MECHANICAL, ELECTRICAL, AND THERMAL PROPERTIES OF MALEIC ANHYDRIDE MODIFIED RICE HUSK FILLED PVC COMPOSITES

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Unmodified and modified rice husk powder filled PVC composites were prepared having different amounts of rice husk powder. Mechanical, thermal, and electrical properties of these composites were determined. The tensile strength of rice husk powder PVC composites having 0, 10, 20, 30, and 40 weight percent of rice husk powder was found to be 33.9, 19.4, 18.1, 14.6, and 9.5 MPa, respectively. Adding of maleic anhydride-modified rice husk powder improved the tensile strength of rice husk powder PVC composites. Flexural strength and flexural modulus of composites increased on treatment of rice husk powder due to the improved bonding between rice husk powder and PVC matrix. Arc-resistance of rice husk powder PVC composites was not affected on increasing loading of the powder. Volume resistivity and surface resistivity decreased with increasing loading due to the presence of impurities and water molecules. Vicat softening temperature increased with rice husk powder loading. Addition of rice husk increased the melting temperature of the composite matrix as compared to pure PVC.

Keywords: PVC; Composites; Thermal; Mechanical

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INTRODUCTION

Organic natural fibers have been used for reinforcement, dating back to prehistoric times when straw was reinforced in bricks during the reign of the Pharaohs. Inca and Maya craftspeople similarly employed plant fiber when making reinforced pottery (Farnfield 1975). Henry Ford constructed an automobile body in 1930 from hemp. Presently automobile manufacturers such as BMW and Mercedes are incorporating hemp into car components (Farnfield 1975). The use of fillers into polypropylene (PP) has been an accepted route to achieve enhancement in material properties and cost saving (Pritchard 1998; Rozman 1998). These fillers can be categorized as inorganic or organic. Inorganic fillers, in particular silica or calcium carbonates, are used in PP composites (Nakamura 1999; Tabtiang 2000; Qiu et al. 2000; Pukanszky 1995; Kim et al. 2006). In the last two decades, organic natural fillers have gained importance over the inorganic fillers due to their low densities, low cost, non-abrasiveness, high loading levels, easy recyclability, bio-degradability, and renewable nature (Chand et al. 1987). These organic fibers can be used either in powder or fiber form.

Recently the utilization of natural fibers and powders derived from agricultural sources, such as sisal, pineapple, banana, and palm oil fruit bunch (Chand and Rohatgi 1994) has become a subject of interest in the polymer composites industry, due to the above advantages. Investigations carried out in this field have shown that stiffness, hardness, and dimensional stability of the polymer could be improved by incorporation of these renewable fillers. These studies have further demonstrated that various functional groups available in the organic filler can be used to modify the filler chemically to improve the compatibility between the fibers and polymer (Darah 1996). Rice husk is one such main agro-waste byproduct, which contains cellulose 35%, hemicellulose 25%, lignin 20%, and ash 17% (silica 94%), by weight (Anon. 2008). Rice husk (RH) has been used as an alternative filler to commercial silica. In a similar study, maleic anhydride has been used to improve the properties of rice husk PP composites (Chand et al. 1987; Ismail 1999). These factors encouraged us to investigate the performance of rice husk powder as a filler for PVC composites. In this study, the effect of rice husk loading on the mechanical properties of rice husk PVC composites has been investigated. Unmodified and modified rice husk powder filled PVC composites have been prepared. A comparison has been made between the properties of rice husk powder filled PVC with treated rice husk powder filled PVC composites.

EXPERIMENTAL

Materials

The poly-vinylchloride (PVC) used in this study was a suspension resin with solution viscosity K-value 67 and grade H 072. This homopolymer PVC is a medium molecular weight resin designed for general purpose and rigid applications. The compounding formulation for PVC was supplied by Manglam Polymer Ltd (India). Rice straws were obtained from Betul Madhya Pradesh (India) in the form of agriculture residues. The maleic anhydride used as compatibilizer (MW 98.06 and M.P. 50.53°C) was supplied by Loba Chemie Bombay. Benzoyl peroxide used as a catalyst (M.P.102°C) was supplied by Central Drug House (India). Xylene (MW106.17) was supplied by Sd Fine-Chem. Ltd. (India).

Methods

Compounding of PVC on high speed mixer

The above supplied ingredients were mixed in an Inalsa Companion mixer grinder (500 w) at 1000 rpm until the desired degree of uniformity was obtained. Mixing was done for 10 minutes.

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Washing of rice straws

Rice straws were washed with water in order to remove dust and mud.

Drying of rice straws

Rice straws were dried under the sunlight for 3 days at 35˚C, and then in a hot air oven for 8 hours at 80 °C.

Grinding of rice straws

The rice straws are generally 80 to 100 cm long. Therefore, before grinding, rice straws were cut into small pieces of length 5 cm. These 5 cm long straw pieces were ground in an Inalsa Companion mixer grinder (500 w) to fine powder.

Sieving of rice straws

Ground rice straw powder was sieved through 710 and 355 μm screen sizes to get uniform particle size. The rice straw powder that remained between 710 and 355 μm sieves was used to make the composites.

Treatment rice husk powder

Rice husk powder was esterified to improve its compatibility with the PVC matrix, using a commercial maleic anhydride (MA) (Loba Chimie India). The rice husk powder was dried at 80˚C in a vacuum oven until a constant weight was reached. The purification of powder was carried out by immersing in water for 24 hrs. to remove all impurities, followed by vacuum filtration.

The esterification reaction was carried out by immersing the rice husk powder in a solution of 340 ml of xylene containing 18.5 g of maleic anhydride and 1.5 g of benzoyl peroxide as catalyst and then heating at reflux temperature of 140˚C for 4 hrs. The esterified powder was separated from the solution and washed with distilled water to remove the unreacted materials. Finally, the powder was dried at 70˚C in a vacuum oven until a constant weight was achieved.

Composite preparation

Both compounded PVC and rice husk powder were mixed as specified in Table 1 at 170˚C with a residence time of 10 min on a two-roll mill. Sheets obtained from the two-roll mill were placed in a rectangular steel mold. A hydraulic oil-heated press with a pressure of 250kN was used for the compression molding. The temperature of the press platens was maintained at 170˚C for 15 min. The 3-mm thick sheet was obtained.

Table 1. Ingredients Used for Making Different Composites

Sample No.	PVC compound %	Rice husk %	Treated Rice husk %
1	100	0	0
2	90	10	10
3	80	20	20
4	70	30	30
5	60	40	40

Testing of Samples

Density

The densities of all the rice husk PVC composites were measured using a Mettler Toledo precision balance having a built-in programme.

Water absorption

Water absorption measurements were performed according to ASTM standard method D 570-99 (ASTM 1999). From each composite, five 3 x 12 x 50 mm^3 samples were cut. The samples were subjected to heat treatment in an oven at 50˚C for about 24 hrs, then immediately weighed (W_o). To measure water absorption of the composite, all of the samples were then immersed in distilled water at ambient temperature for 24 hrs, and then taken out weighed again (W_f). The percent weight gain (PWG) was calculated as:

$$\text{PWG} = [(W_f - W_o)/W_o] \times 100 \quad (1)$$

Tensile testing

The tensile test was performed on a Universal tensile testing machine at a crosshead speed of 10 mm min-1as per ASTM638D. An average of five samples for each composition is reported.

Flexural strength and flexural modulus

Five samples of each composition were used to determine flexural strength and flexural modulus. These quantities were determined with a Universal tensile testing machine as per ASTM 790D.

Hardness

The hardness test was carried out on a HIROSIMA (MODEL PR-21) Durometer on Shore D scale, following the ASTM D 2483 standard with specimen dimensions of 10 x 10 x 3 mm.

Arc resistance

Arc-resistance gives an idea of the resistance of a filled polymer to high power discharge across there surface. Arc-resistance tests, following ASTM D 495, were performed on an arc resistance measuring instrument. This test applies a voltage of 10 KV with a limited current arc discharge of 10mA across the specimen, as the specimen is kept between two chisel-shaped electrodes separated by 0.635cm. The equipment was from Nucleus, Bhopal, India.

Volume resistivity and surface resistivity

Volume and surface resistivity were determined as per ASTM D 257. The size of the specimens used was 100 mm. The sample was tested in the form of a disc. The measurements were performed with a Keithlei electrometer model 610C, giving volume resistivity values according to Eq. 2,

$$\text{Volume resistivity } (\rho)\ (\Omega\text{-cm}) = \frac{A}{t} \times R_v\ , \quad (2)$$

where A is area = 19.6 and t is the thickness of the specimen, and R_V is the volume resistance. The surface resistivity is given by

$$\text{Surface resistivity } (\Omega) = A \times R_s \,, \tag{3}$$

where A is area = 18.8 and Rs is the surface resistance.

Vicat softening temperature

Vicat softening temperature was determined as per ASTM D 1525. The size of specimens used was 10×10 mm in cross section. The temperature at which a flat ended niddle of 1 mm^2 circular cross section was penetrated into the composite specimen to a depth of 1mm.

RESULTS AND DISCUSSION

Figure 1 shows the variation of density with concentration of rice husk powder in PVC composites. Density decreased with increasing rice husk powder loading in the PVC. This decrease is due to porous nature of rice husk powder (Chand et al. 1987). Addition of treated rice husk further decreased the density of the composite. This decrease in density is due to the removal of material during esterification from rice husk powder.

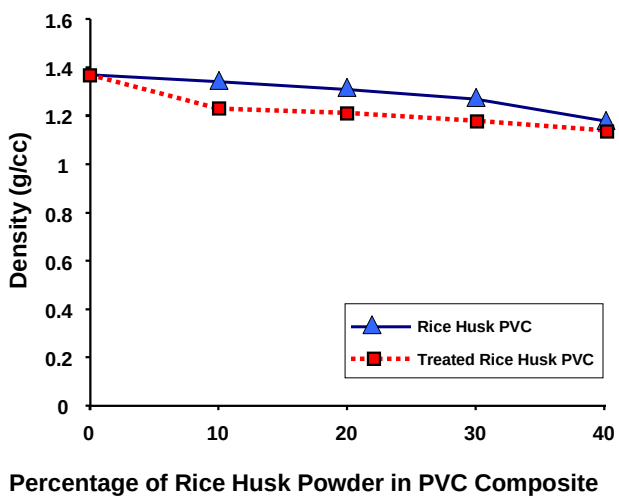

Fig. 1. Variation of density of composites as a function of the content of treated vs. untreated rice husk powder

Figure 2 shows the water absorption of rice husk powder PVC composites. Water absorption increased with increase of rice husk powder loading into PVC matrix, but after treatment of rice husk powder it decreased. This is because rice husk powder is a natural material and its main constituents have hydroxyl groups. These groups are hydrophilic in nature. After treatment, some hydroxyl groups of rice husk powder reacted with maleic anhydride and increased compatibility with PVC matrix. Therefore fewer hydroxyl groups were present in the resulting composites, which resulted in less water absorption.

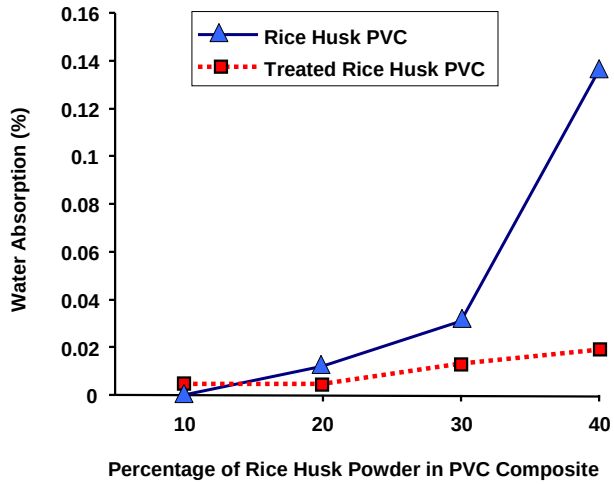

Fig. 2. Water absorption of composites as a function of the content of treated vs. untreated rice husk powder

Figure 3a shows the variation of tensile strength with treated and untreated rice husk powder loading in treated and untreated PVC composites, respectively. Tensile strength of untreated rice husk powder PVC composites decreased with increase rice husk powder loading in PVC matrix. Treated rice husk powder PVC composites showed higher tensile strength than untreated rice husk powder PVC composites. These differences can be attributed to improved compatibilization between rice husk powder and the PVC resin after treatment. As the rice husk powder loading increased, the tensile strength decreased due to the poor interfacial bonding between rice husk powder and PVC matrix.

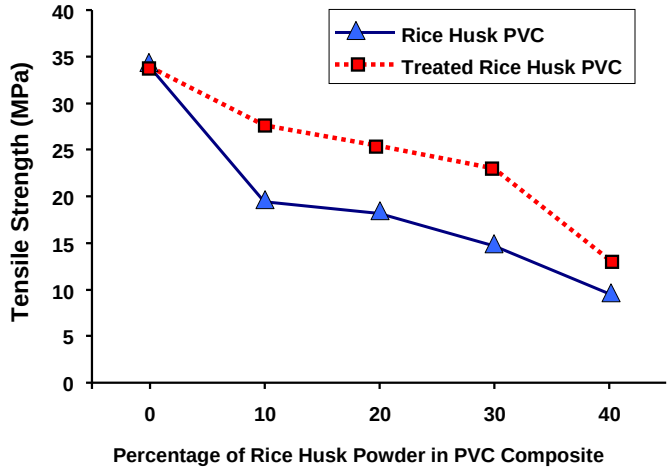

Fig. 3a. Tensile strength (MPa) of rice husk powder PVC composites

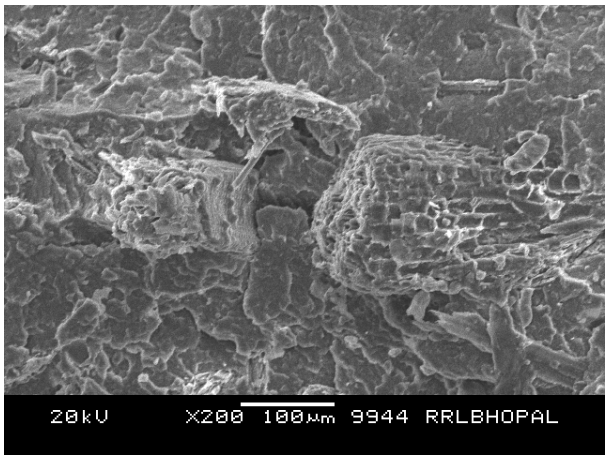

Fig. 3b. Tensile fractograph of rice husk powder (RHP) PVC composites (10% RHP + 90% PVC)

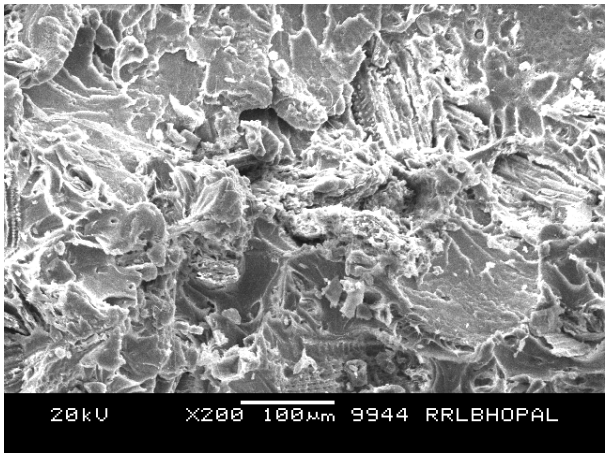

Fig. 3c. Tensile fractograph of treated rice husk powder PVC composites (10% treated RHP + 90% PVC)

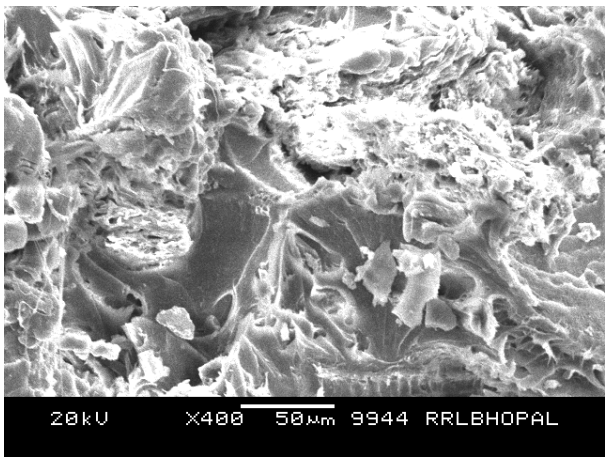

Fig. 3d. Tensile fractograph of treated rice husk powder PVC composites (Magnified 10% treated RHP + 90% PVC)

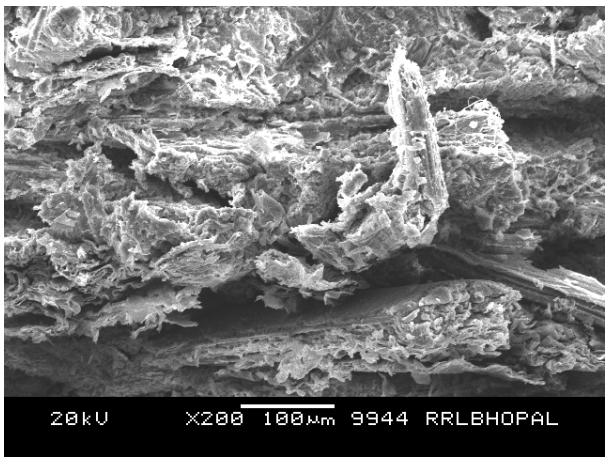

Fig. 3e. Tensile fractograph of rice husk powder PVC composites (20% RHP + 80% PVC)

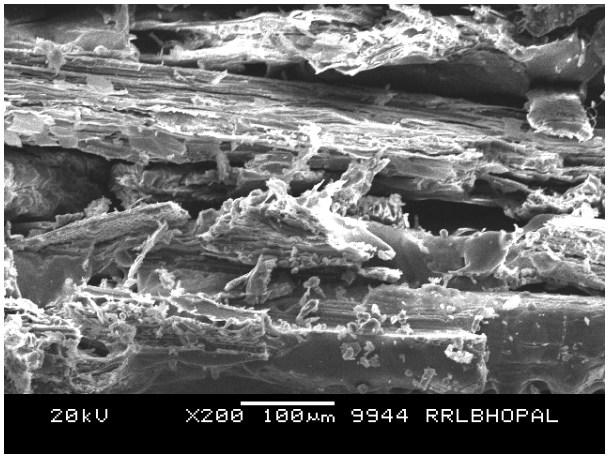

Fig. 3f. Tensile fractograph of rice husk powder PVC composites (40% RHP + 60% PVC)

Figures 3b and 3c show the tensile fractographs of untreated and treated 10 wt% rice husk powder filled PVC composites. The images indicate clear improvement in bonding between rice husk powder and PVC. The magnified microstructure in Fig. 3d demonstrates this in a better way. Figures 3e through 3f show the tensile fractographs of untreated 20 and 30 wt% rice husk powder filled PVC compound composites. These microstructures show increased content of rice husk powder in the composites. Increased content of rice husk powder resulted in decreased bonding between rice husk powder and PVC.

Figure 4 shows the elongation at break of rice husk powder PVC composites. It decreased with increase of rice husk powder concentration in rice husk powder PVC composites. Similar behavior was observed in the case of 10% treated rice husk powder loading. As the rice husk powder concentration increased in composites, the weight fraction of thermoplastic in the composites decreased, which increased brittleness. At higher rice husk loading, bonding between rice husk powder and PVC matrix decreased, which resulted in decrease in elongation.

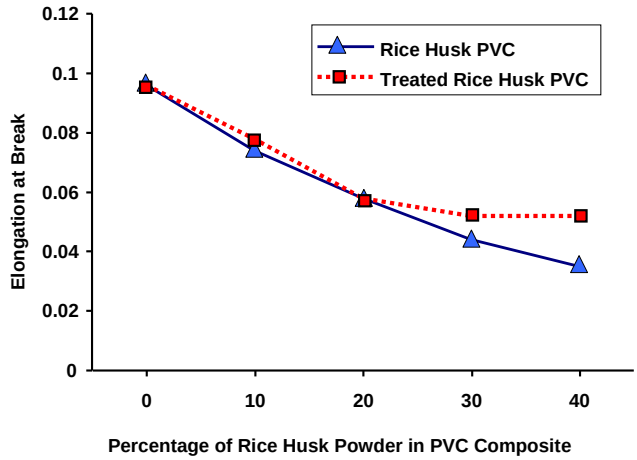

Fig. 4. Elongation at break of rice husk powder PVC composites

Figure 5 shows the variation of flexural strength with rice husk powder loading in PVC composites. Flexural strength of rice husk powder PVC composites decreased with increase of rice husk powder loading. This happened in both the untreated and treated rice husk powder PVC composites. The possible reasons proposed for decrease is poor adhesion between rice husk powder and PVC matrix. Another reason is the hydrophilic nature of rice husk powder and the hydrophobic nature of PVC matrix. Variation in flexural strength values for both treated and untreated rice husk powder PVC composites was within the range of experimental variability.

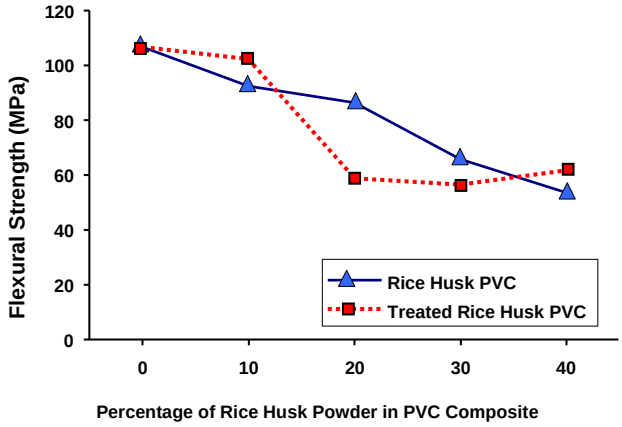

Fig. 5. Flexural strength (MPa) of rice husk powder PVC composites

Variation of flexural modulus with rice husk powder loading in PVC composites is shown in Fig. 6. Flexural modulus decreased with rice husk powder loading in both the treated and untreated rice husk powder PVC composites. This behaviour is similar to the tensile behaviour of treated rice powder PVC composites. This is the effect of filler loading (11). Chemical treatment of rice husk powder improved the flexural modulus. This is due to the increased bonding between rice husk powder and PVC.

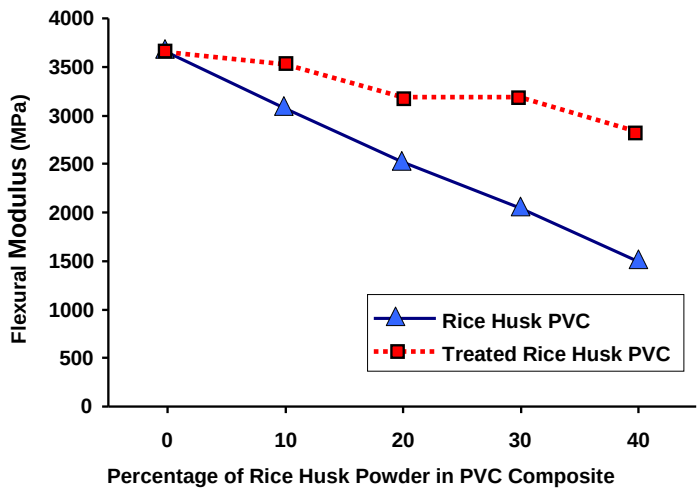

Fig. 6. Flexural modulus (MPa) of rice husk powder PVC composites

Figure 7 shows the variation in Shore D hardness values for treated and untreated rice husk powder PVC composites with rice husk powder concentration in the composites. Hardness gradually increased with rice husk powder loading in both cases. This increase of hardness is due to the brittle nature of lignocellulsic fibers.

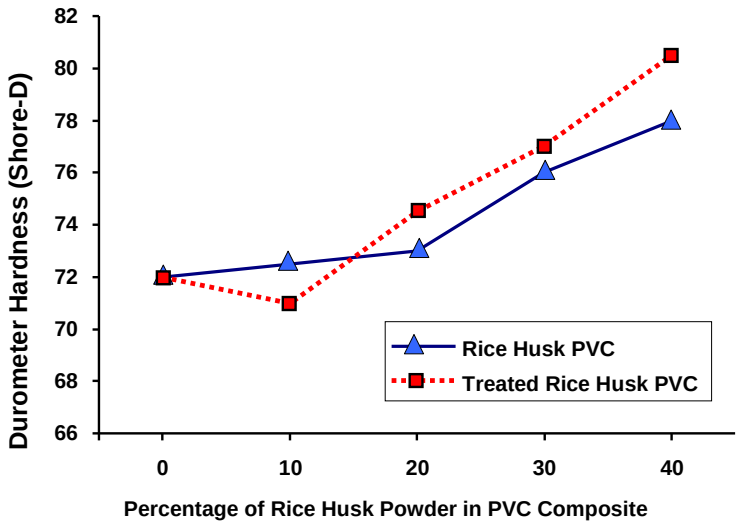

Fig. 7. Durometer hardness (Shore-D) of rice husk powder PVC composites

Figure 8 shows that the dependence of arc- resistance of rice husk powder PVC composites slightly decreased up to 20% rice husk powder loading in PVC matrix. Arc resistance increased on treatment of rice husk powder. Treated rice husk powder PVC composites showed higher arc resistance than untreated rice husk powder PVC composites due to the more compactness between PVC and rice husk powder.

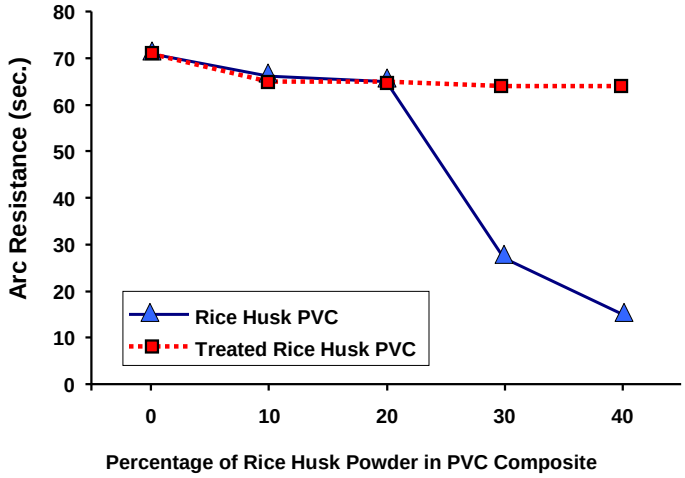

Fig. 8. Arc-resistance (second) of rice husk powder PVC composites

Figure 9 shows the variation of volume resistivity of rice husk powder PVC composites with concentration of rice husk powder in PVC composites. It decreased with rice husk powder loading. There was an abrupt decrease up to 10% rice husk loading; further loading did not result in significant additional change. The same thing happened for treated rice husk powder PVC composites. Volume resistivity of untreated rice husk powder was greater than of treated rice husk powder PVC composites. Rice husk powder having hydrophilic nature showed more affinity toward water absorption, which initially decreased on treatment, and hence increased volume resistivity of 10 wt% rice husk powder PVC composites. Further increase of treated rice husk powder loading in PVC composite reduced the resistivity due to increase in ionic concentration during esterification.

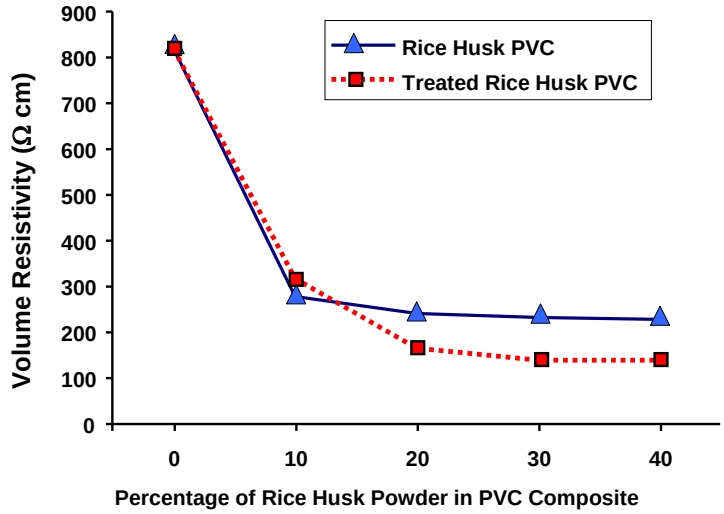

Fig. 9. Volume resistivity of rice husk powder PVC composites

Figure 10 shows the dependence of surface resistivity on rice husk powder concentration in PVC composites. Surface resistivity decreased with increase in loading of both treated and untreated rice husk powder in PVC matrix. This is attributed mainly to the presence of moisture and other impurities on the surface of the specimen. Rice husk powder is an agricultural residue, and its chemical composition depends on type and percentage of cellulose. The cellulose has a great tendency to absorb moisture, therefore increasing rice husk powder loading in the PVC matrix increased the moisture absorption, and hence the surface resistivity decreased.

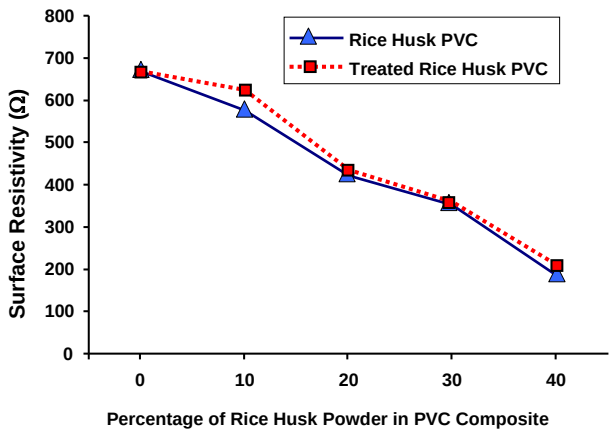

Fig. 10. Surface resistivity (Ω) of rice husk powder PVC composites

Figure 11 shows the variation of Vicat softening temperature (VST) of the treated and untreated rice husk powder PVC composites. It slightly increased with rice husk powder loading in PVC matrix. Addition of 20% rice husk powder kept VST constant, but further addition of rice husk powder increased VST. It can be seen that after 20% loading of rice husk powder, the VST increased slightly in both cases. From the above result it can be concluded that treatment of rice husk powder does not influence the thermal deformation behaviour of the composites.

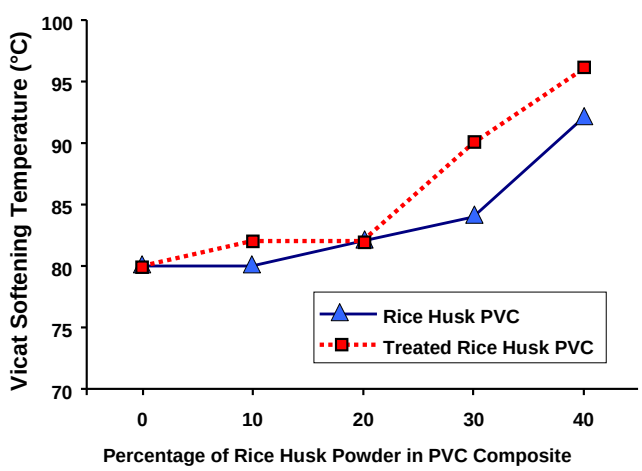

Fig. 11. Vicat softening temperature (ºC) of rice husk powder PVC composites

Figure 12 shows a typical plot for the variation of enthalpy with temperature for PVC compounds, treated and untreated rice husk reinforced PVC composites at 5 ºC heating rate. Table 2 (see Appendix) lists the enthalpy, T_g, and T_m values of composites at different heating rates. This shows that addition of rice husk increased the T_m values for both the treated and untreated rice husk PVC composites as compared to pure PVC. This increase in T_m shows the improved thermal stability of PVC on addition of rice husk powder. Increase of heating rate from 5 to 15°C increased the T_g values of Samples 1 and 2. This shows that addition of rice husk powder filler has improved the flexible structure of PVC.

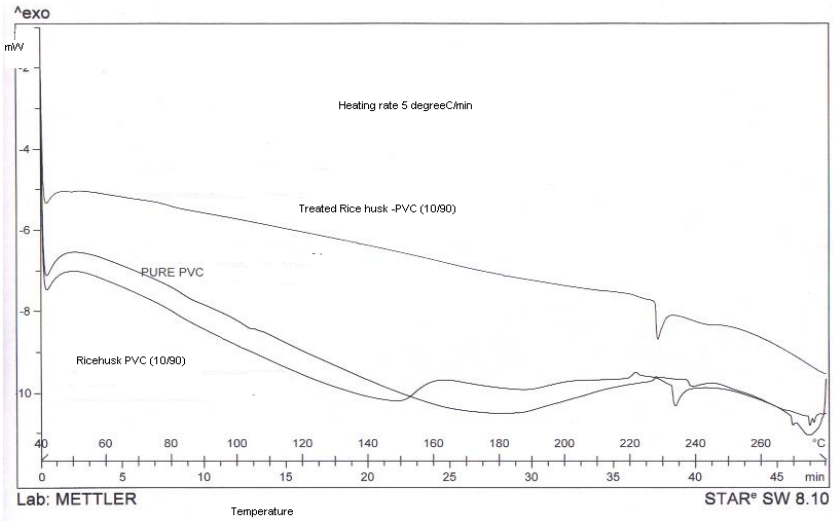

Fig. 12. Variation of enthalpy with temperature for PVC and treated and untreated rice husk PVC composites

CONCLUSIONS

From the above discussion it is concluded that

1. Rice husk powder filled PVC composites could be successfully developed having different rice husk weight percentage.

2. Density rice husk powder PVC composites decreased with increasing rice husk powder loading in the PVC matrix.

3. Tensile strength, flexural strength, and flexural modulus of rice husk powder PVC composites increased on treatment of rice husk powder

4. Arc resistance of rice husk powder PVC composites decreased with increase of rice husk powder loading in PVC matrix.

5. Vicat softening temperature of rice husk PVC composites increased in both treated and untreated rice husk powder filled PVC composites.

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Table 2. DSC Data of Untreated (sample 1) / Treated (sample 2) Rice Husk – PVC Composite (10/90) at Different Heating Rates

Test No.	Sample No.	Heating Rate (ºC)	Tg	Integral (mJ) (Endo.)	Normalized Enthalpy (Jg^{-1})(Endo.)	Onset Endo. (ºC)	Peak Endo. (ºC)	Endset Endo. (ºC)
1	Sample 1	5	81.7	-49.0	-19,300	167.6	187.1	199.4
2	Sample 1	10	82.1	-25.2	-1963.9	180.7	193.1	214.1
3	Sample 1	15	82.1	-11.52	-4643.6	149.6	163.58	180.62
4	Sample 2	5	80.0	-11.8	-3355.3	180.1	181.1	183.6
5	Sample 2	10	80.8	-0.1	-35.6	177.2	181.2	191.0
6	Sample 2	15	80.7	-3.2	-772.2	171.0	182.0	195.1
7	PVC	5	82.8	-256.3			175.2	

Test No.	Sample No.	Heating Rate (ºC)	Tg	Integral (mJ) (Exo.)	Normalized Enthalpy (Jg^{-1})(Exo.)	Onset (Exo.)(ºC)	Peak (Exo.) (ºC)	End Set (Exo.) (ºC)
1	Sample 1	5	81.7	-20.0	-8000.67	232.1	233.3	236.2
2	Sample 1	10	82.1	-32.9	-2569.5	233.2	235.1	239.4
3	Sample 1	15	82.1	-11.8	-4774.9	252.2	253.8	528.2
4	Sample 2	5	80.0	-25.6	-7251.9	227.3	228.1	230.7
5	Sample 2	10	80.8	-11.0	-3320.7	234.0	235.6	240.0
6	Sample 2	15	80.7	-15.3	-3622.1	235.7	258.3	271.8
7	PVC	5	82.8	-271.2				

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