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Physico-Mechanical, Thermal and Morphological Studies of Saw Palmetto Spent - HDPE Composites

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Abstract: ***Composites of Saw Palmetto (Serenoa repens) spent (SPS) with high-density polyethylene (HDPE) were prepared by using 5, 10, 15, and 20 wt % SPS and their tensile, flexural, impact strengths, abrasion resistance, surface hardness, water absorption, density and thermal properties were studied. Addition of SPS affected the tensile, flexural and Izod impact strengths of the composites but tensile modulus of HDPE/SPS composites increased from 609.7 to 713.9 N/mm^2. Heat distortion temperature increased from 62 to 67^{o}C. Slight variation was observed in surface hardness, abrasion resistance, density and water absorption due to incorporation of SPS. There was only marginal variation in melt flow index of composites.***

Keywords: Sawpalmetto; High density polyethylene; Tensile properties; Flexural properties; Abrasion resistance; Injection molding

1. Introduction

The primary purpose of fillers in polymer composites is to improve the properties of the composites and/or reduce the cost and/or increase the biodegradability of the composite material. Good filler should fulfil at least one of the above said requirements. Fillers may be inorganic, organic or natural. Much work has been published on the use of filler materials for the preparation of composite materials which are advantageous. Fillers like glass fibre[1], calcium carbonate [2], boron nitride [3], magnesium hydroxide and aluminium hydroxide [4], Chalk [5], Zinc powder [6], aluminium powder [7], graphite [8], TiO_2 [9], carbon black [10], montmorillonite [11], fly ash[12],wood flour [13], jute [14], Coconut Shell [15], coconut fibre [16], Nutshell Flour [17], pineapple-leaf fibre [18], sawdust[19], Sugarcane bagasse [20], etc., have been used in composite either to improve properties of composites or to reduce the production cost.

Nano materials are currently being used as fillers in composites to improve the properties. The nanofillers that are used in composites are nano clays, nano particles, nano tubes and nano fibers. Use of carbon nanotubes [21 and 22] and nano-oxides [23 and 24] as fillers in polymer composites are of great importance. Utilisation of natural fillers in the fabrication of composites reduces the cost of the product and also advantageous from the environmental point of view. Researchers have also improved the properties of composites by using natural filler [16]. Environment friendly fillers have started now replacing glass fibre in the manufacture of various automotive components [25].

Saw palmetto [Serenoa repens (Bartram) Small] is endemic to the southern United States. Its distribution is mainly in coastal areas from Texas to Carolina. The extract of Saw palmetto fruit is used in the treatment of enlarged prostate (benign prostatic hypertrophy, BPH) [26]. In the present work, Saw palmetto spent (SPS), biomass left after the extraction of active component from the Saw palmetto fruit was used as a filler for HDPE polymer matrix. The composite was fabricated and tested for the physico-mechanical and thermal properties. SEM studies were made to know the dispersion and interaction of SPS particles in the polymer matrix.

2. Methodology

2.1 Materials

Injection grade HDPE (Halene M5018L) was supplied by M/s Haldia Petrochemicals Limited, India. The density and melt flow index of HDPE used were 0.952 g/cm^3 and 17.8 g/10 min respectively. Ethylene vinyl acetate (EVA) copolymer procured from M/s National Organic Chemical Industries, Mumbai, India, with 28% VA content and MFI of 25 g/10 min (190 C/2.16 kg) was used as compatibilizer and binder. Saw palmetto spent used as filler material was supplied by nutraceutical industries, Bangalore, India. Industrially processed spent material was washed thoroughly with double distilled water to remove chemical and physical impurities. The spent was ground to fine powder, washed with distilled water and dried in sunlight. The powder was sieved through ASTM 240 mesh to get ≤ 63 micron size particles, and finally dried in hot air oven at 60^{o}C for 24 hours and stored in air tight containers.

Table 1: Properties of SPS powder

Properties	Values
Colour	Dark brown
Density (g/cc)	0.558
Moisture content (%)	< 2
Charring temperature (^{o}C)	350-450
Particle size (microns)	≤ 63
pH of aqueous slurry	7.8

2.2 Preparative Methods

Slurry of SPS in xylene (75 g SPS in 100 ml xylene) was prepared and EVA granules (25 g) were dissolved in the slurry under boiling condition. After dissolution, the content was poured into a glass mould for solvent evaporation. After complete evaporation for 48 h, thick sheet obtained was cut into small flakes. These flakes were then dried in hot air oven at 50 ^{o} C for 8 h to remove volatile matter. Oven dried SPS flakes were used with HDPE granules for compounding.

HDPE-SPS composites were prepared with SPS concentrations of 5, 10, 15 and 20 wt % using co-rotating twin-screw extruder with a screw speed of 90 rpm. The temperature was set points at 170, 175, 180, 185 and 190°C from feed zone to die zone. The extrudates obtained were water cooled at room temperature, and granulated into pellets. The granules were then fed to injection moulding machine (R.H. WINSOR India) to prepare test specimens. The mould was designed as per ASTM standards to produce specimens which were used for tensile, flexural, abrasion, water absorption and heat distortion temperature (HDT) tests. The specimens after preparation were conditioned before testing as per ASTM D 618.

2.3 Testing

Mechanical properties of the HDPE-SPS composites were evaluated as per ASTM D638 and ASTM D790 standards to study the tensile and flexural properties, respectively. Both the tensile tests and the three-point bending flexural tests were carried out on Universal Testing Machine, (Llyod, UK, Model LR 100K). Shore D hardness test was evaluated using Durometer (M/s. P.S.I Sales Pvt. Ltd., India) as per ASTM D 2240 method. Composite material was tested for abrasion resistance using 100 mm disc as per ASTM D 1044 standards. HDT studies were made as per ASTM D 648 method with HDT-VICAT Tester (ATS FAAR, Italy). Melt Flow Index was performed using melt flow indexer (Devenport, UK, Type 7273) according to ASTM D 1238. Scanning electron microscopy (SEM) analysis was done using a Leo 435 VP. The samples were cryo-fractured to avoid deformation of matrix and then the fractured surface was coated with a fine layer of gold and observed.

Water absorption studies were made as per ASTM D 570 standard, long-term tests were carried out in this respect at room temperature for 24 h. The samples were conditioned by drying in oven at 80°C for 1 h and then cooled to room temperature in desiccators. The conditioned samples were weighed to the nearest to 0.1 mg. The samples were put into container with distilled water at room temperature. After 24 h of immersion the specimens were taken out of water and the surface was wiped with cloth and weighed immediately. Percent of water absorption was calculated using the formula:

$$\text{Water absorption (\%)} = \frac{W2-W1}{W1} \times 100$$

Where, W_1 is conditioned weight and W_2 is the weight after immersion.

3. Results and Discussion

3.1 Tensile properties

The SPS-HDPE biocomposites with SPS load ranging from 0 to 20% wt. were processed by injection molding and their mechanical properties were investigated. Results of tensile strength and elongation of the composites are shown in Fig 1 and 2, respectively. The tensile strength of the composites decreased with increase in the volume percent of the SPS within the matrix of the composite. The composite with the highest volume fraction of filler (20%) had the lowest strength (17.3 N/mm2). The values of tensile elongation also decreased almost ten times for 20% composite. This may be due to poor interaction between SPS and HDPE matrix, which is commonly observed in polyolefin/natural filler composites [27 and 28]. In irregular shaped fillers, strength of the composite material decreased due to inability of the filler to support the stress transferred from the polymer matrix [29]. HDPE/SPS composites follow the general trend of filler loading effects on properties. Several theories have been proposed, to explain the effect of filler volume fraction Φ and geometry on the properties of composites [30 and 31]. A geometric model (1) was developed by Nicolais and Narkis [31] for tensile strength (σ) of a composite with spherical filler particles of equal radius having uniform distribution.

$$\sigma_c = \sigma_0 (1\text{-}1.21\Phi^{2/3}) \text{ .....(1)}$$

Where, σ_c and σ_0 are the tensile strength of composite and matrix polymer, respectively and Φ is volume fraction of filler. The tensile values calculated using eq.(1) (theoretical values) and experimental values are plotted and shown in Figure 1. It is clear that reduction in experimental values are less than that of theoretically predicted values, which may be due to poor interaction and non homogeneous dispersion of filler to take tensile loads transferred from the polymer matrix [32]. Nielsen [7, 8] developed an empirical relationship (2) between volume fraction of the filler and elongation.

$$\varepsilon_c = \varepsilon_0 (1\text{-}\Phi^{1/3}) \text{ .....(2)}$$

Where, ε_c and ε_0 are the elongation values for composite and matrix polymer, respectively. Theoretical (calculated using eq.2) and experimentally obtained tensile elongation values are plotted in Figure 2. The reduction in experimental values in comparison with calculated values may be due to weak interaction of filler with matrix. The tensile modulus increased from 609.7 to 713.9 N/mm^2 (Table 2) with increased filler dosage of 0-20 wt%, this behaviour of the composite may be due to improper dispersion and orientation.

Table 2: Effect of SPS filler loading on tensile properties of HDPE/SPS composites

Composition (%)		Tensile strength (N/mm^2)	Tensile modulus (N/mm^2)	Tensile elongation (%)
HDPE	Saw palmetto spent			
100	0	21.6	609.7	340
95	5	20.8	674.3	145
90	10	18.6	636.4	74
85	15	18.1	612.8	59
80	20	17.3	713.9	43

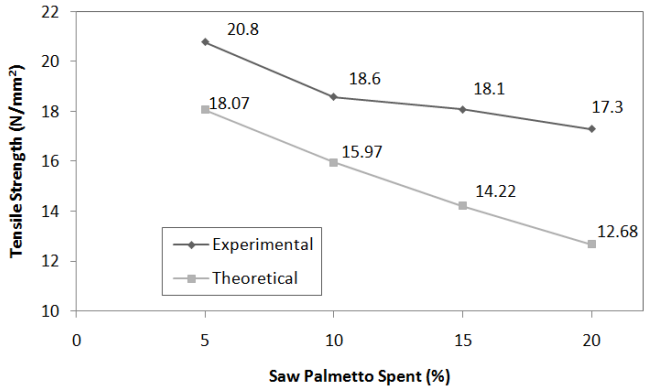

Figure 1: Effect of SPS loading on tensile strength of HDPE/SPS composites

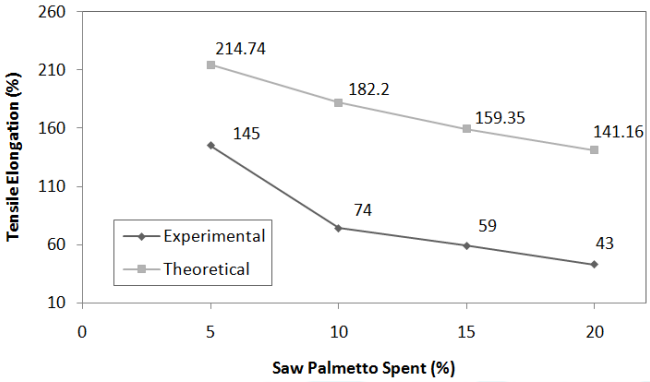

Figure 2: Effect of SPS loading on tensile elongation of HDPE/SPS composites

3.2 Flexural Properties

Flexural strength and flexural modulus values of HDPE/SPS composites are shown in Table 3. It is observed that Flexural strength values decreased from 31.2 to 21.8 N/mm^2 with the increase in filler content from 0-20% wt. Flexural modulus also decreased from 722.3 to 498.7 N/mm^2 with the increase in the filler dosage from 0-20%wt. This reduction in both flexural strength and modulus may be due to poor filler/matrix interfacial adhesion.

Table 3: Effect of SPS filler loading on flexural strength and modulus of HDPE/SPS composites

Composition (%)		Flexural strength (N/mm^2)	Flexural modulus (N/mm^2)
HDPE	Saw palmetto spent		
100	0	31.2	722.3
95	5	28.1	618.6
90	10	25.2	597.1
85	15	24.1	537.8
80	20	21.8	498.7

Table 4: Effect of SPS filler loading on abrasion resistance and surface hardness of HDPE/SPS composites

Composition (%)		Abrasion weight loss (mg)			Surface Hardness (Shore D)
HDPE	Saw palmetto spent	1000 cycles	2000 cycles	3000 cycles	
100	0	14	21	39	63
95	5	16	29	45	64
90	10	17	34	51	64
85	15	21	46	57	65
80	20	42	78	97	65

3.3 Impact strength

Figure 3 shows the effect of filler loading on notched Izod impact strength of SPS filled composites at various leading levels. The strength decreased markedly from 138.7 to 57.3 Kg.cm/cm with the increase in filler loading of 5-20 % wt. Micro spaces between SPS and polymer matrix were induced due to poor interfacial bonding, these spaces results in microcracks when the impact occurs and thereby reducing impact strength of the composites.

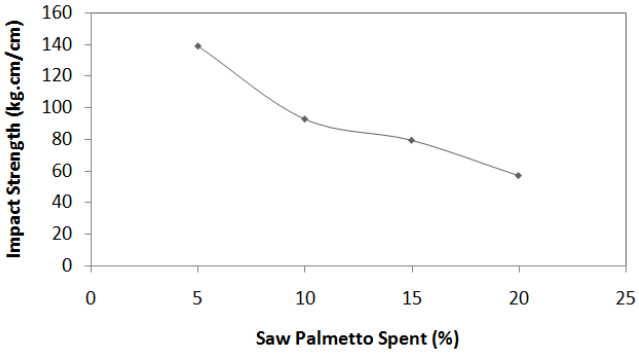

Figure 3: Effect of SPS loading on impact strength of HDPE/SPS composites

3.4 Density and water absorption

No significant change in the density with filler dosage, was observed but there was only a slight increase in density from 0.958 to 1.042 g/cm^3 with increase in the filler content from 0-20% wt (Table 5). The slight increase in density may due to bulky nature of SPS.

Natural fibers are highly hydrophilic; hence incorporation of natural fillers into polymer matrix generally increases the water absorption ability. Table 5 shows the water absorption of HDPE/SPS composites. The water absorption of composites with 20% wt. filler is 0.17%, but it is still higher than pure HDPE.

3.5 Thermal Properties

Presence of fillers in the composites considerably affected heat deflection temperature (HDT). The HDT values for HDPE/SPS composites increased from 62 to 67 ^{o}**C** with the increase in filler dosage from 0 to 20% wt. This increase in HDT values may be due to the increase in modulus. The effects of filler dosage on melt flow index (MFI) values of HDPE/SPS composites are shown in Figure 4. It is observed that, MFI values decreased from 18.6 to 16.4 (g/10 min) as the dosage of filler increased from 0 to 20% wt. The decrease in the value of MFI is due to interruption by SPS particle in the molten polymer to be extrudated.

Table 5: Effect of SPS filler loading on Density, Water absorption and Heat Deflection Temperature of HDPE/SPS composites

Composition (%)		Density (g/cm^3)	Water absorption (%)	Heat Deflection Temperature (°C)
HDPE	Saw palmetto spent			
100	0	0.958	0.02	62
95	5	0.973	0.05	64
90	10	0.995	0.08	64
85	15	1.023	0.11	66
80	20	1.042	0.17	67

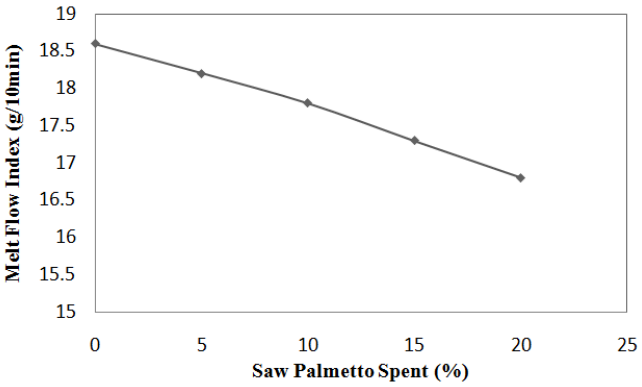

Figure 4: Effect of SPS loading on melt flow index HDPE/SPS composites

3.6 Surface Morphology

The SEM images revealed dispersion of filler particles and voids at the SPS-matrix interfaces. Presence of voids indicates that the extent of adhesion between SPS and HDPE is poor. When elongated these voids coalesce and lead to fracture or breakage. SEM images show non homogeneous dispersion of SPS particles throughout the polymer matrix which might have led to decreased mechanical and other properties of HDPE/SPS composites.

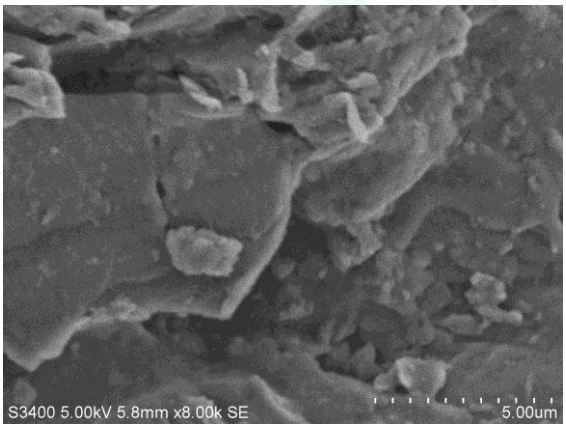

Figure 5: SEM image of HDPE/SPS composites

4. Conclusions

The results obtained, prove that, non-homogeneous distribution of filler in the microstructure of SPS reinforced HDPE composite is the major cause for the decrease in strength. The properties like tensile modulus and HDT which increased from 609.7 to 713.9 N/mm^2 and 62 to 67C, respectively with the addition od SPS. Addition of SPS resulted in a marginal variation of abrasion resistance, surface hardness, density and water absorption of HDPE/SPS composites. SPS could be used as natural, ecofriendly and economical filler to increase biodegradability of the composites and to reduce the cost of production.

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References

[1] Gupta, A. K., et al. (1982). "The effect of addition of high-density polyethylene on the crystallization and mechanical properties of polypropylene and glass-fiber-reinforced polypropylene." Journal of Applied Polymer Science 27: 4669–4686. doi: 10.1002/app.1982.070271214

[2] Xie, T., et al. (2006) "Property transitions in high-density polyethylene/maleated poly(ethylene–octene)/calcium carbonate ternary composites." Journal of Applied Polymer Science101: 3361–3366. doi: 10.1002/app.24029

[3] Zhou, W., et al. (2007). "Study on insulating thermal conductive BN/HDPE composites." Thermochimica Acta 452(1): 36-42. doi.org/10.1016/j.tca.2006.10.018

[4] Hippi, U., et al. (2003). "Compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes." Polymer 44(4): 1193-1201. doi.org/10.1016/S0032-3861(02)00856-X

[5] Badran, B. M., et al. (1982). "High-density polyethylene filled with modified chalk." Journal of Applied Polymer Science 27(10): 3669-3681. doi: 10.1002/app.1982.070271004

[6] Rusu, M., et al. (2001). "Mechanical and thermal properties of zinc powder filled high density polyethylene composites." Polymer Testing 20(4): 409-417. doi.org/10.1016/S0142-9418(00)00051-9

[7] Tavman, I. H. (1996). "Thermal and mechanical properties of aluminum powder-filled high-density polyethylene composites." Journal of Applied Polymer Science 62(12): 2161-2167. doi.org/10.1002/(SICI)1097-4628(19961219)62:12<2161::AID-APP19>3.0.CO;2-8

[8] Krupa, I. and I. Chodak (2001). "Physical properties of thermoplastic/graphite composites." European Polymer Journal 37(11): 2159-2168 doi.org/10.1016/S0014-3057(01)00115-X

[9] Hashimoto, M., et al. (2006). "Enhancement of mechanical strength of TiO2/high-density polyethylene composites for bone repair with silane-coupling treatment." Materials Research Bulletin 41(3): 515-524. doi.org/10.1016/j.materresbull.2005.09.014

[10] Hindermann-Bischoff, M. and F. Ehrburger-Dolle (2001). "Electrical conductivity of carbon black–polyethylene composites: Experimental evidence of

the change of cluster connectivity in the PTC effect." Carbon 39(3): 375-382.
[11] doi.org/10.1016/S0008-6223(00)00130-5 Gopakumar, T. G., et al. (2002). "Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites." Polymer 43(20): 5483-5491. doi.org/10.1016/S0032-3861(02)00403-2
[12] Ahmad and P. Mahanwar (2010) "Mechanical Properties of Fly Ash Filled High Density Polyethylene," Journal of Minerals and Materials Characterization and Engineering 9(3):183-198. doi: 10.4236/jmmce.2010.93016.
[13] Bengtsson, M., et al. (2005). "The effect of crosslinking on the properties of polyethylene/wood flour composites." Composites Science and Technology 65(10): 1468-1479. doi.org/10.1016/j.compscitech.2004.12.050
[14] Mohanty, S., et al. (2006). "Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites." Composites Science and Technology 66(3–4): 538-547. doi.org/10.1016/j.compscitech.2005.06.014
[15] Olumuyiwa, A., et al. (2012). "Study of Mechanical Behaviour of Coconut Shell Reinforced Polymer Matrix Composite." Journal of Minerals and Materials Characterization and Engineering11:774-779. doi: 10.4236/jmmce.2012.118065.
[16] Singh, A. A., et al. (2014). "Coconut Fiber Reinforced High Density Polyethylene Composites By Compatibilizer Process." Applied Polymer Composites 2(3):167-176.
[17] Maldas, D., et al. (1992). "Performance of Surface Modified Nutshell Flour in HDPE Composites." International Journal of Polymeric Materials and Polymeric Biomaterials 17(1-2): 1-16. doi.org/10.1080/00914039208041095
[18] George, J., et al. (1998). "Effects of environment on the properties of low-density polyethylene composites reinforced with pineapple-leaf fibre." Composites Science and Technology 58(9): 1471-1485. doi.org/10.1016/S0266-3538(97)00161-9
[19] Najafi, S. K., et al. (2006). "Mechanical properties of composites from sawdust and recycled plastics." Journal of Applied Polymer Science 100(5): 3641-3645. doi.org/10.1002/app.23159
[20] Mulinari, D. R., et al. (2009). "Sugarcane bagasse cellulose/HDPE composites obtained by extrusion." Composites Science and Technology 69(2): 214-219. doi.org/10.1016/j.compscitech.2008.10.006
[21] Gojny, F. H., et al. (2004). "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content." Composites Science and Technology 64(15): 2363-2371. doi.org/10.1016/j.compscitech.2004.04.002
[22] Yuan, J. K., et al. (2011). "High dielectric permittivity and low percolation threshold in polymer composites based on SiC-carbon nanotubes micro/nano hybrid." Applied Physics Letters 98(3): 032901. doi.org/10.1063/1.3544942
[23] Rong, M. Z., et al. (2001). "Improvement of tensile properties of nano-SiO2/PP composites in relation to percolation mechanism." Polymer 42(7): 3301-3304. doi.org/10.1016/S0032-3861(00)00741-2
[24] Bahadur, S. and C. Sunkara (2005). "Effect of transfer film structure, composition and bonding on the tribological behavior of polyphenylene sulfide filled with nano particles of TiO2, ZnO, CuO and SiC." Wear 258(9): 1411-1421. doi.org/10.1016/j.wear.2004.08.009
[25] Dahlke, B., et al. (1998). "Natural Fiber Reinforced Foams Based on Renewable Resources for Automotive Interior Applications." Journal of Cellular Plastics 34(4): 361-379. doi.org/10.1177/0021955X9803400406
[26] Carrington, M. E. and J. J. Mullahey (2006). "Effects of burning season and frequency on saw palmetto (Serenoa repens) flowering and fruiting." Forest Ecology and Management 230(1–3): 69-78. doi.org/10.1016/j.foreco.2006.04.020
[27] Ismail, H., et al. (2002). "Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent." Polymer Testing 21(2): 139-144. doi.org/10.1016/S0142-9418(01)00060-5
[28] Ismail, H., et al. (2001). "The effect of a compatibilizer on the mechanical properties and mass swell of white rice husk ash filled natural rubber/linear low density polyethylene blends." Polymer Testing 20(2): 125-133. doi.org/10.1016/S0142-9418(00)00013-1
[29] Syed, M. A., et al. (2010). "Development of environmentally friendly high-density polyethylene and turmeric spent composites: Physicomechanical, thermal, and morphological studies." Journal of Applied Polymer Science 118(2): 1204-1210. doi.org/10.1002/app.32330
[30] Li, T. Q., et al. (2001). "Impact behavior of sawdust/recycled–PP composites." Journal of Applied Polymer Science 81(6): 1420-1428. doi.org/10.1002/app.1567
[31] Nicolais, L. and M. Narkis (1971). "Stress-strain behavior of styrene-acrylonitrile/glass bead composites in the glassy region." Polymer Engineering & Science 11(3): 194-199. doi.org/10.1002/pen.760110305
[32] Joseph, P. V., et al. (1999). "Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites." Composites Science and Technology 59(11): 1625-1640. doi.org/10.1016/S0266-3538(99)00024-X