MECHANICAL AND THERMAL CHARACTERIZATION OF HEAT/SURFACE TREATED EGG SHELL FILLER DIFFUSED NATURAL RUBBER GREEN COMPOSITE

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In this present work mechanical and thermal characterization of egg shell fine micro particles reinforced natural rubber composite was investigated. The principal aim of this work is to enhance mechanical and thermal properties of natural rubber by reinforcing 15, 25 & 35wt% of domestic waste egg shell fillers. Egg shell fillers of dimension 800nm were confirmed by particle size analyser. Similarly morphology of spherical shape was confirmed by scanning electron microscopy. Egg shell fillers were surface treated by an amino silane (APTMS) to reduce clustering. Thin sheets of 3mm were made by two roll mill followed by thermo curing was applied. The mechanical and thermal properties were analysed followed by ASTM standards. The mechanical results shows, the additions of egg shell fillers to natural rubber the Visco-elastic properties get affected. But the hardness and wear results were improved. The thermal results showed that the additions of egg shell fillers increased the thermal stability of natural rubber close to 60%. The scanning electron microscopy images confirmed that better dispersion quality of egg shell filler in natural rubber matrix.

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Keywords: Rubber composite; Egg shell; Pin on Disc; SEM; TGA

1. Introduction

Ceramic domestic waste egg shell nano fillers reinforced rubber composites are attractive applications in structural engineering and manufacturing sector due to the capability of improved thermal stability and wear resistance behaviour [1].Requirement of green composites for current engineering sector have huge demand since environmental safety is given loyal preference. Utilization of egg shell fillers improves the process of solid waste disposal where dumped waste products could be converted as a wealth of nation [2]. The improved mechanical and thermal properties on natural rubber increase the demand of such products in many engineering applications. Egg shell fillers could be right choice since they made up of oxides $CaCO_3$. Additions of natural fillers could improve the properties of natural rubber with low cost since egg shell could be available as tons and tons [3]. Heat treatment over the as-received egg shell particles may improve the thermal and wear behaviour since conversion of carbonate to oxide takes place. Two roll mill process of making composites could be cheap and effective method where process parameters are limited [4]. Wear resistance could be improved on natural rubber since egg shell particles contains CaO and $CaCO_3$. Similarly the thermal stability could be improved by acquiring more heat energy by ceramic egg shell particles. Mohamed riza et al [5] concluded that the additions of egg shell particles to natural rubber improve the mechanical and thermal properties. They also concluded that additions of fillers affect the visco-elastric properties but improves novel properties like thermal, wear and shrinkage resistance

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2. Experimental Procedures

2.1 Materials

Natural rubber used for this study was the monomer isoprene (2-methyl-1,3-butadiene purchased from rubber cast India ltd. Curing agent Dibenzothiazole disulphide, Tetra Methyl Thiruram disulfide, Sulphur and ZnO were purchased form carton chemicals Pvt.Ltd. India. Egg shell with as-received condition was procured via domestic agent from southern India.

2.2 Sample preparation

2.2.1 Ball milling process

The as-received egg shell patches were ball milled for 4 hours to get ultra fine fillers. Before ball milling process the egg shell patches were dried finely in room temperature for 48 Hrs. In the part of pre treatment process the cellulose and other impurities from egg shell were removed by manual cleaning. The dried egg shell patches were taken in a mill jar and Tungsten carbide balls of diameter 10mm were selected for milling. The powder to ball ratio was maintained at 1:15. Every half an hour the mill was stopped and egg shell particles were resettled by manual stirring. Figure 1 shows the SEM images of 4 hour ball milled egg shell particles. The particles shape retained spherical which indicates highest equilibrium state of egg shell particles. The surface of particles were looks rough because of high brittle nature of egg shell. Figure 2 shows PSA graph of ball milling process at every 1 hour. It indicates that at initial stage particles dimensions were reduce as faster rate. Whereas milling after 4 hours did not fetch any reduction on particles size. This is because of lower collision rate of particles to ball mill tungsten carbide balls [6].

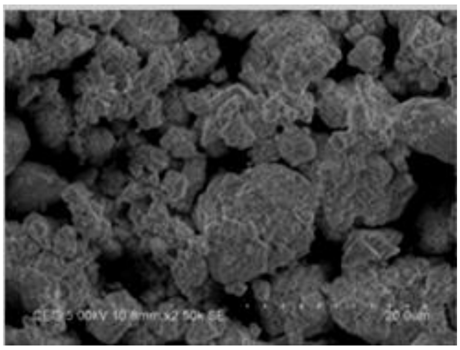

Fig. 1 SEM image of Egg shell ball milled particles.

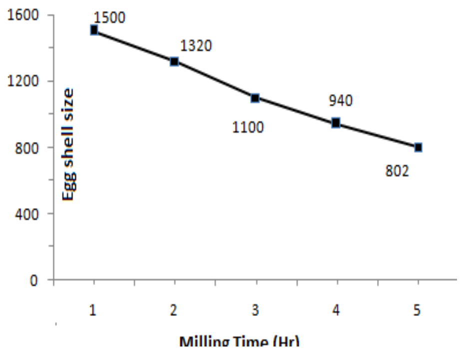

Fig. 2 PSA graph of Egg shell powder to milling time

2.2.2 Heat treatment process

The ball milled 800nm egg shell fillers were heat treated to eliminate the formed moisture and conversion of $CaCO_3$ to CaO. The milled fine 800nm particles were taken in a silica crucible and kept over an electric furnace. The temperature was then raised to 1200ºC. During heating oxygen was supplied via special opening to enhance oxidation process [7].

The temperature was maintained at same level for 6 hrs to get complete conversion of CaO. The heat treated fillers then allowed to cool in room temperature and taken out from silica crucible. Figure 3 shows SEM images of heat treated CaO particles which indicates finer structure.

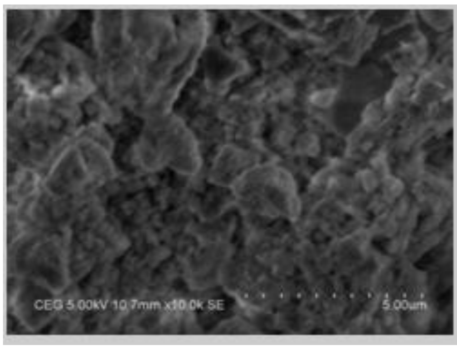

Fig. 3 SEM image of Heat treated egg shell Powder

2.2.3 Surface modification of egg shell particles

The heat treated egg shell particles were surface treated by a silane (APTMS) via aqueous solution method. In this fixed quantity of egg shell particles were taken in ethanol-water solution. 2 wt% of silane substance was then added in to the ethanol –water solution to form silinal groups. The surface treated egg shell particles then taken away from ethanol-water solution and allowed to dried in hot oven for 1 hour thus created the Si-O-Si structure on egg shell fillers [8]. Figure 4 shows surface modification reaction on egg shell particle surface.

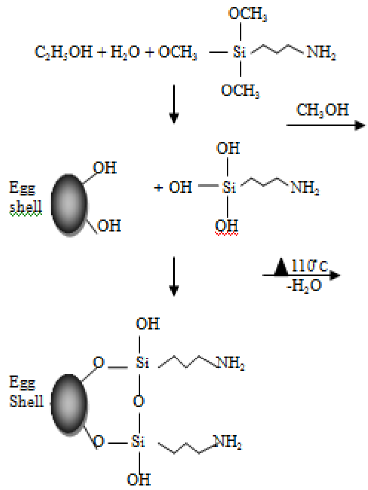

Fig. 4 Reaction of APTMS on egg shell filler surface.

2.2.4 Fabrication of Egg shell rubber composite

A fixed quantity of natural rubber and 15, 25, 35 wt % of egg shell particles were mixed and rolled in a two roll mill. More no of passes were done to ensure homogeneous mixture of natural rubber and egg shell particles. The rolled NR-ES compound was then settled in a mould for curing process. MBTS (Dibenzothiazole disulphide) of 10g, TMT (Tetra methyl thiruram disulfide) of 5g, Sulphur of 20g and Zinc oxide of 25g were added to it separately. After 2 hours of curing with applied pressure thin 3mm sheets were made [9]. The prepared NR-ES composite sheets were inspected for visual defects and cleaned for further study.

2.2.5 Specimen preparation

The prepared NR-ES composite sheets were cut from moulded sheets by shearing process. Test specimens of ASTM dimensions based samples were prepared carefully. The composite designations and compositions were given in Table 1.

Table 1. Composition and designation of composites

Material Designation	NR (wt%)	Egg Shell (wt%)
NR	100	0.0
NRES1	85	15.0
NRES2	75	25.0
NRES2	65	35.0

NR- Natural rubber; ES- Egg Shell

2.3 General Characterization

2.3.1 Particle size analyser

The size of ball milled egg shell particles were measured with a particle size analyser (Malvern V 2.2, Germany). Ball milled powder samples of refractive index 2.71 were dispersed in distilled water of refractive index 1.333, viscosity of 0.88 and ultrasonically stirred for 10 min with 70 Hz before testing.

2.3.2. Scanning electron microscopy

Surface morphology of ball milled egg shell particles and fractured surface of composite materials were analysed using scanning electron microscope (HITACHI S-3400 JAPAN). The surface of the samples was coated with gold before scanning.

2.3.3. Mechanical characterization

The tensile behaviour of egg shell natural rubber composite were tested based on ASTM-D638 with a universal testing machine having 5 ton of loading capacity and digital encoder attached at a cross head speed of 2.5 mm/min(FIE. India). The wear properties were investigated using a pin-on-disc followed by G99. The tear test was done using a tensile tester followed by IS: 3400. The hardness of composites was tested using Durometer (shore-A) as per ASTM-D 2240. Five identical specimens were tested for each material designation.

2.3.4. Thermal analysis

The thermal behaviour of composite was analysed with a DSC/TGA analyser (NETZSCH STA Jupitar 409 PL Luxx, Germany)under N_2 atmosphere. Samples were scanned from 0 to 600ºC at heating rate of 101ºC/min and sample crucible material was Al_2O_3.The thermo gravimetric analysis was performed to study the mass loss of NR diffused egg shell composite with rise in temperature. Similarly the DSC test was conducted to know the glass transition temperature of rubber composites. The thermal conductivity behaviour of composite was analysed with Lee’s disc method. Three circular specimens of diameter 11.2 cm were tested to take average value of thermal conductivity.

2.3.5. Volume swell test

The chemical resistance of egg shell diffused natural rubber composite was tested by immersion test. Test samples of 60mmX60mm were taken for test and weight difference was taken as a result.

3. Results and discussions

3.1 Mechanical properties

The result of tensile, wear, tear and micro hardness of egg shell nano particles reinforced natural rubber composite is presented in Table 2. The tensile result shows that additions of egg shell particles in to natural rubber reduced its tensile behaviour. This is because of diffused egg shell particles affected the degree of curing of rubber monomers with curing catalyst. The results show that the least tensile strength of 0.9 N/mm^2 is observed for composite designation $NRES_3$. This is because of incorporation of large weight percentage of egg shell particles affect the Isoprene molecular network formation and decreased degrees of ordering [10]. The decreased tensile strength for composite designations $NRES_1$, $NRES_2$& $NRES_3$ is 40%, 56% &71%. Similarly the percentage of elongation of natural rubber and egg shell disused rubber composites results were displayed in Table 2. It is observed that the percentage of elongation also get decreased when filler loading increases. It is observed that the percentage of elongation is a direct proportional variable with tensile strength. The decreased elongation percentage of 45, 51 & 57 was observed for composite designations $NRES_1$, $NRES_2$& $NRES_{3.}$ This is because of high randomness of natural rubber molecules lost its visco-elastic properties and became a harder one; hence the percentage of elongation is decreases [11]. Table 2 shows the tear test result of egg shell diffused natural rubber composite. It shows decreased values. The decrement of 18%, 32% &42% were observed for composite designations $NRES_1$, $NRES_2$& $NRES_3$ respectively. This decreased result is because of poor rubber molecular structure. The diffused egg shell fillers replaced the rubber molecules and formed an awkward structure, which affect the tear strength. Due to high randomness in molecular structure crack may initiate and propagate easily thus affected the tear resistance [12]. Figure 5 shows the fracto-graphy of tensile specimen which indicates the presence of egg shell particles and medium visco-elastic rubber matrix. The dimple formation is quit less which indicates the egg shell diffused rubber specimen became harder than the natural rubber.

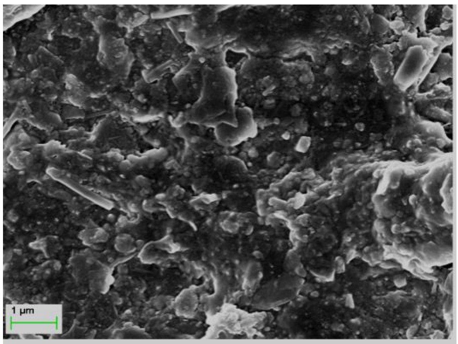

Fig. 5 Fractography of tensile specimenunder axial loading

Table 2 shows the wear rate of different composites. It is observed that the natural rubber gives wear rate of $0.1446mm^3/m$. Whereas additions of heat treated egg shell fillers to natural rubber decreased the wear rate of natural rubber. The improved wear resistance of 14%, 35% &64% were observed for composite designations $NRES_1$, $NRES_2$& $NRES_3$ respectively. This improvement is because of additions of heat treated egg shell particles reduce the direct contact of natural rubber in to the rubbing abrasive wheel. When contact surface area is decreases by the replacement of egg shell the wear rate is significantly reduced. Figure 6 shows the worn out surface of 30wt% of egg shell filler reinforced natural rubber composite, which indicates almost flat surface which refers that the worn out surface is rather hard than natural rubber.

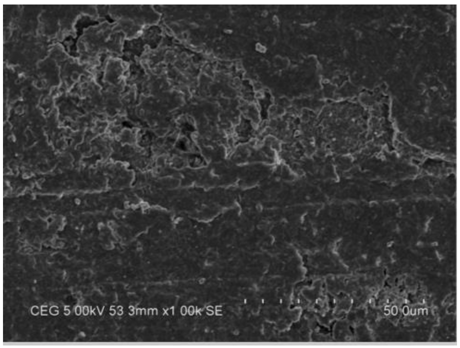

Fig. 6 Worn surface morphology of wear test specimen

Table 2 shows the shore A hardness of natural rubber and egg shell diffused rubber composite. It is observed that additions of egg shell particles to natural rubber increased the hardness of natural rubber. The improvement of 10%, 22% &32% were observed for composite designations $NRES_1$, $NRES_2$& $NRES_3$ respectively. This is because of additions of egg shell particles get placed in void contents of natural rubber and increase the cross linking density [13]. The improved cross linking increase the isoprene monomer density per unit volume. This improved the hardness of natural rubber.

Table 2 Mechanical properties of egg shell natural rubber composite

Composite designation	Tensile strength (N/mm^2)	Elongation (%)	Tear Strength (Kg/mm)	Wear rate mm^3/m	Hardness (Shore –A)
NR	3.2	368	2.8	0.14	44
$NRES_1$	1.9	202	2.3	0.12	49
$NRES_2$	1.4	178	1.9	0.095	57
$NRES_3$	0.9	158	1.6	0.05	65

3.2 Thermal properties

Fig. 7 shows the graphs of TGA and thermal conductivity of natural and egg shell diffused natural rubber composite. The results show that additions of egg shell particles increased the mass loss resistance of natural rubber. This is because of additions of egg shell particles occupy the void contents of natural rubber. When temperature increases the egg shell particles absorbs the heat energy and maintains the isoprene monomers as inactive. Hence large quantity of heat is required to activate the secondary molecules in natural rubber. The Figure 7 shows the thermal conductivity values of NR and egg shell diffused NR. It indicates that no drastic changes were observed by the incorporation of egg shell particles. A small reduction in thermal conductivity was observed for egg shell reinforced natural rubber composites. This is because of ineffective particle network formation on rubber matrix [14].

Figure 8 shows the glass transition temperature of rubber composite in cooling. The graph indicates that additions of egg shell particles greatly served in glass transition temperature. The glass transition temperature was increased 15%, 24% & 36% for composite designations $NRES_1$, $NRES_2$& $NRES_3$ respectively. This is because of additions of egg shell particles reduced the free volume of natural rubber which increased the glass transition temperature [15].

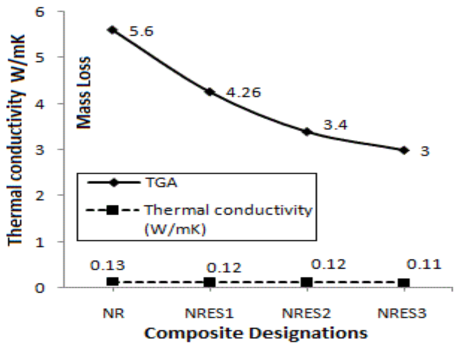

Fig. 7 Thermal properties of egg shell NR composites.

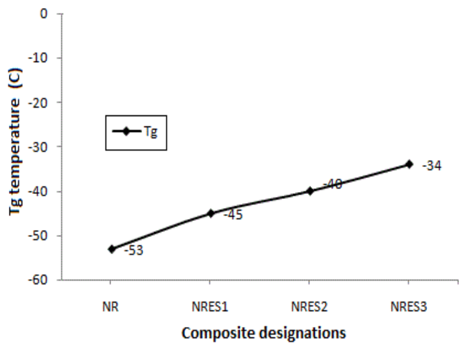

Fig. 8 Glass transition temperature of egg shell NR composites

3.3 Volume swell percentage

Fig. 9 and 10 shows the volume swell percentage of natural rubber and egg shell reinforced natural rubber. The volume swell of natural rubber in ASTM-3 Oil is about 130% whereas additions of egg shell particles increased the resistance of swell as 9%, 15% & 24% similarly in water it is 30%, 47% & 57% for composite designations $NRES_1$, $NRES_2$& $NRES_3$ respectively. This is because of reduced void content of natural rubber. When void content is reduced the amount of water and oil uptake phenomenon gets decreased. Since the reaction between egg shell and water and also ASTM 3 oil is absolutely nil the egg shell diffused natural rubber composites are improved in water up take resistance [16].

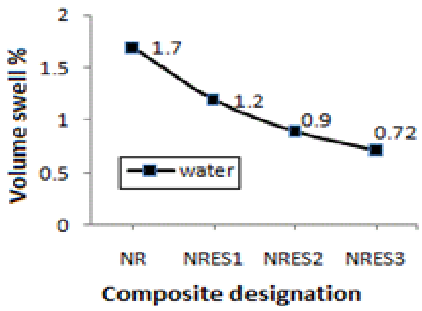

Fig.9 Volume swell percentage of egg shell NR composites in water.

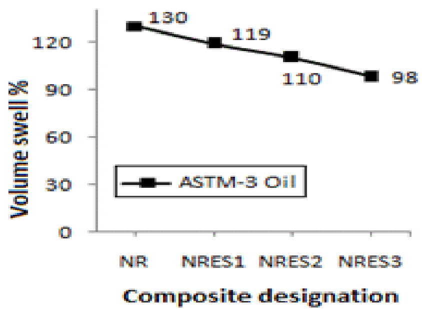

Fig.10 Volume swell percentage of egg shell NR composites in ASTM oil.

4. Conclusions

The following results have obtained from the study. The additions of egg shell particles to natural rubber increased the thermal, wear, volume swell and hardness properties. While the properties like tensile strength, elongation percentage and tear strength get decreases. The scanning electron microscopy results revealed that the egg shell particles were well bounded with natural rubber. Thus the thermally improved natural rubber may be used in heat prone zone where rubber could be sealing material. High wear resistance of egg shell toughened natural rubber could be used in structural application where shear force is a predominant factor. Thus selection of egg shell fillers improved the usage of natural rubber in engineering sector and also the domestic waste could be converted as a wealthy product.

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