Performance Characteristics of Industrial waste-N_{330}, N_{550} and N_{660} Carbon Black Hybrid Natural Rubber Composites

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Summary: In this research work, natural rubber (NR) hybrid composite was prepared by incorporating industrial waste such as marble sludge with three different types of carbon black (CB_{dt}) to be precise as CB_{N330}, CB_{N550} and CB_{N660}. Samples were mixed on two roll mill and vulcanized at 150° C. The effects on the curing characteristics, mechanical and swelling properties of NR hybrid composites of CB_{dt} with MS were evaluated in CB_{dt} and hybrid combinations of MS/CB_{dt}. It was found that gradual increment of CB_{dt} in MS/CB_{dt} hybrid composite decreased the scorch and cure times, however the minimum and maximum torques increased with increasing CB_{dt} in particular hybrid composite. The overall mechanical properties tended to increase, however the % elongation at break, resilience and abrasion loss decreased with increasing CB_{dt}. The swelling ratio has also been observed to be decreasing and cross link density and shear modulus increasing with CB_{dt} incorporation.

Keywords: Hybrid composites, Carbon black, Marble sludge, Curing characteristics, Mechanical properties.

Introduction

Considering an imperative rather of polymer material, natural rubber is widely used owing to its high and reversible deformability. Nevertheless the basic properties such as strength and modulus are low therefore an additional reinforcing component is essential for the practical implementation of rubber products [1-3]. Rubber is commonly reinforced with carbon black, silica, silicates and fibers. Carbon black (CB) is an important reinforcing material in polymers and usually improves performance related properties. Reinforcement of CB in elastomers has been investigated by numerous researchers [4-14].

At present many attention has been directed towards the hybrid filler composition in rubber compounds using varieties of two or more different kinds of filler in a polymer matrix to elucidate some innovative outcomes [15]. Among them, CB-silica hybrid filler system, glances to be the most popular and successful. The CB-silica dual phase filler is commercially manufactured by Cabot Corporation for the applications of truck tire [16]. The CB-silica hybrid filler system has overall improved mechanical properties compare to individual one. It also illustrates the almost favorable balance of various properties, for example wet traction, wear resistance and rolling resistance [17].

In our previous work the natural rubber hybrid composites were prepared by using marble sludge alone and with rice husk derived silica hybrid composites and the resultant composites showed satisfactory performance [18-20]. For further continuation of research work in said field the preparation and properties of three different kinds of carbon black along with marble sludge incorporated to natural rubber is investigated. Marble sludge is waste material remaining after cutting and polishing of large pieces of marble.

The key objective of the present exploration is to fabricate the constructive hybrid NR composite tailor-made cure characteristics, mechanical, swelling as well as aging properties. Thus, in this work we investigated the effects of marble sludge hybrid composites with three different natures of CB namely CB_{N330}, CB_{N550} and CB_{N660} added in natural rubber to get cost effective and good performance hybrid composites

Results and Discussion

Characterization of Marble Sludge

Marble sludge is composed of calcium/ magnesium compound in large amount and silica, aluminum and iron oxide in small amount as shows in Table-1. The values obtained for metal component of MS from the complexometric titration (CaO, 68.13%, MgO, 22.88%), gravimetric analysis (SiO_2 4.26 %, Al_2O_3 2.55 % and Fe_2O_3 0.585 %) and AAS (Fe_2O_3 0.581 %, Cr_2O_3 0.20 %, ZnO 0.23 %, TiO_2 0.560 %, Mn 0.0059% and Sb, Ni, Pb and Na compound not detected) are approximately same with those obtained from WDX-ray fluorescence spectrometer.

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Table-1: Analysis of MS using WDX-ray fluorescence Spectrometer.

Component	Wt (%)
Calcium Oxide	68.6
Magnesium Oxide	22.13
Silica	3.89
Aluminum Oxide	2.785
Iron Oxide	0.603
Chromium Oxide	0.24
Zinc Oxide	0.20
Titanium Oxide	0.549

Cure Characteristics

Table-2 illustrates the cure characteristics values of NR composites with different hybrid combinations of MS with different types of CB filled NR composites. The optimum cure time (t90) shows the variation with variable amount of CB replacing MS for a given in MS/CB_{dt} content within the NR hybrid composite. The t90 reduces with an increase in the amount of CBs in NR hybrid composites. Although some investigation specified that the accelerated amount of CB could cause hindrance to the initiation of the vulcanization [21]. For a given combination in MS/CB_{dt} filler, the CB_{N330} filled hybrid system reveals the highest t90 value compare with CB_{N550} and CB_{N660} containing hybrid systems. The scorch time (ts2) showed a reduction after the addition of CBs in the corresponding MS/CB_{dt} hybrid NR composite. Same pattern as to t90 also found in ts2. In combination with the different CB in the NR hybrid composites, for a particular result, the CB_{N330} containing hybrid NR composite reveals the highest ts2. This specifies the better scorch safety of CB_{N330} comprising NR hybrid composites.

The CRI as shown in Table-3 has found higher values of as compare to MS filled NR composite, however, at higher CB_{dt} content, the CRI shows no significant effect. The hybrid filled sample with carbon black showed the highest CRI. This surveillance obviously shows the better reinforcing proficiency of all three types of carbon black in NR hybrid composite.

The minimum (ML) and maximum (MH) torque shown in Table-2 increases with gradual increases CBs amount in MS/CB_{dt} hybrid NR composite. For a given hybrid ratio, CB_{N330} containing hybrid ratio showed the lowest MH value. The highest MH value is scrutinized for CB_{N660} filled hybrid NR composite. This observation is related to the different CB in the degree of reinforcement. The highest reinforcement is observed in the case of CB_{N330} that is merged with its lesser particle size as compared to CB_{N550} and CB_{N660}. The allocation of CB_{N330} particles in the NR matrix is more consistent which gives a better reinforcement.

Mechanical Properties

The tensile strength (TS) of MS/CB_{dt} NR composite is shown in Fig. 1. All three type of carbon black exhibited an increasing trend up to maximum (60 phr) content. The hybrid ratio at 10/50 MS/CB_{N33} has optimum value as compare to other two combinations. The TS increased radically as the content of CB concentration incorporated in-place of MS in NR hybrid composite. The variation in TS is in compromise with the reinforcing aptitude of the fillers. The tensile properties, dynamically depends on numerous aspects such as the filler reinforcement and rubber matrix properties, filler content, particle size and surface area of the filler The enhancement in TS may be caused by the very well dispersion of CBs in the NR matrix, which leads to a strong interaction between the NR matrix and CB particles. These sounds-dispersed CBs might have the effect of cross linking positions, therefore increasing the tensile strength [22]. The distinction in TS is in accordance with the reinforcing ability of the fillers. MS/CB_{N660}, comprising the biggest particle size, illustrates the lowest reinforcement in their corresponding hybrid composite. Similarly CB_{N330} having the lowest particle size in corresponding NR composite exhibit a better reinforcement level. However the CB_{N550} shows an intermediary behavior in their hybrid NR composite. In the particulate filled rubber matrix, the fillers proceed as stress deliberators. Lesser the particle size of fillers more competent will be the stress transmitting from the matrix to the fillers [23].

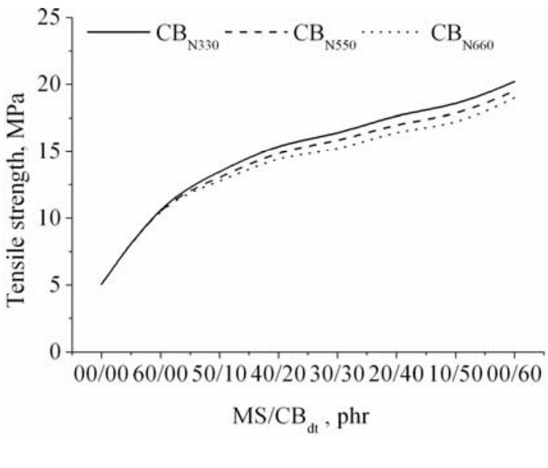

Fig. 1: Tensile strength of MS/CB_{dt} hybrid combination with NR composite.

Table-2: Cure characteristics measurement of MS/CB_{dt} hybrid NR composites.

MS/CB_{dt}	Hybrid composition	Cure characteristics at 150 ºC				
		Scorch time, min	Cure time, min	Min. Torque, dNm	Max. Torqued, Nm	CRI, min^{-1}
00/00	Unfilled	2.34	4.22	0.23	2.56	0.532
60/00	MS-60	1.67	4.55	0.39	3.45	0.348
50/10	MS/CB_{N330}	1.62	4.32	0.41	3.52	0.370
	MS/CB_{N550}	1.60	4.29	0.42	4.53	0.371
	MS/CB_{N660}	1.57	4.26	0.44	4.57	0.371
40/20	MS/CB_{N330}	1.56	4.24	0.44	4.60	0.373
	MS/CB_{N550}	1.54	4.24	0.46	4.60	0.370
	MS/CB_{N660}	1.54	4.21	0.48	4.62	0.374
30/30	MS/CB_{N330}	1.52	4.20	0.47	4.64	0.373
	MS/CB_{N550}	1.49	4.17	0.50	4.68	0.373
	MS/CB_{N660}	1.47	4.15	0.51	4.68	0.373
20/40	MS/CB_{N330}	1.40	4.10	0.52	4.70	0.370
	MS/CB_{N550}	1.37	4.05	0.53	4.72	0.373
	MS/CB_{N660}	1.35	4.03	0.55	4.75	0.373
10/50	MS/CB_{N330}	1.30	4.00	0.57	4.77	0.370
	MS/CB_{N550}	1.27	3.96	0.59	4.81	0.371
	MS/CB_{N660}	1.25	3.92	0.60	4.81	0.374
00/60	MS/CB_{N330}	1.22	3.90	0.63	4.86	0.373
	MS/CB_{N550}	1.18	3.86	0.64	4.88	0.373
	MS/CB_{N660}	1.15	3.84	0.67	4.92	0.371

A good interface between the fillers and the rubber matrix is very significant for a material to situate the stress. Under load, the matrix allocates the force to the CBs that take most of the applied load.

Fig. 2 demonstrates the effect of MS/CB_{dt} content within the NR hybrid composite on 300 % modulus. The same trend as for the tensile strength was also observed for 300 % modulus. It was evidently shown that the presence of CB with MS contained NR hybrid composite has significantly improved the 300 % modulus. Hybrid NR composite reinforced with three types of CB, showed a remarkable increase of modulus with gradually increasing CB. CB_{N330} content shows a maximum value of 300 % modulus at 10/50 MS/CB_{N330} which shows that the modulus increases with increase in the amount of CB in their individual hybrid system. The improvement of modulus is owing to the high modulus of CB and well dispersion exhibiting accurate stress transfer [24].

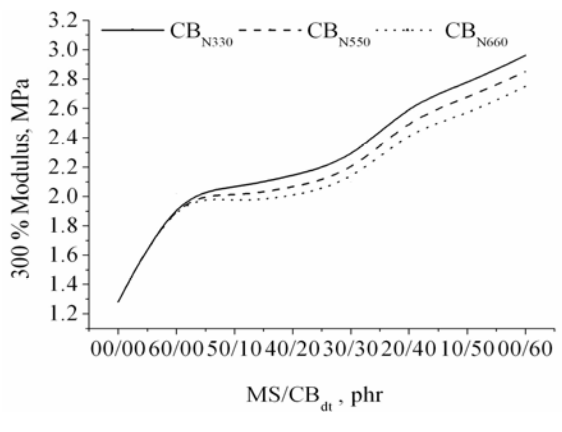

Fig. 2: 300 % Modulus of MS/CB_{dt} hybrid combination with NR composite.

Fig. 3 illustrates the tear strength of MS with three different types of CB incorporated in NR hybrid composite. The tear strength of the composites generally depends on the nature of the filler and their hybrid composition. The same trend as for the tensile strength also observed in tear strength results. The tear strength increased with the increasing quantity of different types of CB incorporated in place of MS in NR hybrid composite, as expected. A higher dispersion of the filler in the NR matrix can be observed in the maximum quantity of carbon black in 10/50 MS/CB ratio or at 60 phr CB loaded NR composite. A more uniform dispersion of CB_{N550} in NR matrix can be viewed. The tear strength of the hybrid composite becomes more uniform at 10/50 MS/CB phr loading compare to that at 50/10 MS/CB phr loading. This clearly supports better tear strength of MS/carbon black composite at 10/50 phr loading compare to those with lower filler content.

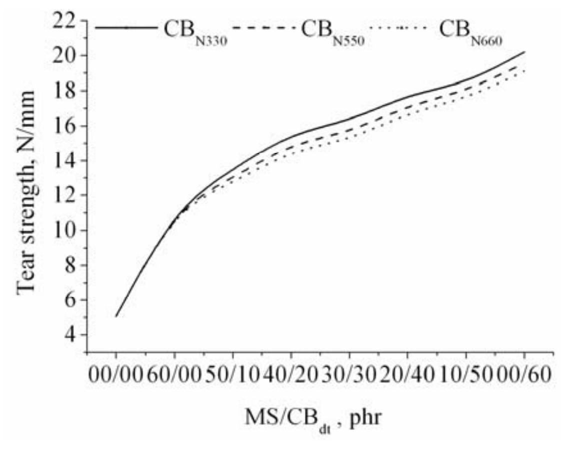

Fig. 3: Tear strength of MS/CB_{dt} hybrid combination with NR composite.

The % elongation at break of MS/CB_{dt} is shown in Fig. 4. The elongation at break decreased with the increase in the quantity of different types of CBs. It may be attributable to the marked reinforcing effect of CB. As the CB content in the NR hybrid composite increases, the stress level gradually increases but at the same time, the strain of the hybrid composites decreased. This is because the carbon black included in the NR matrix behaves like physical cross-linking points and restrict the movement of polymer chains. This shows that the addition of carbon black makes the NR matrix stronger but more brittle.

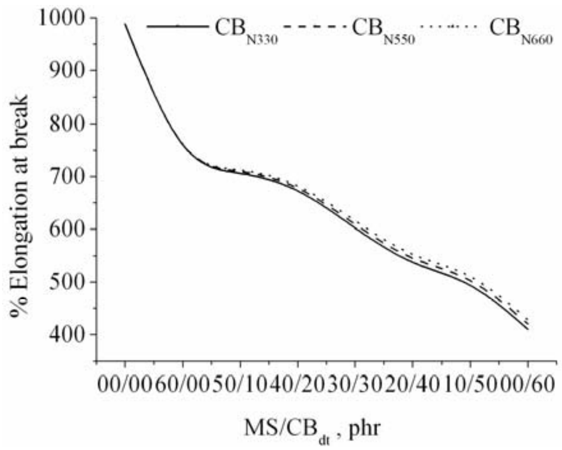

Fig. 4: % elongation at break of MS/CB_{dt} hybrid combination with NR composite.

The hardness curve for MS/CB_{dt} is shown in Fig. 5. The hardness of the composites is another property that may be varied by the combination and the addition of filler in rubber matrix. It has been observed that the hardness of the hybrid composite increases with gradual CBs loading in all the cases of hybrid NR composite attaining highest value for MS/ CB_{N330} filled hybrid samples followed by CB_{N550} and CB_{N660} filled samples.

Fig. 6, illustrate the % rebound resilience of the relevant hybrid composites, It is found to be lower than the unfilled NR compound and has been established to be in the sequence $CB_{N330} > CB_{N550} > CB_{N660}$ comprised NR hybrid composites. The rebound resilience of the respective hybrid composites has been observed to be decreasing with the increasing amount of CBs. It may be due to the polymer chain mobility within the matrix and is lower for CB_{N660} filled NR hybrid composite as compare to CB_{N550} and CB_{N330} containing sample.

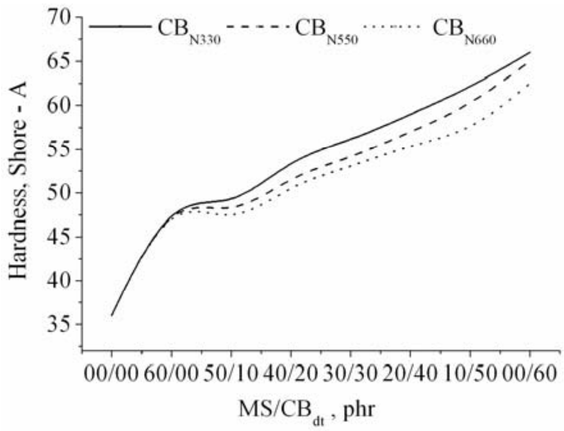

Fig. 5: Hardness of MS/CB_{dt} hybrid combination with NR composite.

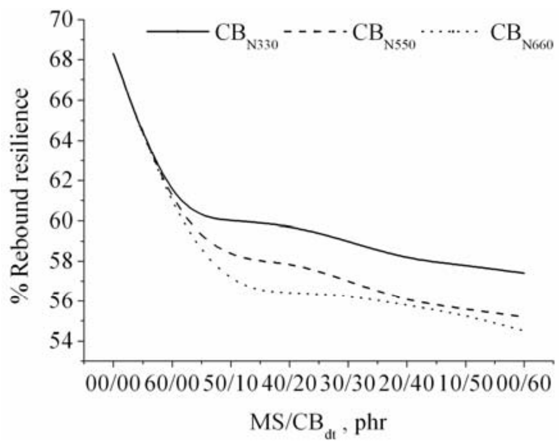

Fig. 6: % Rebound resilience of MS/CB_{dt} hybrid combination with NR composite.

The abrasion resistance expressed as volume loss of unfilled, MS filled and MS/CB_{dt} hybrid NR composite have been examined and shown in Fig. 7. A higher volume loss shows the lower abrasion resistance. The unfilled NR compound has lowest volume loss however MS filled hybrid has the highest value. With gradual increase of the CB amount in MS/CB_{dt} reduced the abrasion loss. The CB_{N330}-filled NR hybrid composite exhibited highest abrasion resistance as compare to CB_{N550} and CB_{N660}. The high value of abrasion resistance of the CB_{N330} containing NR hybrid composite corresponded to its highest hardness and cross-link density lowest abrasion loss [25]. Furthermore explained that the abrasion resistance of rubber vulcanizates was dependent upon their hardness and cross-link density value

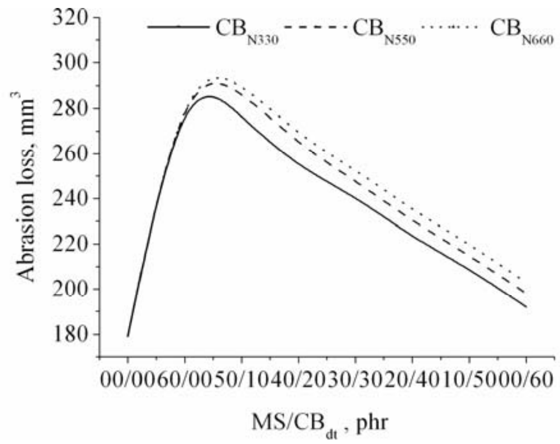

Fig. 7: Abrasion loss of MS/CB_{dt} hybrid combination with NR composite.

Swelling Properties

The swelling ratio is the ability with that the sample swells the effect of CB_{dt} replacing by MS on swelling ratio of unfilled, MS filled and the subsequent hybrid composites, that was immersed in toluene for five days are presented in Table-3. It is evident that the rate of solvent uptake decreased with the incorporation of the CB_{dt}. This trend could be attributed to the presence of the CB_{dt} dispersed, that decreased the rate of transportation by increasing the average diffusion path length in the NR matrix [26]. The subsequent hybrid composites evidently posses that CB_{dt} are uniformly dispersed in the NR, this is in contrast to the unfilled and MS filled NR that has poor dispersion of the MS, hence results show increased solvent uptake. The progresses established to be lower for MS/ CB_{N330} filled hybrid samples pursued by CB_{N550} and then CB_{N660} filled samples.

Chemical cross-linking density is mole of effective network chain per cubic centimeter. In the present study the value of the chemical crosslink of the MS/ CB_{N330} filled hybrid filled NR compare with the unfilled and MS filled NR is shown in Table-3. The result shows that there was effective cross-linking of the CB_{dt} filler with NR during vulcanization and this increase with increasing CB_{dt} dosage in NR hybrid composite [27]. This further confirms the reality that there is better filler-rubber interaction for CB_{dt} containing hybrid sample than the unfilled and MS filled NR composite. It has been inaugurated to be in the order CB_{N330} > CB_{N550} > CB_{N660} occupied NR hybrid composites

The shear modulus of MS/CB_{dt} hybrid NR composite of hybrid composites is also given in Table-3. The shear modulus also follows the same trend as that of crosslink density.

Table-3: Swelling performance of MS/CB_{dt} hybrid NR composites.

MS/CB_{dt} Hybrid composition		Swelling performance		
		Swelling ratio	Crosslink density x 10^{-4} mol/cm^3	Shear modulus, MPa
00/00	Unfilled	3.70	1.557	0.351
60/00	MS-60	2.58	2.53	0.570
50/10	MS/CB_{N330}	2.47	1.748	0.362
	MS/CB_{N550}	2.53	1.168	0.263
	MS/CB_{N660}	2.55	1.428	0.322
40/20	MS/CB_{N330}	2.35	1.850	0.417
	MS/CB_{N550}	2.43	1.499	0.338
	MS/CB_{N660}	2.46	1.453	0.327
30/30	MS/CB_{N330}	2.30	1.988	0.448
	MS/CB_{N550}	2.38	1.561	0.352
	MS/CB_{N660}	2.42	1.580	0.356
20/40	MS/CB_{N330}	2.23	2.016	0.454
	MS/CB_{N550}	2.30	1.606	0.362
	MS/CB_{N660}	2.35	1.593	0.359
10/50	MS/CB_{N330}	2.19	2.183	0.492
	MS/CB_{N550}	2.27	1.697	0.382
	MS/CB_{N660}	2.33	1.625	0.366
00/60	MS/CB_{N330}	2.00	2.206	0.497
	MS/CB_{N550}	2.10	1.700	0.383
	MS/CB_{N660}	2.18	1.626	0.366

Experimental

Materials and Test samples

The materials, natural rubber (RSS-1) and carbon blacks (N_{330}, N_{550}, and N_{660}), provided by Rainbow rubber industry Karachi, (CB_{N330} high-abrasion furnace black, average primary particle diameter 30 nm, CB_{N550} fast-extruding furnace black, average primary particle diameter 50 nm and CB_{N660} general purpose furnace black with 65 nm average primary particle diameter) have been cross linked by sulfur vulcanization. MS was collected from the marble processing industry. The MS was dried at 80° C for 24 h in the oven and then crushed in finer form. The ground MS was passed through sieve to obtain 37 µm. The filled natural rubber hybrid compounds contain 00/00, 60/00, 50/10, 40/20, 30/30, 20/40, 10/50 and 00/60 of MS/CBs per hundred grams of rubber (phr). Furthermore to the raw rubber and filler, the other constituents were Tetramethyl thiuram disulfide (a fast curing sulfur-donor accelerator), zinc oxide (ZnO and stearic acid as activator), sulfur as curing agent, 3-Dimethylbutyl-N-phenyl-p-phenylenediamine (anantioxidant), 3-Dimethylbutyl-N-phenyl-p-phenylenediamine (Antioxidant) used were commercial grade and all purchased from local market.

The characterization of MWP was carried out with a XRF spectrometer (PIONEER with the Bruker AXS SPECTRA) to corroborate the composition of the MWP. XRF spectrometer result of MWP was to analyze the composition of MWP.

The formulation is presented in table 4. The composites were managed as depicted previously [28-30]. The cure characteristics of the compositions were examined as in our prior works [31, 32]. Mechanical, swelling and other properties of prepared hybrid composites were carried out as expressd previously via ASTM [33, 34]

Table-4: Formulation Used in the Preparation of MS/CB_{dt} hybrid filler NR composites.

Ingredients	Formulation, phr
Natural Rubber	100
$MS:CB_{dt}$ Hybrid combination	00:00, 60:00, 50:10, 40:20, 30:30, 20:40, 10:50, 00:60
Zinc oxide	05
Stearic acid	02
Tetra methylthiuram disulphide	2.4
Sulphur	1.6
Antioxidant	1.5

Conclusion

In this work, the MS with CB_{N330}, CB_{N550} and CB_{N660} hybrid NR composites were fabricated and the cure characteristics, mechanical and swelling behavior were measured.

The scorch as well as cure time of the NR hybrid composite revealed a decreasing trend with increasing CB_{dt} amount in MS/CB_{dt} while the minimum and maximum torque exhibited an increasing tendency. The tensile strength, modulus, tear strength, hardness, cross link density and shear modulus has been found to be increased with increasing the amount of CB_{dt} in MS/CB_{dt} hybrid NR composite. Along with the hybrid composites, the CB_{N330} filled hybrid models showed the highest overall properties pursued by CB_{N550} and CB_{N660} filled hybrid samples. The elongation at break, resilience, abrasion loss decreased and swelling ratio was established to be decreased with increasing the amount of CB_{dt} in MS/CB_{dt} hybrid NR composite

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