and the treated composites; a high modulus value with moderate tensile and impact properties.

Suitable applications for the RHA composites would be in components demanding high stiffness, excellent dimension stability with reasonable tensile and impact properties. Although the rice husk ashes do not perform superbly as reinforcing fillers, one may still consider that the economic and ecological benefits plus their ability to perform as low cost extenders (without significantly affecting the properties of interest in the composites) are of considerable advantages in their application as fillers in polypropylene.

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