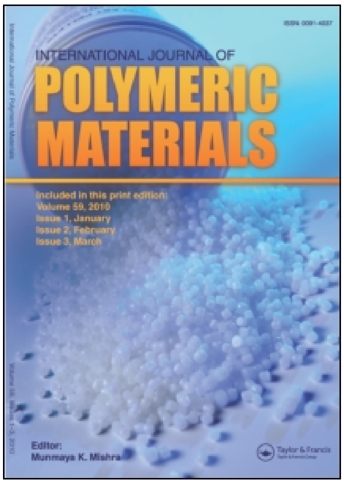

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Performance of Surface Modified Nutshell Flour in HDPE Composites†

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The nutshells of different mesh sizes, e.g. 100, 200 and 325, were modified by polymer grafting with maleic anhydride [MA] (1–3% by weight of filler), dicumyl peroxide [DPO] (1% by weight of filler) and high density polyethylene [HDPE] (5% by weight of filler). The mechanical properties of both compression molded and injection molded composites containing HDPE and modified or unmodified nutshell have been investigated. The mechanical properties of modified nutshell-filled composite materials are generally higher than those of unmodified ones. Moreover, both strength and modulus of modified nutshell-filled composites improve even compared to those of unfilled polymer.

The maximum improvements in mechanical properties, except those of modulus which increases continuously with the addition of more and more fillers to the composites, occur between 20% and 30% filler content, but in a few cases they occur even at 40%. Moreover, 3% MA seems best as far as the concentration of MA is concerned and properties improve more when 200 mesh nutshells are used as a filler compared to those of mesh sizes 100 and 325. The impact strength of the composites is inferior to that of the original polymer. Experimental results as well as cost analysis indicate that surface modified nutshells are a potential reinforcing filler for thermoplastic composites.

KEY WORDS Thermoplastic composites, high density polyethylene, nutshell flour, maleic anhydride, surface modification, mechanical properties, cost analysis.

Agro-wastes and agro-forest materials, e.g. woodflour, pulpmill wood residue, bark, nutshells, bagasse, straw, corncobs, bamboo, etc., have played an important role in the plastic industry.[1–12] Moreover, compared to inorganic fillers, the organic fillers impart added benefits such as weight reduction. For instance, a window shutter of polypropylene (PP) filled with 40% calcium carbonate weighs 5.1 lb, while a shutter made of PP and filled with 20% rice hulls weighs in at 3.6 lb.[13] Similar to other organic fillers, nutshells are low-cost and they are an abundant

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waste product.[4,14] Moreover, when they are used in a thermoplastic resin has a lower water absorption than woodflour.[4,5,7]

But demand for unmodified fillers that reduce costs but contribute little to property improvement has risen only marginally.[15] Due to the wide difference in polarity, cellulosic materials do not easily disperse in non-polar thermoplastics, e.g. polyethylene. When they are modified by grafting with a compatible and hydrophobic polymer, using a coupling agent, e.g. isocyanate or maleic anhydride or phthalic anhydride, prior to being mixed with the plastics, the affinity of the filler particles for the base polymer can be greatly increased.[16–23] As a result, filler particles can combine well with the composites and cohesion of all the components can thus be enhanced. The impact of such grafting treatments using a compatible polymer, e.g. polyethylene and a coupling agent, e.g. maleic anhydride, as the modification components on the mechanical properties of nutshell flour-filled polyethylene composites, have been investigated.

MATERIALS

Thermoplastic

High density polyethylene (HRSN 8907) was supplied by Novacor Co., Calgary, Alberta, Canada.

Fillers

Blends of peanut hull and pecan shell flour of mesh sizes 100, 200 and 325 were supplied by Southeastern Reduction Co., Valdosta, Georgia, U.S.A. The physical properties of the filler as manufactured by the above-mentioned company are listed in Table I. The fillers were oven-dried by circulating air at 55°C for 5–7 days.

Monomer and peroxide

Maleic anhydride and dicumyl peroxide were supplied by Anachemia, Montreal, Canada.

EXPERIMENTAL PROCEDURE

Surface modification

Fillers were surface modified with HDPE (5% by weight of filler), maleic anhydride (1%, 2% and 3% by weight of filler) and dicumyl peroxide (1% by weight of filler) with the help of a Laboratory Roll Mill (C. W. Brabender, Model No. 065) at 170°C for 5 min. The surface modified fillers were passed through a screen of mesh size 20 by a Granu Grinder, C. W. Brabender Instruments, Inc.

TABLE I

Physical properties of fillers as manufactured

Mesh Size:	100	200	325
Composition:			
Peanut hull flour[a]	90%	90%	—
Pecan shell flour[b]	10%	10%	100%
Property:			
Appearance	Gold-tan	Gold-tan	Light-tan
Moisture content	6–7%	4–5%	4–6%
pH in neutral H_2O	5.4	5.4	5.0
Ash content	2.4%	2.4%	2.0%
Particle size analysis:			
% retained on US 80 mesh	7.7	2.1	0.0
% retained on US 100 mesh	1.9	0.6	0.0
% retained on US 200 mesh	19.0	11.9	3.0
% retained on 325 mesh	13.5	14.4	17.0
% through 325 mesh	57.9	70.5	80.0
Microbiological content in fillers:			
Total aerobic plate count (no/g)	3,600,000	3,780,000	15,000
Yeast and mold (no/g)	70,000	60,000	2,000
Total coliform (MPN/g)	46,000	15,000	9
E. coli (MPN/g)	3[c]	3[c]	3[c]
Total aflatoxins (microgram/kg)	5[c]	5[c]	5[c]

[a] Ground product of torn/sheared fibers from the peanut hulls.
[b] Pecan shell particles are low aspect ratio angular particulates.
[c] None found, if present less than.

Compounding

Usually, 50 grams of polymer and unmodified/modified filler (10%, 20%, 30% and 40% by weight of composites) were mixed with a roll mill at 170°C. After mixing 5–10 times, the resulting mixtures were ground once again to mesh size 20.

Compression molding

The compounded mixtures were molded into shoulder-shaped test specimens (ASTM D 638, Type V). The resulting mixture was molded in a laboratory size single opening hydraulic press. Standard molding conditions were: initial pressure 2.7 MPa for 15 min at room temperature; temperature, 155°C; pressure during heating and cooling, 4.34 MPa; heating time, 5 min; cooling time, 10 min.

Injection molding

The mixtures werc injection molded with a Minishot-2 injection molding machine (Model AE130). Standard molding conditions were: pressure 0.68 MPa; mold temperature, 140°C; injection temperature, 210°C.

Width and thickness of each specimen were measured with a micrometer.

Mechanical tests

The mechanical properties (e.g. tensile strength, elongation and tensile energy at maximum point, as well as the secant modulus (at 0.1% strain) of all the samples were measured with an Instron Tester (Model 4201) following ASTM D 638. The mechanical properties were automatically calculated by a HP-86B computer. The strain rate was 10 mm/min. The impact strength (Izod, unnotched) was tested with an Impact Tester (Model TMI, No. 43-01) supplied by Testing Machine Inc., U.S.A. The samples were tested after conditioning at 23 ± 0.5°C and 50% relative humidity (RH) for at least 18 h in a controlled atmosphere. Mechanical properties were reported after taking the statistical average of the measurements of at least five specimens for compression molded samples and at least three specimens for injection molded samples. The coefficients of variation, 2.5–8.5%, were taken into account for each set of tests to obtain a reliable average and standard deviation.

RESULTS AND DISCUSSION

Tables IIA and IIB show the variation in mechanical properties, e.g. tensile strength, modulus, elongation and energy, on the concentration of both unmodified and modified nutshells in compression molded HDPE composites. The effect of particle size, e.g. mesh sizes 100, 200 and 325, on the performance of the composites is also presented in the same Tables IIA and IIB. It is evident from Table IIA that modulus increased, while tensile strength declined for unmodified nutshell-filled composites as substitution rate of filler increases beyond 10%. This can be explained by the poor adhesion between unmodified nutshell and the polymer.[21] The tensile strength of short fiber reinforced composites is strongly dependent on the degree of adhesion between fibers and matrix, while modulus is more strongly affected by the orientation of the fiber and less by the polymer-fiber adhesion.[24] The improved tensile strength at the 10% level (unmodified 100, 200 and 325 mesh) is partially attributed to the particle shape (fibrous characteristic) that is beneficial for reinforcement.

Table IIA also reveals that the tensile strength of modified nutshell-filled composites is superior to that of unmodified ones. Generally, strength increases, whereas modulus remains more or less unaltered, with the rise in concentration of MA. Furthermore, strength for composites containing 2% or 3% of MA is superior in most cases, even to that of the original polymer. But modulus for coated nutshell-filled composites is always superior to the virgin polymer. According to Table IIA, the maximum improvements in mechanical properties, except those of modulus which increases continuously with the addition of more and more fibers to the composites, occur between 20% and 30% filler content, but in a few cases they occur even at 40%. Moreover, 3% MA seems best as far as the concentration of MA is concerned, and properties improve more when 200 mesh nutshells are used as a filler compared to those of mesh sizes 100 and 325.

Table IIB shows that elongation of the composites decreases compared with the virgin polymer and it continues to decrease with the increase of filler content in the composites. Once again, the elongation of the composites containing 200 mesh

TABLE IIA

Mechanical properties of compression molded composites comprising HDPE and surface modified[a] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Tensile Strength (MPa)				Secant Modulus (MPa)			
Fiber wt.%:		10	20	30	40	10	20	30	40
100	0	22.9	18.6	15.7	13.2	972	1073	1134	1201
100	1	22.6	22.8	23.1	22.3	1224	1289	1328	1446
100	2	23.0	24.0	25.5	27.1	1115	1259	1346	1576
100	3	23.7	23.9	25.2	25.5	1148	1266	1399	1514
200	0	22.2	20.1	17.4	13.6	1051	1116	1187	1295
200	1	24.6	25.2	26.6	26.2	1239	1317	1396	1571
200	2	26.5	26.0	27.0	26.9	1201	1301	1400	1494
200	3	25.8	28.1	29.5	26.0	1099	1341	1429	1559
325	0	21.6	18.7	16.0	13.7	1029	1118	1183	1236
325	1	24.6	24.2	22.4	21.5	1320	1368	1374	1576
325	2	23.1	23.1	25.8	26.6	1219	1265	1431	1646
325	3	25.4	25.2	26.5	27.3	1353	1385	1472	1611

[a] Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

Properties of HDPE : strength, 20.9 MPa and modulus, 695 MPa.

filler is higher compared with the other mesh sizes, e.g. 100 and 325. The energy of the composites (see Table IIB) follows a more or less similar trend to that of elongation. Generally, as tensile strength increases in value, a given product increases in stiffness; this usually occurs at the expense of elongation properties. But unlike elongation, the energy of the composite materials containing 10 wt. % of 200 mesh fiber with 2% MA, as well as up to 30 wt. % of same mesh size and with 3% MA, is comparable to that of the virgin polymer.

The improvement percentages of the composite materials compared to those of the virgin polymers were calculated and listed in Table IIC. This table clearly indicates that the properties of the modified nutshell-filled composites are generally superior to the virgin polymer, with some exceptions (e.g. elongation and energy); other properties increase even compared to unmodified nutshell-filled composites. The great improvement in tensile strength and modulus (e.g. up to +41% strength and +127% modulus) in the modified formulations demonstrates the success of the present objective.

TABLE IIB

Mechanical properties of compression molded composites comprising HDPE and surface modified[a] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Elongation (%)				Tensile Energy (mJ)			
Fiber Wt.%:		10	20	30	40	10	20	30	40
100	0	7.2	5.5	2.8	1.7	96.0	60.0	25.0	15.0
100	1	6.6	4.6	4.5	4.1	82.6	58.9	52.7	51.5
100	2	6.9	5.8	5.7	5.3	84.5	79.0	76.2	70.9
100	3	6.6	5.9	5.2	4.2	78.7	73.1	73.1	57.9
200	0	6.6	5.3	3.1	1.5	82.0	61.0	30.0	11.0
200	1	6.9	5.9	5.5	3.7	98.5	82.4	82.8	52.1
200	2	7.7	6.4	6.0	4.6	120.4	94.4	92.6	72.3
200	3	7.4	7.0	6.7	6.3	108.3	115.0	109.6	93.3
325	0	7.1	5.6	3.1	1.7	92.0	64.0	29.0	14.0
325	1	6.5	5.0	3.8	3.3	79.8	55.2	50.9	40.4
325	2	6.6	6.0	6.0	4.8	88.0	91.9	87.5	69.8
325	3	6.6	6.4	6.3	6.0	85.6	86.6	90.6	78.6

[a]Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

Properties of HDPE : elongation, 10.1 % and energy, 126.4 mJ.

The influence of the same modification compositions, e.g. HDPE (5 wt. % of filler) + DCP (1 wt. % of filler) + MA (1–3 wt. % of filler), on the mechanical properties of injection molded HDPE composites were investigated and illustrated in Tables IIIA and IIIB. It appears from the experimental results that, in general, although numerical values differ, the mechanical properties follow more or less similar trends as discussed earlier for compression molded composites. Because of the high viscosity and pseudoplastic character of the high filled blends, the injection had to be relatively rapid (with high injection pressure) in order to ensure good mold filling.[25] Unfortunately, since the maximum operating pressure of our injection machine was very low (e.g. 0.68 MPa), difficulties with mold filling and release already appeared at 20 weight % of filler, and problems with discoloration arose

TABLE IIC

Comparison of the property improvement[a] of compression molded composites comprising HDPE and surface modified[b] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Fiber (Wt.%)	Improvement Percentage			
			Tensile Strength	Elongation	Tensile Energy	Secant Modulus
100	0	10	+ 9.6	-28.7	-24.1	+ 39.9
100	1	30	+10.5	-55.2	-53.4	+ 91.0
100	2	40	+29.8	-47.9	-43.9	+126.8
100	3	30	+20.3	-48.5	-42.2	+101.3
200	0	10	+ 6.2	-34.7	-35.2	+ 51.2
200	1	30	+27.3	-45.8	-34.5	+100.8
200	2	30	+29.3	-40.9	-26.7	+101.4
200	3	30	+41.1	-33.6	-13.3	+105.6
325	0	10	+ 3.4	-29.7	-77.1	+ 48.1
325	1	20	+15.9	-50.9	-56.3	+ 96.8
325	2	30	+23.4	-40.8	-30.8	+105.9
325	3	30	+26.7	-38.1	-28.3	+111.8

[a]Based on the original polymer.

[b]Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

as well. Thus, the practical limit for filler loading was 20% by weight. In addition, elongation values for injection molded samples were significantly higher than the compression molded ones. On the other hand, other mechanical properties of injection molded composites seem inferior when compared to the performance of compression molded ones. In the presence of peroxide, free-radical centers may be generated in PE and as a result, cross-linking of PE may take place. The differences in mechanical property values for two different molding processes may therefore be due to differences in cross-linking of PE associated by different processing conditions.

Table IV shows the Izod impact strength of the composite materials as percentage of the impact strength value of unfilled polymer. This table reveals that the impact strength of both compression and injection molded composites is inferior to that of the unfilled polymer and impact strength decreases with the increase of filler content and particle size of filler. Improved stiffness in the composites results in a

TABLE IIIA

Mechanical properties of injection molded composites comprising HDPE and surface modified[a] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Tensile Strength (MPa)		Elongation (%)		Tensile Energy (mJ)		Secant Modulus (MPa)	
Fiber Wt.%:		10	20	10	20	10	20	10	20
100	0	20.4	18.1	17.8	15.4	2.1	1.6	614	646
100	1	19.7	20.0	18.6	18.6	2.1	2.1	420	420
100	2	22.0	22.6	19.6	17.4	2.5	2.2	643	647
100	3	21.9	22.7	19.3	18.6	2.4	2.4	666	530
200	0	20.1	19.3	18.5	14.4	2.2	1.5	608	643
200	1	21.2	22.5	19.2	18.3	2.4	2.4	714	665
200	2	22.0	22.4	19.6	17.8	2.5	2.3	408	355
200	3	21.9	22.3	19.8	20.3	2.5	2.7	688	739
325	0	19.3	17.5	21.1	17.3	2.4	1.9	612	653
325	1	19.6	19.9	18.7	16.0	2.1	1.8	472	529
325	2	20.6	20.5	17.4	16.4	2.0	1.9	652	556
325	3	20.5	21.0	19.6	20.6	2.3	2.5	521	462

[a]Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

Properties of HDPE : strength, 19.8 MPa; elongation, 21.7 %; energy, 2.5 mJ and modulus, 472 MPa.

decrease in impact strength compared to the original unfilled polymer. For compression molded composites 10% of 100 mesh size nutshell with 3% MA seems best, while 10% of 200 mesh size with 3% MA ranked best as far as injection molded composites are concerned.

The general improvements in the mechanical properties due to the addition of MA to the composites indicate that the compatibility between hydrophilic cellulosic materials and hydrophobic polymer has increased, and MA acts as a coupling agent. The function of the MA can be explained in the following way. When polyethylene is used as the thermoplastic material, cellulose (nutshell) as a material containing —OH groups and MA as the coupling agent in the presence of an initiator, e.g. dicumyl peroxide, the polyethylene and cellulose are linked together by means of the MA forming a block copolymer containing a succinic half ester bridge between

TABLE IIIB

Comparison of the property improvement[a] of injection molded composites comprising HDPE and surface modified[b] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Fiber (Wt.%)	Improvement Percentage			
			Tensile Strength	Elongation	Tensile Energy	Secant Modulus
100	0	10	+ 3.3	-18.0	-16.0	+30.1
100	1	20	+ 1.0	-14.3	-16.0	-11.1
100	2	20	+14.1	-19.8	-12.0	+37.1
100	3	20	+14.7	-14.3	- 4.0	+12.3
200	0	10	+ 1.5	-33.6	-12.0	+28.8
200	1	20	+13.6	-15.7	- 4.0	+40.9
200	2	20	+13.1	-18.0	- 8.0	-24.8
200	3	20	+12.6	- 6.5	+ 8.0	+56.6
325	0	10	+ 2.5	- 2.8	- 4.0	+29.7
325	1	20	+ 0.5	-26.3	-16.0	+12.1
325	2	20	+ 3.5	-24.4	-20.0	+17.8
325	3	20	+ 6.1	- 5.1	- 8.0	- 2.1

[a]Based on the original polymer.

[b]Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

cellulose and polyethylene segments.[23] The polyethylene becomes, in this manner, a side chain of the cellulose. The reactions which occur may be represented in Figure 1. Moreover, the —OH group of cellulose also has the ability of forming hydrogen bonds with the —COOH group of the MA segment. In this way, MA develops an overlapping interface area between cellulose and polymer matrices. Moreover, prior grafting of the nutshell with polymer and MA contributes to the formation of a soft film of hydrophobic materials on the surface of the hydrophilic material. As a result, the phase separation between the two different matrices might be reduced. In addition, strong fiber-fiber interaction due to intermolecular hydrogen bonding has also been diluted, which leads to better dispersion of the nutshell particles. Mechanical properties improve independently of the concentra-

TABLE IV

Comparison of the impact strength of compression and injection molded composites comprising HDPE and surface modified[a] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Percentage of Unfilled Polymer Value					
		Compression Molded				Injection Molded	
Fiber Wt.%:		10	20	30	40	10	20
100	0	54.8	45.6	40.6	27.4	18.9	13.9
100	1	43.7	44.6	41.2	26.4	21.0	14.4
100	2	43.5	40.2	40.4	33.3	23.2	23.6
100	3	57.7	50.9	42.1	32.9	30.5	26.9
200	0	49.0	44.0	38.9	25.5	18.9	12.9
200	1	33.7	32.1	26.2	24.7	25.8	30.9
200	2	48.1	38.1	37.3	34.2	40.5	25.8
200	3	50.6	42.9	40.6	33.9	33.0	29.2
325	0	41.5	37.5	33.1	23.2	20.9	15.3
325	1	41.5	24.1	16.3	15.9	29.3	19.1
325	2	38.1	30.8	29.1	26.4	29.8	22.5
325	3	41.0	36.8	34.3	31.8	28.4	27.8

[a]Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

Un-notched Izod impact strength of HDPE : compression molded, 47.8 J/m and injection molded, 410.3 J/m.

tion of MA because with the rise in concentration of MA in the composite, the possibility of formation of interfacial area increases.

It is a well-established fact that fiber length is a critical parameter in the evaluation of the properties of the composites.[21,26] In the present study, composites having mesh size 200 provided the best performance compared to those of the other two mesh sizes (e.g. 100 and 325).

The orientation of the fibers in the matrix plays an important influence on the ultimate properties of composite materials. The orientation of the fiber can be controlled by the selection of suitable molding techniques.[27-29] Accordingly, fibers are partially oriented in injection molded composites, while they are rather randomly oriented in compression molded composites. As a result, the injection molded

REACTIONS:

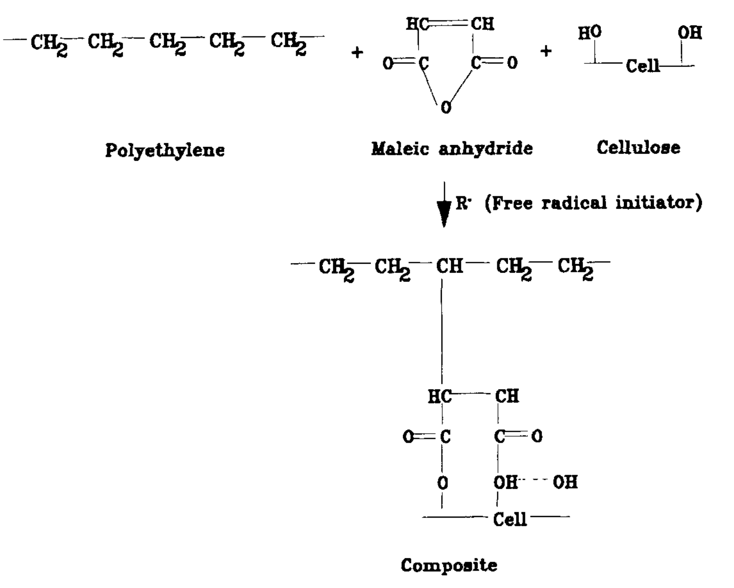

FIGURE 1 Chemical reactions of polyethylene—maleic anhydride-cellulose.

composites should provide better performance compared to those of compression molded ones. The experimental results indicate that the mechanical property values for elongation and impact strength were higher for the injection molded composites; however, the compression molded composites had slightly higher values for tensile strength and modulus. As we mentioned earlier that PE may be cross-linked due the radicals generated in the presence of peroxide, degree of cross-linking depends on the degree of radicals generated during different processing conditions. Higher tensile strength and modulus indicates greater cross-linking of PE, while higher elongation and impact strength indicates less cross-linking of PE. Moreover, this can also be explained by minor damage of the organic fibers due to higher injection temperature (e.g. 210°C) and by the higher shear forces of injection molding. In fact, the components of cellulose are supposed to remain stable[30,31] up to 180°C. Therefore, it is recommended that molding temperature for cellulosic composites be less than 200°C. This would easily be possible with commercial size injection molding equipment having sufficient pressure to inject composite materials at lower temperatures. Pressure was a limiting factor (e.g. 0.68 MPa) on the laboratory equipment in this study.

The density of the surface modified nutshell-filled composites is presented in Table V. The density of the composites increases slightly with the increase in the concentrations of fiber and MA. Moreover, the density of the composites containing more than 10 wt. % of coated nutshell is higher than that of the original polymer. Generally, when cellulosic materials are coated with hydrophobic polymer prior

TABLE V

Density of compression molded composites comprising HDPE and surface modified[a] nutshell flour

Fiber (Mesh Size)	MA (Wt.%)	Density (g/cc)			
	Fiber Wt.%:	10	20	30	40
100	0	0.92	0.95	1.00	1.05
200	0	0.93	0.97	1.02	1.04
325	0	0.95	0.97	1.03	1.04
100	3	0.94	0.95	1.00	1.05
200	1	0.95	0.97	1.02	1.04
200	2	0.95	0.97	1.02	1.05
200	3	0.95	0.98	1.02	1.05
325	3	0.96	1.00	1.03	1.06

[a] Fibers were coated with maleic anhydride [MA] (1%-3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).

Density of HDPE : 0.96 g/cc (literature value) and
0.87 g/cc (experimental value).

to being mixed with the plastics, the coating penetrates into the pores of the filler particles and increases the density of the filler particles.[16,17]

The estimated cost of surface modified nutshell fibers and their composites appears in Table VI. The cost analysis has taken into account the delivered cost of filler, bonding agents, and the additional compounding cost to incorporate the filler into the polymer. Compounding cost is estimated at US $100 per ton and is based on literature from Werner and Pfleiderer Corporation[32] using one of the more expensive compounding systems (twin-screw extruder). Table VI demonstrates that at filler substitution rates of 30% and 40%, there is obvious economic incentive for use. The actual break-even substitution rates are 27 for 3% maleic anhydride coated 200 mesh filler. However, it is noted that all optimum formulations have improved tensile properties over unfilled polymer. It could be possible to reduce costs further if less composite plastic was required to achieve equivalent product performance characteristics.

Three other possibilities exist to reduce costs: i) the use of lower costing peroxides than the dicumyl peroxide; ii) the use of optimum but minimum percentage of peroxide, particularly less than 1%; and iii) the use of manufacturing technique

TABLE VI

Estimated cost of surface modified nutshell flour and HDPE—modified nutshell flour composites

Coating Composition (% by Weight of Fiber)			Price[a] (US $)/ton				
MA	DCP	HDPE	Coated-Fiber	Composites (Fiber Wt.%) 10	20	30	40
Mesh size 200:							
1	1	5	449.6	901.0	861.9	822.9	783.8
2	1	5	459.8	902.0	864.0	825.9	787.9
3	1	5	469.9	903.0	866.0	829.0	792.0
Mesh size 325:							
1	1	5	435.6	899.6	859.1	818.7	778.3
2	1	5	446.0	900.6	861.2	821.8	782.4
3	1	5	456.3	901.6	863.3	824.9	786.5

[a] Including processing cost as 100 US $/ton.

Cost of raw materials: HDPE, 840 US $/ton; nutshells mesh 200, 323 US $/ton; nutshell mesh 325, 308 US $/ton; maleic anhydride (MA), 1340 US $/ton and dicumyl peroxide (DCP), 9380 US $/ton.

called "masterbatching." The last possibility would involve compounding at higher filler substitution rates (+50%) and reblending this "masterbatch" with unfilled polymer to achieve the desired substitution rate.

Table VII presents a list of commercial polymers on the market in 1990 with similar mechanical properties to the optimum composite formulations listed in the same table. It is noted that the vast majority of the commercial polymers are injection moldable grades. Most of the uses for these polymers are in the target utilization for disposable items entering the municipal solid waste stream. Some of the commercial polymers have higher elongation % values than the compression molded composites. It is also noted that elongation is highly related to the original unfilled polymer characteristics and to the molding process. In fact, the injection molded test specimens showed higher elongation % values than the compression molded ones (see Table IIB and IIIA).

TABLE VII

List of commercial polymers with similar properties to the optimum composite formulation

Commercial/ Composite Name	Molding Method	Tensile Strength (MPa)	Secant Modulus (MPa)	Elongation (%)	Uses
Commercial polymer:					
Bapolene 2082	Injection	28.3	NL[1]	NL[1]	caps/thin walled uses
Sclair 2908/ Sclair 2909	Injection	31.1	NL[1]	10	housewares, bottle bases toys[2]
Dow 30060M	Injection	28.3	NL[1]	NL[1]	housewares, containers[2]
Marlex EMN TR-885	Injection	31.1	NL[1]	10	thin containers
Petrothene LB 832	Blow/Extru.	26.2	876	25	housewares, bottles[2]
Petrothene LB 861	Injection	27.6	897	25	housewares, toys[2]
Petrothene LB 742	Blow	26.2	925	25	pharmaceutical/ cosmetic containers[2]
Petrothene Ls 630	Injection	31.1	1001	25	five gallon pails
F-20TC-0360	Injection	25.5	1035	15	housewares, pharmaceutical/ cosmetic containers[2]
HDPE-nutshell (NS) composites with various substitution rate (SR):					
HDPE-NS 200 (SR-10%)[3]	Compression	26.5	1201	7.7	
HDPE-NS 200 (SR-20%)[4]	Compression	28.1	1341	7.0	
HDPE-NS 200 (SR-20%)[4]	Compression	29.5	1429	6.7	
HDPE-NS 325 (SR-20%)[4]	Compression	27.3	1611	6.0	
HDPE-virgin	Compression	20.9	695	10.1	

[1] Not listed in the International Plastics Selector.
[2] Information obtained by phone contact with supplier.
[3] Fibers were coated with maleic anhydride [MA] (2% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber).
[4] Fibers were coated with maleic anhydride [MA] (3% by weight of fiber), dicumyl peroxide (1% by weight of fiber) and HDPE (5% by weight of fiber)

CONCLUSION

The findings of this study indicate that mechanical properties, particularly tensile strength and modulus of the surface modified nutshell filled composites are generally superior to those of unmodified polymer. Mechanical properties increase even compared to unmodified nutshell-filled composites. Moreover, the mechanical property values for elongation and impact strength are higher for the injection molded composites; however, the compression molded composites had slightly higher values for tensile strength and modulus. Experimental results as well as cost analysis demonstrates that at filler substitution rates of 30% and 40%, there is obvious economic incentive for use. The actual break-even substitution rates are 27 for 3% maleic anhydride coated 200 mesh filler.

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