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Curing and Physical Properties of Natural Rubber/ Wood Flour Composites

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Summary: Natural rubber based composites were prepared by incorporating Wood flour of two different particle size ranges (250–300 μm) and (300–425 μm) and concentrations (15 and 30 phr) into the matrix, using a Banbury® internal mixer according to a base formulation. Curing characteristics of the samples were studied. Influence of particle size and loading of filler on the properties of the composites was analyzed. Results obtained show that the addition of wood flour to natural rubber increased scorch time and curing time and caused improvement in modulus at 300% strain and in tear properties. However, it decreased tensile strength and elongation at break. The particle size range of 300–425 μm was found to offer the best overall balance of mechanical and dynamic properties (tan δ and viscous torque). Swelling behavior of the composites in toluene was also analyzed in order to determine the rubber volume fraction and crosslinking density. Composites with the bigger particle size wood flour were found to have greater crosslinking density than the ones with smaller particle size, fact that could possibly indicate a better rubber-filler interaction in the former. Major percentage of filler increased slightly this interaction. Water absorption behavior of the composites with wood flour reached a maximum of 12% w/w when 30 phr of filler were incorporated; nonetheless, particle size did not affect this property. The ageing study in presence of air at 70 °C revealed that natural rubber composites with wood flour maintained the same classification cell with temperature as the pure rubber. A compound with 30 phr of carbon black was prepared for comparative purposes. Results obtained were as expected. Scorch time decreased and higher values of modulus at 300% strain and tensile strength were achieved, due to strongest interaction between filler and elastomer.

Keywords: composites; elastomer; fillers; particle size; wood flour

INTRODUCTION

During the last years, the effects of different types of fillers on Natural Rubber compounds have been studied, in search of improvements on its physical and mechanical properties. Amongst these fillers are carbon black, silica, calcium carbonate, etc. Recently, the application of fillers of organic nature has attracted interest due to their low cost, renewable and environment friendly nature. Several cellulosic wastes such as ground wood waste, nut shells, bamboo, white rice husk, cassava starch and cereal straw have been used as fillers for rubber[1–4] Fillers have an important direct action on the physico mechanical properties of rubber blends. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a

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complex interaction of several filler related parameters. These include filler size, filler shape, filler dispersion, surface area, surface reactivity, filler structure and bonding quality between fillers and rubber matrix.[5]

Thus, it is the aim of this contribution to assess the potential utilization of wood flour, obtained from typical trees of Venezuela, in Natural Rubber compounds. So, the objective of the present investigation is to study the influence of wood flour content and particle size on the rheological, mechanical, dynamical and ageing behavior of NR composites. A secondary objective concerns a comparative study with conventional filler such as carbon black

Experimental

Materials employed were Natural Rubber (NR) SMR-20 and wood flour originated from tropical trees, Puy (*Tabebuia chrysantha*) and Algarrobo (*Prosopis pallida*). Two concentrations were used: 15 and 30 phr. Wood flour (WF) was sifted, so different particle sizes could be obtained. Sieves where wood flour was retained were 40 mesh (300–425×10^{-6} m) (WF_{40}) and 50 mesh (250–300×10^{-6} m) (WF_{50}). Figure 1 shows a SEM micrograph of a 40 mesh wood flour.

The curing system employed was conventional. The other components of the compound, stearic acid, zinc oxide (ZnO), cyclohexylbenzothiazyl sulphenamide (CBS) and sulphur (S) were all laboratory reagent grade. GPF Carbon black (CB) with an average particle size of 70 nm and with secondary aggregates particle size measured of 850–2000 μm,was used for comparative purposes. Both fillers (WF and CB) were ground and woodflour was previously air dried at 60 °C for 48 h (172.8×10^3 s). Table 1 shows the rubber compound used.

Compounds were prepared using a Farrel Banbury® internal mixer, with a capacity of 1 lt and a fill factor of 0.75, at a rotor speed of 77 rpm. Firstly, rubber was masticated during 105 s. Then, ZnO was mixed for other 60 s. Half of the filler was then incorporated and mixing continued for 90 s; the remaining half was added at that time and after 90 s of mixing, stearic acid was added and mixing continued for another 60 s. Curatives (S and CBS) were added in a second step using the same equipment. The compound obtained was then passed through a two roll mill to form sheet.

Cure characteristics were studied using a Rotorless rheometer model EKT-2.000SP at 160 °C and 0.5° oscillation according to ASTM D5289 procedure. This equipment

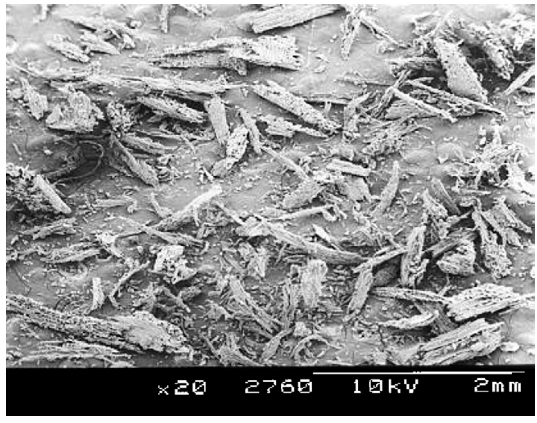

Figure 1.
SEM micrograph of a 40 mesh wood flour sample.

Table 1.
NR formulations

Formulation (phr)	F1	F2	F3	F4	F5	F6
NR SGR-10	100	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
WF_{40}	—	15	30	—	—	—
WF_{50}	—	—	—	15	30	—
Carbon Black	—	—	—	—	—	30

also permits the determination of dynamic parameters such as complex torque, elastic torque (S′) and viscous torque (S″) as a function of time. The mechanical loss factor (tan δ) is calculated by dividing S″ by S′.

All rubber compounds were compression molded into sheets in a Carver hydraulic press at 160 °C, according to their t_{90} and to their thickness. All specimens were then cut from the vulcanized sheets.

Tensile and tear properties of vulcanized blends were determined using a Lloyd Instruments machine model EZ20 according to ASTM D412 and ASTM D624 procedures, respectively.

Test for hardness was carried out using a Shore type A Durometer in accordance to ASTM D2240.

Ageing was carried out in a Heraeus air-circulating oven at 70 °C for 70 h (252×10^3 s) following ASTM D573 and ASTM 2000 procedures.

Crosslinking density was determined according to equilibrium swelling measurements in toluene, for 72 h (259.2×10^3 s) at room temperature. The swollen samples were then weighed, the solvent removed in air during three days, and the dried pieces were weighed again. The volume fraction of the rubber in the swollen vulcanizates (V_r) was then calculated through the equation:[6]

$$V_r = \frac{(m_1/\rho_r) - V_f}{(m_1/\rho_r) - V_f + (m_2 - m_3)/\rho_s} \quad (1)$$

Where: m_1 is the initial weight of the specimen; m_2 is the weight of the swollen specimen; m_3 is the weight of specimen after solvent evaporation; V_f is the volume of the filler, ρ_r is the density of rubber; and ρ_s is the density of the solvent (866.9 kg/m^3 for toluene).[7]

V_r was then substituted in the Flory-Rehner equation:

$$M_c = -\frac{\rho_r V_0 (V_r^{1/3} - V_r/2)}{\ln(1 - V_r) + V_r + \mu V_r^2} \quad (2)$$

Where M_c is the molecular weight of polymer chains between two crosslinks, μ is the polymer-solvent interaction parameter ($\mu = 0.42$ for NR-toluene)[6], and V_0 is the molar volume of solvent ($V_0 = 106.2 \times 10^{-3}$ m^3/mol for toluene).[6] Crosslinking density (υ) can be calculated as $1/2M_c$.

To evaluate water absorption behavior, the samples were vacuum dried at 40 °C until a constant weight was reached, prior to be fully inmersed in a static deionized water bath at room temperature. The specimens were periodically taken out of the water, wiped with tissue paper to remove surface water, reweighed and dimensions remeasured; and immediately put back into the water. At least three specimens were used for each sample. Specimens weight was measured daily for the first two weeks and afterwards, every alternate day. Total span time of immersion was 110 days.

Water absorption (WA) was calculated according to the following equation:

$$WA = 100(M_f - M_0)M_0^{-1} \quad (3)$$

Where M_f is the mass of the sample after immersion and M_o is the mass of the sample before immersion.

Results and Discussion

Table 2 summarizes the values of minimum (S′min) and maximum (S′ max) elastic torque, scorch time (t_s) and time needed to reach 90% of maximum torque (t_{90}) of all formulations prepared. The t_{90} and t_s of those formulations filled with woodflour are slightly superior to those of NR. These parameters differ more when filler has a bigger particle size (WF_{40}) and when it is present in greater amount. Ismail et al[8]

Table 2.
Cure characteristics, elastic and viscous torques and tan δ

Formulation	S′ min	S′ max	t_s	t_{90}	S″	tan δ
	(N.m)	(N.m)	(s)	(s)	(N.m)	
F1	0.059	0.8	90	204	0.048	0.060
F2	0.062	1.07	108	240	0.075	0.070
F3	0.075	1.27	120	264	0.099	0.078
F4	0.058	1.10	96	216	0.083	0.075
F5	0.061	1.30	102	240	0.105	0.081
F6	0.060	1.10	78	198	0.069	0.063

found that for Epoxidized NR compounds with 15% oil palm wood flour, the scorch time and t_{90} decrease, when compared to the unfilled compound. They report that this behavior is partly due to the humidity and water content that is usually present in this type of fiber, which according to Buttler et al[9] causes a decrease in scorch times and an increase in cure rates. In this present investigation, woodflour was previously dried, so the effects of humidity and water content are negligible.

Maximum and minimum elastic torque values are higher for those filled formulations. The presence of fillers imparts restriction to the deformation, and consequently, the composite becomes harder and stiffer.[8] This behavior will be confirmed when mechanical properties are analyzed. If torque maximum values are compared for both particle sizes at equal content, one can see that they are similar. However, when minimum torque is analyzed, the influence of particle size is noticeable, since bigger particle size (WF_{40}) has stronger effect on compound viscosity.

Concerning carbon black, the behavior obtained during curing is as expected for this type of filler: there is a slight decrease in scorch and curing time. The authors obtained the same tendency for carbon black filled EPDM vulcanizates.[10] Also, Ramesan et al[11] studied the influence of carbon black on SBR/NBR blends. They associate the decrease in scorch and curing time with the higher crosslinking density obtained when loading of carbon black increases.

The mechanical loss factor tan δ (loss angle between the storage modulus E′ and the loss modulus E″ in viscoelastic materials) is a parameter widely used to measure the degree of imperfection on the elasticity of a rubber. It is a measure of the absorbed energy fraction that is not stored but dissipated. It is directly related with hysteresis and resilience, but it's most important issue is that within ranges of practical interest, it is insensitive to changes in deformation amplitude so it can be almost considered as an intrinsic property of the material. This fact can be explained since E′and E″ change in the same way when use conditions vary, so its quotient is basically unaltered. However, hysteresis and resilience do vary with test conditions.[12]

Figure 2 illustrates the variation of tan δ while curing of formulations takes place. As it can be seen both in Figure 2 and in Table 2, unfilled NR (F1) exhibits the lower values of tan δ. This property is increased when filler is added, independently of its nature. It should be emphazised that the value of tan δ expressed in Table 2 corresponds to the point where the vulcanizate is totally cured. For wood flour filled compounds, it can be noticed that the ones with the bigger size particles (F2 and F3) present lower values than its analogous pairs of smaller size. With respect to the compound filled with carbon black, it exhibits the lowest value of tan δ, which could be indicating that resilience was affected in a lesser extent.

Caruthers et al[12] concluded in their work on carbon black reinforced NR, that the interaction between filler particles is one of the factors that mostly affects the value of tan δ. They demonstrated that the energy consumed by the material during deformation that is not stored, is used for breaking up the primary aggregates of carbon black particles. So, while the elastomer-filler interaction is higher, a less variation on tan δ will be obtained.

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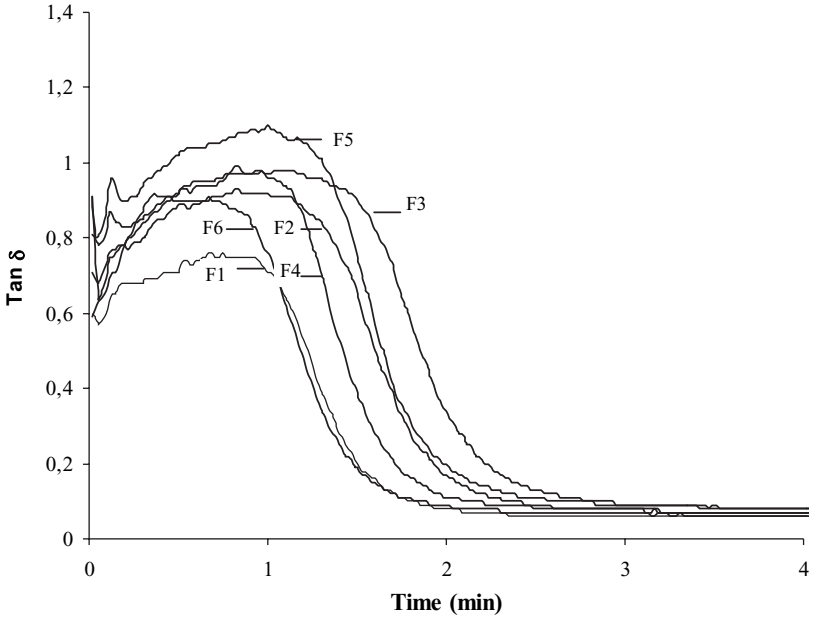

Figure 2.
Tan δ variation with time at 150 °C.

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Besides, Wang[13] found that a stronger filler network contributes to higher elastic modulus and lower hysteresis. He suggested that the breakdown and deformation of the filler network, accompanied by releasing the trapped rubber from the filler network, would cause an energy dissipation process during dynamic strain.

Figure 3 shows how curing time affects the viscous torque (S″). It should be reminded that the rotorless rheometer employed in this study measures this variable which is directly proportional to the loss Modulus E″. The tendency obtained for S″ is the same as for tan δ, as it is shown in Table 2. The increase in this variable when filler loading increases could be partially attributed to the hydrodynamic effect, since the addition of unstrained particles of wood flour to the rubber matrix would result in a high viscosity compound.

Table 3 presents several properties of the vulcanizates, one of which is the crosslinking degree (υ) obtained from the swelling tests. It can be noticed that the crosslinking degree of all filled vulcanizates is slightly higher than the one of the pure rubber. When the bigger particle size of wood flour is employed (F2 and F3) the degree of crosslinking attained is higher.

In this case, the wood flour employed is of fibrous nature, as determined previously by the authors[14], so the aspect ratio (relation between length and average diameter of filler) of the larger-sized filler (W_{40}) is higher. This is reflected on the higher values of V_r obtained (see Table 3), as an indicative of a decrease in the extent of swelling caused by the higher polymer-filler interaction.

When the filler is carbon black, the highest value of crosslinking density and V_r of all vulcanizates is obtained. It is well known that this type of filler promotes the

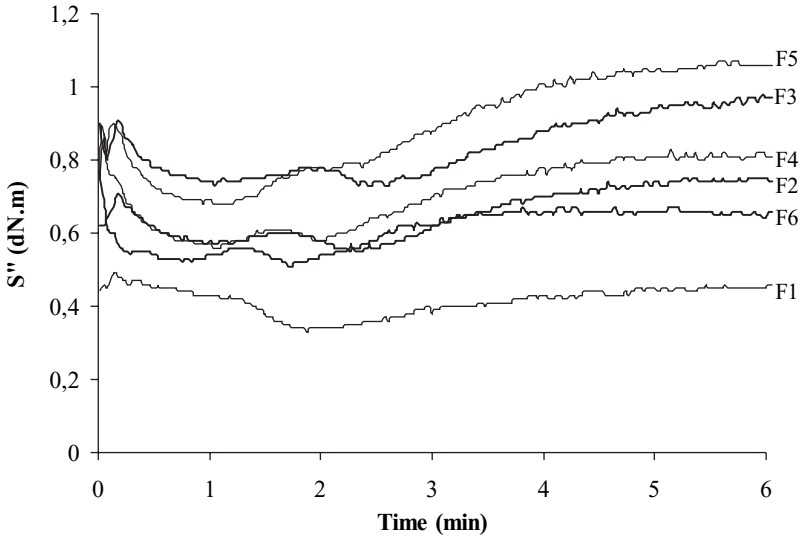

Figure 3.
Viscous torque variation with time at 150 °C.

formation of the so-called bound rubber, due to the strong interaction between filler and rubber, which in turn comprises physical adsorption, chemisorption and mechanical interaction.[15]

Studies on reinforcement generally agree that the surface interaction (physical or chemical) between fillers and rubber molecules or network segments promotes better final properties. [16] In particular, the adhesion between a filler particle and an elastomer enhances the mechanical properties of the cured vulcanizates.

Table 3 shows that moduli at 300% strain (σ_{300}) of compounds tend to increase when fillers are present. This observation highlights the fact that the incorporation of fillers into the rubber matrix can improve the stiffness of the compound. Also, it is observed that tensile strength (σ_r) of NR decreases with wood flour content, tendency also observed by authors such as Ismail et al[8] and attributed to the geometry of WF fillers.

For irregularly shaped fillers, the strength of the composites decreases due to the inability of the filler to support stresses transferred from the polymer matrix. In addition, particle size seems not to affect considerably this property. In a previous paper[17] the authors reported the effect of filler content and size on the mechanical properties of polypropylene/wood flour composites. It was found that the composites filled with large size filler showed higher modulus and tensile strength

Table 3.
Physical and mechanical properties of the NR-Wood flour vulcanizates

Parameter	F1	F2	F3	F4	F5	F6
σ_{300} (MPa)	1.60	2.42	2.93	2.19	2.75	4.92
σ_r (MPa)	18	13	10	12	9	26
Elongation at break (%)	963	803	683	819	715	789
Tear strength (kN.m)	5.1	7.9	8.4	6.6	6.2	6.1
Hardness (Shore A)	42	52	59	52	58	62
V_r	0.2049	0.2087	0.2101	0.2016	0.2057	0.2271
υ (10^5) mol/kg	7.0	7.4	7.5	6.8	7.1	9.0

because the wood flour fillers seem to act as fibrous type fillers where larger size improves the strength properties. On the other hand, when carbon black is the filler tensile strength does improve as expected, reflecting a real reinforcing effect. This is due to the greater NR-filler interaction which favors a higher reticulation degree, as discussed previously.

Table 3 also reflects that formulations of filled NR show lower elongation at break (ε_b) due to the formation of filler aggregates between the flexible chain segments, which act as obstacles to their sliding. Nonetheless, elongation at break could be slightly improving for the small particle size vulcanizates (F4 and F5) probably due to the better dispersion of the filler, which in turns reduces the tendency of filler-filler interactions. Similar results were found by Anna et al.[18] They studied the influence of two organic fillers (cotton fibre and wood flakes) on PP composites. When analyzing the mechanical properties, they found that the longer fibre size (cotton fibre) prevents the elongation, resulting in a lower elongation at break. The higher elongation at break of the wood flake containing composite was due to the shorter fibre size of the wood flakes, which allows the orientation and movement of the matrix polymer chains during the tensile test.

If tear properties (TS) are analyzed, the expected effect is to obtain a rise in this property with filler content, since filler offers opposition to tear patterns, making the crack propagation more difficult. This tendency is clearly observed for 300–425 μm particle size (see Table 3) due to the fibrous nature of wood flour, which imparts greater restriction to crack propagation.

Hardness Shore A was modified when filler was added to the NR compounds; an increase of 24 % was obtained for 15 phr of wood flour (see Table 3). Moreover, higher hardness was reached when amount of filler increased, passing from a hardness of 52 to 58–59 Shore A when wood flour content increased from 15 phr to 30 phr. This behavior could be due to the reduction of the volume fraction of the elastomer and seems to be independent of particle size.

If compared to carbon black, one can see that hardness obtained for wood flour filled compounds is lower than the corresponding value for carbon black compounds.

Table 4 presents changes produced on tensile ($\Delta\sigma_{300}$, $\Delta\sigma_r$, $\Delta\varepsilon_b$) and tear properties (ΔTS), and hardness (ΔH) due to the accelerated ageing of NR and formulations with woodflour. Results indicate that the variation on properties for all the studied formulations is within the requirements specified by ASTM D2000 for a material classified as AA grade "2".

Figure 4 shows water absorption with time for all rubber-wood flour compounds. It is noticeable that water absorption increases with wood flour content. This behavior is totally predictable since NR is hydrophobic while wood flour is highly hygroscopic.

The water absorption of all NR-wood flour vulcanizates is generally low (<12 wt %) indicating that the wood flour particles are well encapsulated within the rubber matrix. Similar results were obtained by Vladokova et al[19] for wood flour filled NBR compounds.

However, there is no clear behavior of the influence of particle size on this property. In this study, the difference in particle size or in avaibalility of OH groups might not have been enough so a real different behavior in water absorption could be attained. Moreover, after about 110 days of soaking time the samples reached a constant moisture content (equilibrium).

Table 4.
Change of mechanical properties of aged NR and its composites at 70 °C for 70 h

Formulation	$\Delta\sigma_{300}$ (%)	$\Delta\sigma_r$ (%)	$\Delta\varepsilon_b$ (%)	ΔTS (%)	ΔH (shore A)
F1	+20	−16	−19	+6	+3
F2	+30	+22	−5	−30	+5
F3	+26	+6	−13	−31	+6
F4	+14	−25	−21	−15	+6
F5	0	−32	−22	−7	+3

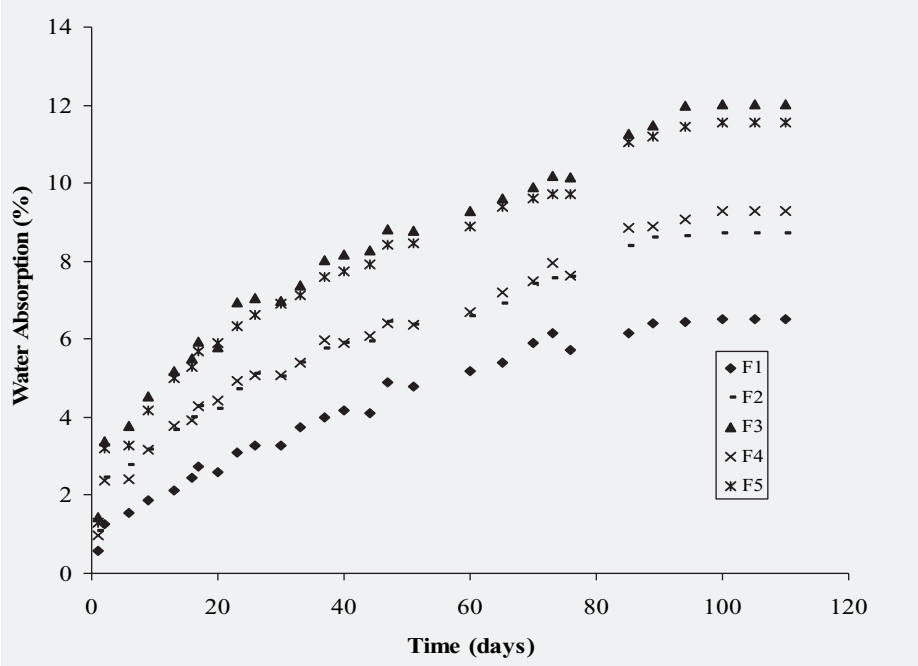

Figure 4.
Water absorption of NR-Wood flour composites at room temperature.

Conclusions

The influence of filler particle size and content on wood flour/natural rubber composites was evaluated. Results obtained showed that the addition of wood flour to NR increased scorch and curing time and caused an improvement in modulus at 300% strain and in tear properties. However, it decreased tensile strength and elongation at break. The particle size range of 300–425 μm was found to offer the best overall balance of mechanical and dynamic properties, as well as a higher degree of crosslinking density. Water absorption behavior of the composites with wood flour reached a maximum of 12% w/w when 30 phr of filler were incorporated; nonetheless, particle size did not affect this property.

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