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A study of thermo-mechanical properties of NBR-rice husk ash composites

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Abstract

This paper reveals the result of a study for the property improvement for nitrile rubber (NBR) using rice husk ash (RHA) as filler and MA-g-NBR as a compatibilizer (C). In this work, NBR is compounded with RHA in the presence of compatibilizer. Different concentrations of RHA (0, 0.5, 1, 1.5, 2, 2.5 and 3) and compatibilizer (5, 10, 15 and 20) were used. Cure time and scorch time were increased in both uncompatibilized and compatibilized composites. Characterization of RHA and composites were done by Fourier Transform infrared spectroscopy (FTIR). The compatibilized NBR-RHA composites have a tensile strength about 76% higher than that of virgin NBR. Tear strength, hardness and abrasion resistance were also increased in compatibilized composites compared to uncompatibilized composites. TGA study shows that uncompatibilized as well as compatibilized NBR-RHA composites have excellent thermal stability. The results prove that RHA is a valuable reinforcing material for NBR and the environmental pollution arising from RHA can be eliminated in a profitable way by this technique

Keywords: *NBR, RHA, compatibilizer, compatibilzed composites, mechanical properties, thermal properties*

1. Introduction

Composite materials are well known to mankind since pre-historic times and used for many applications ranging from house hold appliances to aeronautics [1]. Polymer composites have unique flexibility in designing and other characteristics such as ease of manufacturing, high specific strength, stiffness, corrosion resistance, durability, adaptability and cost effectiveness have attracted the attention of engineers, material scientists and technologists [2]. The composites performance mainly depends on the reinforcing effect of filler present in it. In practical applications, elastomers have been reinforced with mineral fillers such as silica or carbon black to improve their physical and mechanical properties.

RHA is an industrial waste obtained after burning the rice husks. RHA contains 55-97% silica with trace amounts of various elements such as potassium, sodium, magnesium and calcium. The major impurity is in the form of trapped carbon. RHA is in partially crystalline and amorphous forms depending upon the prior combustion conditions. RHA is more reactive in amorphous state. It is thermally stable and a tough material possessing high specific properties. It is also a low-cost material and readily available. RHA has hydrophilic nature [3]. One way to improve the final performance of the blend by using interfacial modifier or compatibilizing agents acting from the matrix side [4,5]. In our study, NBR used as matrix and RHA used as filler. To improve interfacial adhesion between NBR and RHA, maleic anhydride grafted NBR (MA-g-NBR) used as compatibilizer.

2. Materials and methods

Acrylo nitrile butadiene rubber grade-KNB 35L. Zinc oxide (activator) and stearic acid (co-activator) were supplied by M/s Meta Zinc Ltd., Mumbai, and by Godrej Soaps Pvt. Ltd., Mumbai, respectively. Cyclohexyl benzothiazole sulphenamide (CBS) and tetramethyl thiuram disulphide (TMTD) (accelerator) used in the present study were obtained from Polyolefins Industries, Mumbai. Sulphur (Crosslinking agent) was supplied by Standard Chemicals Co. Pvt. Ltd., Chennai. Maleic anhydride (MA) was obtained from SD fine-chem Ltd., Mumbai, and dicumyl peroxide (DCP) was supplied by Merck, India. Derivative of trimethyl quinoline (antioxidant) (TQ) and Methyl ethyl ketone (MEK) were of reagent grade and used as such.

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2.1. Preparation of RHA

Rice husk collected from rice mill. It was washed clean with distilled water to remove grit and dried in an oven at a temperature of 100ºC for 2h. It was burnt in 550ºC in a muffle furnace for 6h. This incineration time was found to give concordant values of ash content at each temperature.

2.2 Preparation of compatibilizer (MA-g- NBR)

Maleated NBR prepared by grafting reaction of NBR with maleic anhydride (MA) in presence of dicumyl peroxide (DCP) at molten state. NBR was first cut into small pieces. It was then dried in a vacuum oven at 40°C for 24 h. The internal mixer (Brabender Plasticorder) was then used to masticate it at 100°C with a rotor speed of 60 rpm for 2 min. 1g of maleic anhydride and 0.125g of DCP were then added into the internal mixer. The mixing was continued for 10 min at 100°C. The blended product was then dumped out onto the two-roll mill, sheeted out and cut into small pieces.

Table.1 *Formulations used in the preparation of NBR-RHA composites*

Ingredients	Weight
NBR	100
S	1.5
ZnO	4.5
Stearic acid	2
RHA	Varying concentration (0.5, 1, 1.5, 2, 2.5, 3)
Compatibilizer (MA-g-NBR)	5, 10, 15, 20
HS	1

2.3 Preparation of NBR- RHA composites

Compounding of NBR was done on a two-roll mill as per the formulation given in Table1. NBR was masticated for 2 minutes on a two-roll mill ((16×33cm^2) and the ingredients were added in the order shown in Table 1. Varying concentrations of filler and compatibilizer were added (in parts per hundred rubbers, phr) into it. The samples were then cured at 160^{0}C in an electrically heated hydraulic press to their respective optimum cure time at a pressure of 200 Kg/cm^{2}in a specially designed mould to get sample sheets having thickness 1.5 mm approximately.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of representative samples were recorded on a Thermo Nicolet FTIR Spectrometer Model Avatar 370. Samples in the form of thin films, <1 mm thickness, were employed.

2.5. Cure characteristics

Cure characteristics of the mixes were determined at 160°C, as per ASTM standard D 2084-07 [6]. The cure times (T_{90}), scorch time (t_2), minimum torque (ML) and maximum torque (MH) were obtained from the rheograph. Cure rate index (CRI) is a measure of the speed with which the cure reaction is taking place and is calculated using the equation:

$$\mathrm{CRI} = \frac{100}{\mathrm{t_{90}} - \mathrm{t_2}} \tag{1}$$

2.6 Mechanical properties

The tensile tests were done on dumb-bell shaped specimens punched out from vulcanized sheets of 2 mm thickness. The measurements were carried out on a Universal Testing Machine (10 KN), Shimadzu Autograph AG-I series with a grip separation of 40 mm as per ASTM D 412-06 [9]. The experiments were conducted at room temperature. These tests provided the tensile strength, elongation-at-break and modulus values of the NBR-RHA composites. Tear strength was determined by ASTM D 624-00(2007) [7]. The testing speed for tensile and tear properties was 500 mm/min.

2.6.1 Hardness

The hardness (Shore A) of the moulded samples was determined using Bareiss Digital hardness tester in accordance with ASTM D 2240-03 [8]. The tests were performed on unstressed samples of 30 mm diameter and 6 mm thickness.

2.6.2 Abrasion resistance

The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53,516) [9]. Samples having a diameter of 6 ± 0.2 mm and a thickness of 6 mm were kept on a rotating sample holder and a 10 N load was applied. Initially a pre run was given for the sample and its weight taken. The weight after final run was also noted. The abrasion loss in cc^3/h was calculated using the formula:

$$\text{Abrasion loss} = \frac{\text{loss of weight}}{\text{specific gravity}} \times \frac{60}{2.2} \tag{2}$$

2.7 Thermogravimetric analysis (TGA)

Thermo gravimetric analyses of the samples were carried out in a TGA Q-50 thermal analyzer (TA Instruments) under nitrogen atmosphere was employed in order to remove all corrosive gases. The samples were heated from room temperature to 800°C at a heating rate of 10°C/min and a nitrogen gas flow rate of 40–50 cm^3/min. Sample weight varied from 5-10mg. The onset of degradation temperature, the temperature at which weight loss is maximum (T_{max}), and residual weight in percentage, etc. were evaluated.

3. Results and discussion

3.1. Determination of cure characteristics

Cure characteristics of NBR RHA and compatibilized NBR RHA composites ex-pressed in terms of optimum cure time (T_{90}), scorch time (t_2), maximum and minimum torque values and cure rate index values were also given in tables 2 and 3 respectively.

Table. 2 *Cure characteristics of NBR- RHA uncompatibilized composites*

Concentration of filler (phr) at constant 10% C (MA-g-NBR) loading	T_{90}	t_2	Minimum Torque (dNm)	Maximum Torque (dNm)	Cure rate index (CRI)
0.5	3.51	1.3	0.108	3.249	45.2488
1	3.55	1.29	0.15	3.354	44.2477
1.5	3.58	1.3	0.155	3.4789	43.8596
2	3.68	1.31	0.158	3.5809	42.1941
2.5	3.76	1.32	0.16	3.685	40.9836
3	3.8	1.34	0.163	3.701	40.6504

Table. 3 *Cure characteristics of NBR - RHA compatibilized composites*

Concentration of filler (phr) at constant 10% C (MA-g-NBR) loading	T_{90}	t_2	Minimum Torque (dNm)	Maximum Torque (dNm)	Cure rate index (CRI)
0.5	3.59	1.31	1.01	3.445	46.0827
1	3.63	1.39	1.04	3.558	44.6428
1.5	3.76	1.4	1.15	3.575	42.3728
2	3.98	1.6	1.25	3.625	42.0168
2.5	4.2	1.65	1.28	3.698	39.2156
3	4.3	1.69	1.32	3.752	38.3141

Table 2 and 3 summarize the values of optimum cure time (T_{90}), scorch time (t_2) and minimum and maximum torque values of uncompatibilized NBR -RHA and compatibilized NBR- RHA composites. Cure time (T_{90}) increases with increasing filler loading in uncompatibilized and compatibilized NBR-RHA composites. This is due to the fine particle sized rice husk ash which has polar groups (e-g., -OH) attached to its surface, adsorbs the accelerators, thereby blocking accelerators effective participation in the vulcanization process [10]. Scorch time (t_2) also increases with increasing filler loading in compatibilized and uncompatibilized composites. The increase in minimum and maximum torque values with an increase in RHA loading is due to the increased stiffness and hardness of the nitrile rubber composites. The presence of the filler in the rubber matrix reduces the mobility of the rubber's macromolecular chains and hence the maximum and minimum torque values will be increased. The decreased CRI values for the composites compared to pure NBR also suggest a deceleration of the crosslinking reaction.

3.2 FTIR analysis

Fig.1 shows the FTIR of RHA and compatibilized NBR-RHA composites. The FTIR spectrum of RHA shows a peak at 1106cm^{-1} corresponding to Si-O-Si the stretching vibration. Another peak at 750cm^{-1} is for the vibration frequency of Al_2O_3. The spectrum of the compatibilized NBR-RHA composite shows peaks at 2912cm^{-1}, 1429cm^{-1} and 962cm^{-1} corresponding to the olefinic C-H stretching frequency, the CH_2 blending vibration frequency and C-H out-of-plane blending frequency of NBR structure respectively. The peak at 2229cm^{-1} shows the vibration frequency of CN group from NBR structure. A peak at 1735 assignable to symmetric stretching of C=O group present in ester moieties.

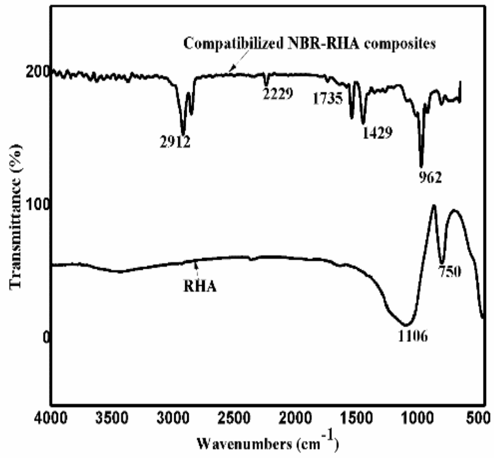

Fig.1 *FTIR of NBR and NBR- RHA compatibilized composites*

3.3 Mechanical properties of NBR-RHA uncompatibilized composite

Figs. 2 and 3 show the tensile strength, modulus and tear strength of uncompatibilized NBR composites in the presence of RHA loading. Tensile strength shows an increase upto 2 phr filler loading and then decreases. Due to filler agglomeration at higher filler loading leads to lowering of tensile strength of the composites. Addition of RHA into NBR improves stiffness of the composites and hence modulus increases at three different percentages of elongations. Addition of RHA fillers to rubber reduces the tear strength due to its poor rubber – filler interaction. Tear strength is affected by the particle size and surface area of the filler particles. For this reason, tear strength is decreased with increased loading of RHA.

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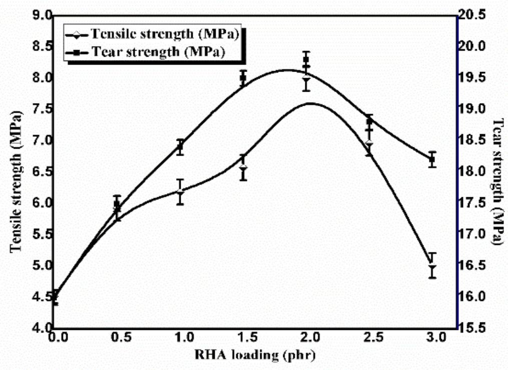

uncompatibilized composites

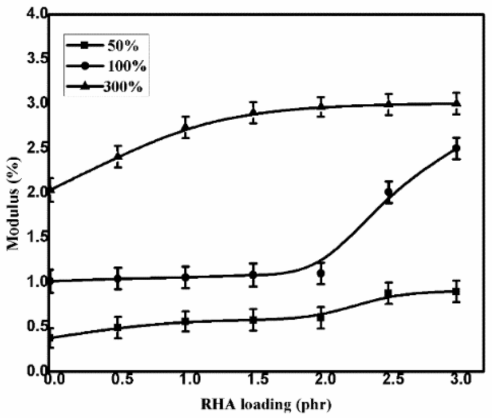

Fig. 3 *Modulus of NBR-RHA uncompatibilized composites*

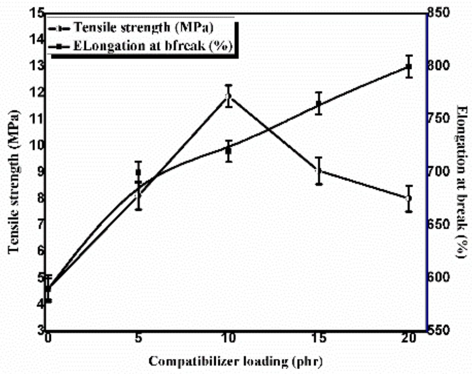

Fig. 4 *Tensile strength and elongation at break of NBR-RHA compatibilized composites*

3.4 Optimization of compatibilizer

In the preparation step of compatibilized NBR RHA vulcanizates, varying concentrations of (5, 10, 15, 20) compatibilizer were added to constant concentration (2phr) of RHA. After that these blends subjected to mechanical testing. Then 10phr compatibilizer added blends showed maximum tensile strength and elongation at break. Modulus increased with increasing compatibilizer loading. Fig. 4 shows the tensile strength, of NBR matrix in the presence of compatibilizer. Tensile strength showed a tendency to increase upto 10phr and then decreases. This is due to the availability of more NBR from compatibilizer to interact with NBR matrix.

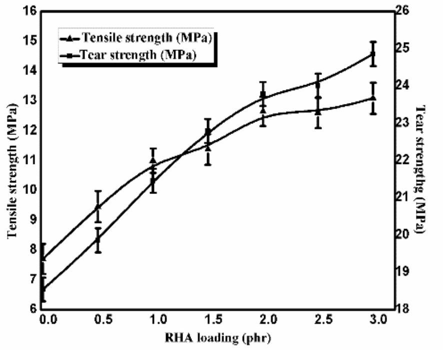

Fig. 5 *Tensile strength and tear strength of NBR-RHA compatibilized composites*

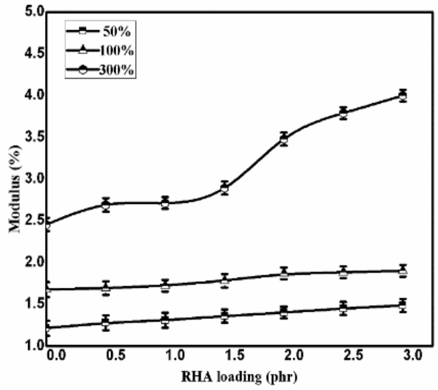

Fig. 6 *Modulus of NBR-RHA compatibilized composites*

3.5 Mechanical properties of compatibilized composites

Figs. 5 and 6 show the effect of RHA content on the tensile strength, tear strength and modulus of compatibilized NBR/RHA composites. The mechanical properties of the composites in the presence of the compatibilizer are become superior. The use of the compatibilizer has proven to be effective in enhancing the dispersion, adhesion and compatibility of the filler with NBR matrix. The tensile strength of the compatibilized NBR-RHA composite also shows an increasing tendency with increasing filler loading. The breaking elongation of the composite also shows the same trend. When the composites under exterior stress, the filler helps to distribute the stress evenly and delay the rupture of the material. Modulus of the composites increases with increasing filler loading. The interfacial adhesion is increased by the presence of the compatibilizer and the high surface area of the filler gives rise to increased modulus and strength.

3.5.1 Hardness

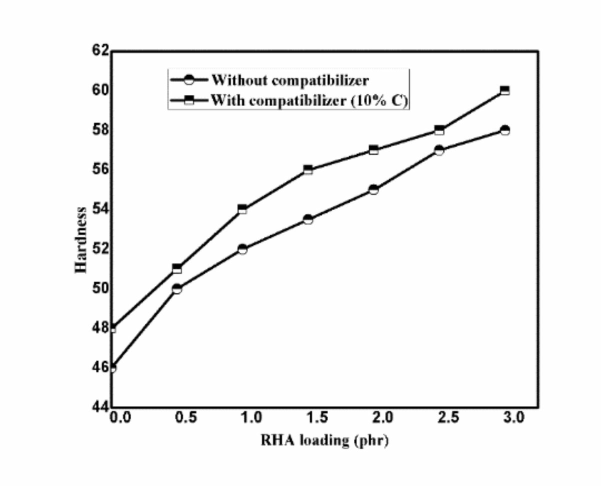

Fig. 7 *Hardness of NBR-RHA uncompatibilized and compatibilized composites*

Fig. 7 shows that hardness increases with increasing filler loading in both compatibilized and uncompatibilized NBR-RHA composites. Due to the presence of filler particles in the rubber matrix, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates. RHA is a hard and stiff inorganic (not pure silica) material in particulate form. The presence of RHA in the rubber matrix would reduce the flexibility of rubber chain and, consequently, the vulcanizates become harder and stiffer [11].

3.5.2 Abrasion resistance

From the graph, it is clear the abrasion loss of uncompatibilized and compatibilized composites have been influenced by the addition of RHA. The lower filler- filler interaction leads to higher abrasion resistance. The addition of RHA gradually decreases abrasion loss and increases abrasion resistance of the composites. In uncompatibilized composites, at high phr loading of RHA leads to filler –filler attraction. Hence abrasion loss values after 2phr of RHA addition decreased. It is well known that the abrasion resistance of filled rubber is basically determined by filler characterization, especially its morphology and surface reactivity [12]. In compatibilized composites filler particles have less tendency to agglomerate. Fine particles actually reflect their greater interface between the filler and the rubber matrix, thus providing a better abrasion resistance than that of the coarse particles.

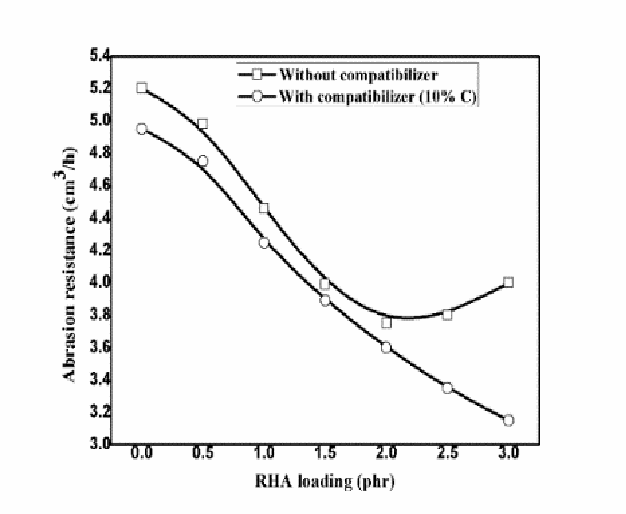

Fig. 8 *Abrasion resistance of NBR-RHA uncompatibilized and compatibilized composites*

3.6 Thermal gravimetric analysis

From the table, it is clear that by the addition of 0.5 phr RHA into NBR, the temperature of onset degradation is shifted to 332.91°C from 329.63°C and maximum peak temperature of degradation increases from 454.78°C to 458.37°C. At the maximum addition of RHA (3 phr) the onset degradation temperature and maximum peak temperature shifted to 340.16 and 466.44°C respectively. Enhancement of thermal stability of the rice husk ash composites is attributed to the organic/inorganic interaction between the polymer and rice husk ash where inorganic filler delays the volatilizations of the products generated at the temperature of carbon–carbon bond scission of the polymer matrix [13].The inorganic ash can also absorb the heat generated during the degradation and help to decelerate the overall degradation process. The same trend is shown by the presence of compatibilizer in the NBR-RHA composites. The compatibilized composites show enhanced thermal stability than uncompatibilized composites. Because the compatibilizer (10 phr) improves the better interfacial addition between NBR matrix and RHA particles. This has the effect of making the blend less susceptible to thermal degradation. The higher residual values of the composites are due to the better interaction between NBR and RHA.

Table.3 *TGA analysis of NBR and NBR-RHA uncompatibilzed and compatibilized composites*

Sample	Onset T (^{0}C)	Peak T (^{0}C)	Endset T (^{0}C)	10% weight loss (^{0}C)	20% Weight loss (^{0}C)	50% weight loss (^{0}C)	Residue (%)
NBR	329.63	429.15 454.78	503.73	375.88	410.11	444.74	6.783
NBR+1phrRHA	333.18	432.8 459.12	506.43	378.35	413.96	449.32	8.11
NBR+2phrRHA	337.21	436.28 462.19	508.23	381.25	415.2	452.32	11.56
NBR+3phr RHA	340.16	439.74 466.44	510.54	384.66	417.5	454.1	14.71
NBR+10phr C+1phr RHA	344.54	443.89 469.87	515.45	386.94	420.3	456.81	13.05
NBR+10phr C+2phr RHA	348.16	447.91 472.87	518	388.69	423.02	458.55	14.31
NBR+10phr C+3phrRHA	350.11	449.79 474.95	523.68	391.58	425.89	460.22	15.68

4. Conclusion

Addition of RHA into NBR matrix increases cure time and scorch time of the both composites. Rubber filler interaction study reveals that NBR like polar rubber has ability to interact with hydroxyl groups on RHA and this interaction can be enhanced by the incorporation of compatibilizer. Addition of 2phr RHA increases tensile strength and tear strength by 73% and 23% respectively when compared to gum NBR. In the presence of 10phr of MA-g-NBR, compatibilized composites show 76% and 32% improvement in tensile strength and tear strength. Other mechanical properties like hardness and abrasion resistance show an increasing trend in both composites. The thermally stable RHA enhances the thermal stability of NBR-RHA composites in both uncompatibilized and compatibilized condition. The results prove that a pollutant material like RHA can be used advantageously to reinforce NBR.

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