Filler Surface Treatment with Hydrophobic Esters

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ABSTRACT

The use of fillers in polyolefin polymer composites has escalated in recent years in conjunction with the need for improved physical properties and the increased costs of petroleum-based polymers. Fillers, used as inert extenders and reinforcing agents, present problems when added to organic polymers that are different in chemical nature and physical form. Use of surface-treatment additives has been developed to overcome problems that originate in the interfacial region where the organic resin phase must wet out the inorganic filler being compounded. Achieving optimal physical and chemical properties in a filled compound, by the use of hydrophobic esters derived from castor oil as wetting and encapsulating agents, was evaluated. The hydrophobic esters improved the dispersion and distribution of filler particles throughout the organic medium. The surface treatment with the esters resulted in a lowering of viscosity and better ability to control the rheology of the compound, raise the extender filler loadings and an upgrading of mechanical properties of the filled resin. It was shown that the use of hydrophobic esters as a surface filler treatment resulted in increased tensile strength, higher impact strength and improved processing of filled polymer composites.

INTRODUCTION

It is often stated that we now live in the age of plastic composites. If one defines composites as compounded polymers, then it can be concluded that the plastics age has always been an age of composites. Few plastics would have their wide application usage without the use of additives. When components of differing chemical nature and physical forms are combined, new technology must evolve to achieve optimal properties required for specific applications.

Advances in filler and reinforcement technology in filled polymer composites are widely distributed across performance level parameters. This paper confines itself to the surface treatment of fillers which are generally classified as inert extenders or reinforcing agents that reduce the volume of resin and can reduce cost while improving specific physical properties. The addition of fillers normally enhances physical properties such as flexural strength, flexural modulus, heat deflection temperature and overall stiffness and resistance of the composite to greater loads and at higher use temperature. Negative aspects of filler addition are loss of impact strength and development of plastic composites which are more difficult to process. The market for filler and extender pigments is predicted to rise to $1.2 billion in 1987, up 60% from the $750 million in 1982 (1).

Consumption of calcium carbonate extender in plastics was 1,362,000 metric tons in 1982 and estimated to reach 1,525,000 metric tons in 1983 (2). Surface modifiers and treatments that function as processing aids or coupling agents are entering a period of reintensified development. New products for filler surface treatment that increase the extender loading and decrease the final cost of the resin composite have met several obstacles. For mineral-filled thermoplastic composites, the high cost of the surface modifiers, their exotic chemistry and handling complexities act as deterrents to their use.

DISCUSSION

Surfaces of most fillers are hydrophilic in nature and it is difficult to achieve a strong interfacial bond between the continuous polymer phase and the discontinuous filler reinforcement phase. Achieving optimal properties in a filled polymeric compound, when components of differing chemical and physical form are present, requires a stable, homogenous dispersion of filler in the resin. The wet-out of the filler is critical to the problems which originate in the interfacial region where the organic resin must spread over the inorganic filler and allow the filled particles to be distributed through the organic resin phase. To overcome the difficulties in achieving a bond between dissimilar phases, a variety of surface-treatment additives have been promoted and utilized on a commercial basis. Silanes and organotitanates are effective coupling agents for improved properties and aging of plastic composites (3-6). Silane coupling agents such as vinyl trichloro, vinyl triethoxy and gamma-aminopropyl triethoxy silanes are effective with glass fiber-reinforced composites. Methyl acrylochromium complexes and allyl trichlorosilane resorcinol have also been used with a variety of fillers and reinforcements (7). Mica that has been surface-treated with sulfonilazido silane has increased flexural and tensile properties in thermoplastics. Two component organosilicon surface treatments of 50% mica-filled high density polyethylene and polypropylene show significant improvements in mechanical properties such as flexural strength, tensile strength at break and notched Izod impact strength (8). Chlorinated paraffins have been used with mica-filled polypropylene (9). Stearic acid-treated calcium carbonate and amine-treated calcined clay have been commercialized (10).

Calcium carbonate is the most widely applied nonfibrous extender pigment or filler for plastics and is used in commercial polyvinylchloride, polypropylene, polyethylene, phenolics, epoxies, polyester, polyurethanes and ethylene propylene diene monomer (EPDM) compounds, as well as experimental impact styrene and nylon compounds. New commercial grades of surface-treated calcium carbonate are being marketed in increasing quantities (11). It is estimated that over 50 million lb of stearic acid-coated calcium carbonate was sold in 1982. Polymeric hydrophobic wetting and dispersing agents have been used to displace water from the filler surface and optimize filler wet-out by the resin (12).

Although there are numerous filler surface treatments that function at the interface of a polymer-filler system, many are expensive and the equipment and procedures involved in treating the fillers requires high energy input. The use of a hydrophobic wetting agent that would encapsulate fillers and produce a low-cost, highly filled thermoplastic composite was evaluated.

Castor oil and castor oil esters are noted for their ability to carry high concentrations of dyes and pigments used in cosmetics, plastics and rubber applications. The derivatives serve as hydrophobic wetting agents that encapsulate fillers by displacing air and water from the surface, thereby optimizing wet-out to produce stable and homogenous dispersions. The hydroxyl group functionality also serves to control the rheology of pigmented dispersions and their unique chemistries permit surface interaction with organic polymers as well as inorganic fillers (13-15). Ability of liquid esters to lower the viscosity of a composite blend allows an increase in the extender filler loading for improved economics, along with increased and improved flow for high quality moldings. A study of several ricinoleic acid esters was undertaken to evaluate their effect on polyolefin composites with various filler loadings.

Experimental Procedures

Two ricinoleic acid esters, namely, methyl acetyl ricinoleate (MAR) and glyceryl triacetoxy stearate (GAS), were evaluated as surface-treatment additives. The esters are low viscosity liquids which can be readily incorporated with standard compounding procedures. Polymers investigated included polypropylene (PP), high density polyethylene (HDPE) and low density polyethlene (LDPE). Calcium carbonate ($CaCO_3$), was chosen as the prime filler for performance evaluation since it has been used as the nonfibrous enhancer of choice in most extended polyolefins. Studies centered on the efficiency of the surface treatment in relation to the average filler particle size and impact properties of the composite. Calcium carbonate, having an average mean particle size of 2.5 microns, was chosen as a base for extended studies. The effect of parameters such as compounding methods and processing technique were also investigated.

To examine the efficiency of the organic surface treatment in relation to filler particle size, the particle size of $CaCO_3$ was varied and incorporated at a 30% level into HDPE. Tensile impact tests performed on compression molded stocks showed a 3% surface treatment with MAR to be most effective in improving the tensile impact strength. Table I shows a sharp decrease in impact properties when $CaCO_3$ with particle size distribution greater than 2.5 microns or finer than 0.7 micron was employed.

To determine a use level of MAR surface treatment, a 2.5-micron $CaCO_3$ was pretreated in 0.5% increments ranging from 0.5 to 5% using a high speed blender. The treated $CaCO_3$ was subsequently fluxed at 30% loading in HDPE for 10 min on a two-roll mill heated to 275 F (144 C). Tensile impact tests were performed on compression molded slabs and the results are displayed graphically in Figure 1, which shows a significant improvement in tensile impact strength where a surface-treated $CaCO_3$ filler was used. The results indicate an optimum use level of 3.5% and a use range of 2.5-4.5%, based on the filler weight.

The effect of filler loading in HDPE and PP composites containing 30, 50 and 70% loading of 2.5-micron $CaCO_3$ were prepared and examined for tensile impact strength and room temperature Gardner impact strength. A similar study was performed with 10 and 20% $CaCO_3$ filled LDPE composites and examined for low temperature brittleness and impact properties. Results of the testing are shown in Tables II and III. With polypropylene, the addition of 3% MAR was more efficient at filler loading levels of 50-70% $CaCO_3$. The data in Table II show a significant improvement in both tensile and Gardner impact properties when the MAR surface treatment is applied. Polypropylene composites with 70% treated $CaCO_3$ developed ductility properties similar to a 30% loading of untreated calcium carbonate.

TABLE I

Effect of $CaCO_3$ Particle Size (30% Filled HDPE): Tensile Impact Strength $CaCO_3$ Particle Size)

Filler	Mean particle size (microns)	Tensile impact strength (ft lb/in.^{2}) Treatment: None	3% MAR[a]
None	–	123	130
A	6.0	62	67
B	2.5	64	107
C	2.5	81	114
D	0.7	61	96
E	0.06	49	64

[a] 3% Methyl acetyl ricinoleate (MAR) based on $CaCO_3$ weight.

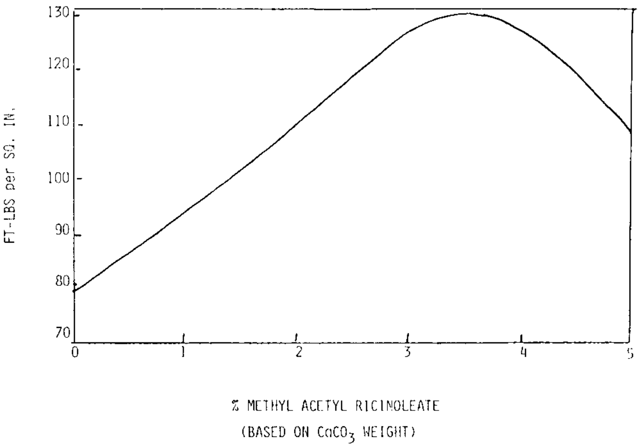

FIG. 1. Tensile impact strength vs surface treatment level HDPE/2.5μ $CaCO_3$ (70/30).

TABLE II

Effect of Filler Loading on Impact Strength of Compression Molded Composites

Filler[a] (%)	MAR[b] (%)	Tensile impact (ft lb/in.^{2})	Ductility (msec)	Gardner impact (ft lb/mil) X 10^2
		Polypropylene/$CaCO_3$)		
0	0	129	1.3	5.6
30	0	83	1.0	6.1
30	3	144	2.0	9.5
50	0	68	0.8	3.4
50	3	125	1.9	5.2
70	0	34	0.1	0.2
70	3	73	0.9	2.4
		High Density Polyethylene/$CaCO_3$		
0	0	134	1.7	10.0
30	0	81	1.2	10.0
30	3	114	1.6	10.5
50	0	54	0.4	10.5
50	3	73	1.4	8.0
70	0	17	0.1	0.3
70	3	62	0.1	1.4

Impact tests run at 75 F.

[a] 2.5-micron uncoated $CaCO_3$.

[b] Methyl acetyl ricinoleate based on weight of $CaCO_3$ percentage used.

Table II shows that the tensile impact and Gardner impact strengths improve significantly with the use of surface-treated $CaCO_3$ in HDPE. The efficiency of the organic surface treatment also improves as the filler concentration of the composite is increased. A near 4-fold increase in tensile and Gardner properties was observed in the 70% $CaCO_3$ filled HDPE composites.

The tensile impact strength data given in Table III show a substantial improvement in this property with the use of the MAR surface treatment, without effect on the low temperature brittleness at 10 or 20% $CaCO_3$ loading in LDPE.

The performance of glyceryl triacetoxy stearate (GAS) as a surface treatment for 40% mica-filled polypropylene composites was also evaluated. Three grades of mica (Suzorite) from Marietta Resources International Ltd. were coated with 2% by weight of GAS. The mica was coated using a Henschel mixer and Polypropylene Homopolymer 6523PM added to the respective coated grade of mica and mixed further for an additional 2 min. Precompounded blends were injection molded directly in a 50-ton Van Dorn injection molding machine. The blends were injected at a low temperature cycle of 370-420 F (180-213 C). The blends were easily processed and the molded specimen showed a smooth and glossy surface. No warpage or shrinkage was observed in the molded specimen. The physical properties – Gardner impact, tensile impact, notched and unnotched Izods, tensile strength and elongation – were determined by ASTM methods.

Results of the study are shown in Table IV. Improvements in physical properties of the GAS-coated mica composite over the polypropylene composite containing uncoated mica were substantially higher as tabulated by the percentage improvement.

Since filler surface-treatment additives require good thermal characteristics for high temperature processing of the composites, the thermogravimetric analysis of GAS was compared to stearic acid now in commercial use. Table V shows glyceryl triacetoxy stearate to have better thermal stability than stearic acid.

The critical requirement for incorporation of fillers in a plastic composite relates directly to a properly treated filler surface for intimate contact at the interface of the organic and inorganic phases. Direct pretreatment of the filler with the surface-treatment additive can be accomplished in high intensity mixers. The physical nature of the additives, whether solid or liquid, will govern the processing temperatures, mixing time and intensity.

Evaluations of compounding and processing techniques were made with blends of homopolymer polypropylene and various loadings of both treated and untreated $CaCO_3$. Powder blending was done in a Patterson Kelly V-Blender. Also, blends of $CaCO_3$ and resin were pelletized by extruder compounding. Injection molding of these composites was performed in a Van Dorn 50-ton, reciprocating screw injection machine equipped with a mold to produce tensile and impact specimens. Conditions for the extrusion and injection molding are listed in Table VI.

In processing the composites, it was observed that temperature conditions for surface-treated $CaCO_3$/PP are higher than for unfilled PP, but substantially lower than for untreated $CaCO_3$/PP blend. The surface treatment of the filler leads to a definite processing advantage as shown by the plotted extrusion data (Fig. 2). The output per hour versus the screw rpm shows an increase factor of ca. 1.5 for the surface-treated $CaCO_3$ over that of the unfilled polypropylene at screw speeds of 30-60 rpm.

TABLE III

Physical Properties of Compression Molded Low Density Polyethylene/$CaCO_3$ Composites

$CaCO_3$ [a] (%)	MAR[b] (%)	Low temperature Brittleness[c] (C)	Tensile impact strength (ft lb/in.^{2})
0	0	-65	366
10	0	-65	225
10	3	-65	328
20	0	-65	185
20	3	-65	282

[a] 2.5-micron $CaCO_3$.
[b] Methyl acetyl ricinoleate percentage based on $CaCO_3$ weight.
[c] ASTM D-746-73.

TABLE V

Thermogravimetric Analysis

Conditions	Glycery triacetoxy stearate	Stearic acid
	Temperature (C)	
Air atmosphere		
Thermal stability (onset of decomposition)	280	200
Decomposition (complete decomposition)	400	320
Nitrogen atmosphere		
Thermal stability (onset of decomposition)	320	210
Decomposition (complete decomposition)	480	340

TABLE IV

Physical Properties 40% Mica/60% Polypropylene Composites: Surface-Treated vs Untreated Mica

	Mica 60s		Mics 200s		Mica 325s	
Surface treatment (wt % gas of mica)	0	2	0	2	0	2
Tensile impact strength (ft lb/in.^{2})	12	22	19	31	18	34
% Improvement	–	+83	–	+63	–	+89
Notched Izod Impact (ft lb/in.)	0.85	1.15	0.78	1.04	0.70	1.04
% Improvement	–	+35	–	+33	–	+49
Unnotched Izod impact (ft lb/in.)	2.2	4.78	2.5	6.07	2.4	5.22
% Improvement	–	+117	–	+143	–	+118
Elongation (%)	3	9	5	14	4	9.5
% Improvement	–	+200	–	+180	–	+138

TABLE VI

Processing of Polypropylene/Calcium Carbonate Composites

Extrusion

Samples	Barrel temperature (C)	Pressure (psi)
Polypropylene	202-213	1000
Polypropylene/$CaCO_3$ (untreated 60/40)	219-263	725-750
Polypropylene/$CaCO_3$ (treated 60/40)	202-230	625-650

Injection molding

Samples	Barrel temperature (C)	Injection pressure (psi)
Polypropylene	213-225	11,000
Polypropylene/$CaCO_3$ (untreated 60/40)	257-329	11,000
Polypropylene/$CaCO_3$ (treated 60/40)	235-246	9,000

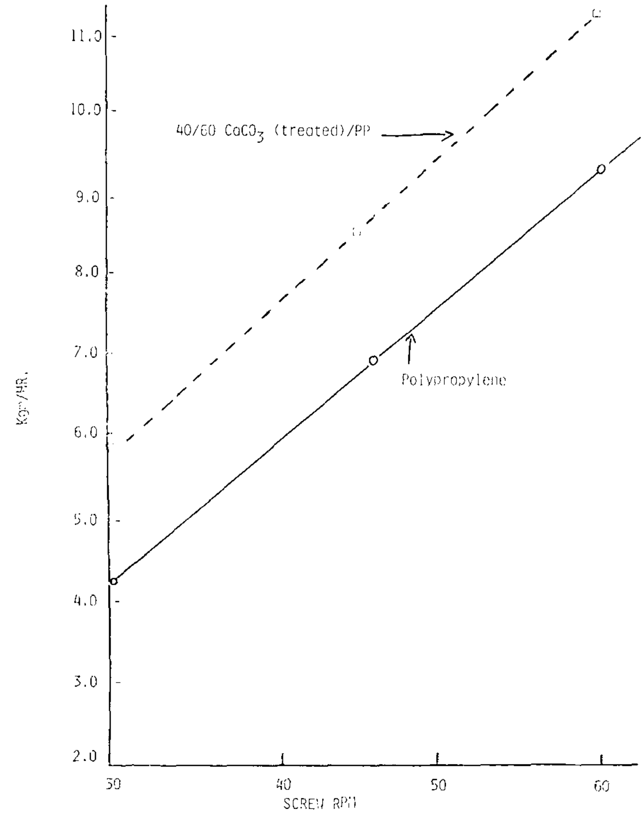

FIG. 2. Output/hr vs screw rpm.

TABLE VII

Physical Properties – Powder Blending vs Pellets Blending in Surface-Treated $CaCO_3$ in Polypropylene

Property	Unfilled polypropylene	(Surface-treated) $CaCO_3$/PP Powder blending	(Surface-treated) $CaCO_3$/PP Pellet blending
Tensile strength (psi)	4470	3550	3000
Izod impact strength (notched) ft lb/in.	0.9	0.95	1.05

TABLE VIII

Melt Flow

	Melt flow index (g/10 min)[a]	Characteristics
Polypropylene	0.78	Smooth flow
40/60 $CaCO_3$/PP (untreated)	0.73	Poor flow
40/60 $CaCO_3$/PP (treated)	3.65	Good smooth flow

[a] Condition L ASTM D-1238.

Comparison of compounding procedures shows the method to have an effect on the mechanical properties of the final composite. Table VII shows the pretreated powder blended composite containing 40% $CaCO_3$ to give a higher tensile strength than equivalent composite prepared by blending pretreated $CaCO_3$ with pellets. The powder blending offers an economic advantage over extrusion in terms of energy usage and yields better tensile properties in the composite. The surface treatment of $CaCO_3$ with 2% methyl acetyl ricinoleate improved the melt flow characteristics of 40% $CaCO_3$/60% PP composites by a factor of 4.5 over that of the unfilled polypropylene. The physical characteristics of the extruded composites show the treated 40% $CaCO_3$/60% PP to be easy flowing and smooth. The uncoated 40% $CaCO_3$/60% PP requires increased temperature to achieve the same viscosity and the extrudate is observed to be rough with poorer flow behavior. Melt flow results are shown in Table VIII.

Polypropylene composites containing 50% by weight of both untreated $CaCO_3$ and surface-treated $CaCO_3$ at various levels of methyl acetyl ricinoleate were compared. The use of surface treatment resulted in significant improvement in physical properties. The surface-treated $CaCO_3$ composite showed ca. 33% improvement in tensile strength at a low (1%) concentration of surface treatment. Table IX provides a summary comparison between the properties of treated PP composites containing 50% by weight of $CaCO_3$. The observed increase in impact strength by use of the

TABLE IX

Physical Properties – 50% $CaCO_3$ Filled PP

Polypropylene	100	50	50	50	50
$CaCO_3$ (wt %)	0	50	50	50	50
Surface treatment (wt % of $CaCO_3$)	0	0	1.0	1.5	2.0
Tensile strength (psi)	4470	3125	4030	3700	3380
Elongation (%)	120	30	30	40	80
Tensile impact strength (ft lb/in.^{2})	138	96	108	115	140
Notched Izod impact (ft lb/in.^{2})	1.27	0.90	0.90	0.99	1.06
Unnotched Izod impact (ft lb/in.^{2})	15	11	NB	NB	NB

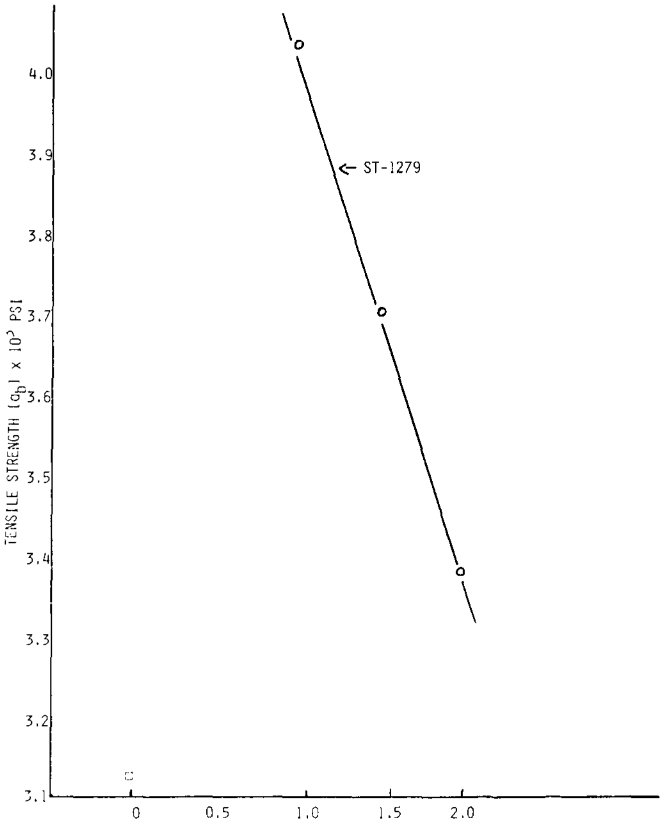

FIG. 3. Tensile strength vs surface treatment level pp/$CaCO_3$ (50/50).

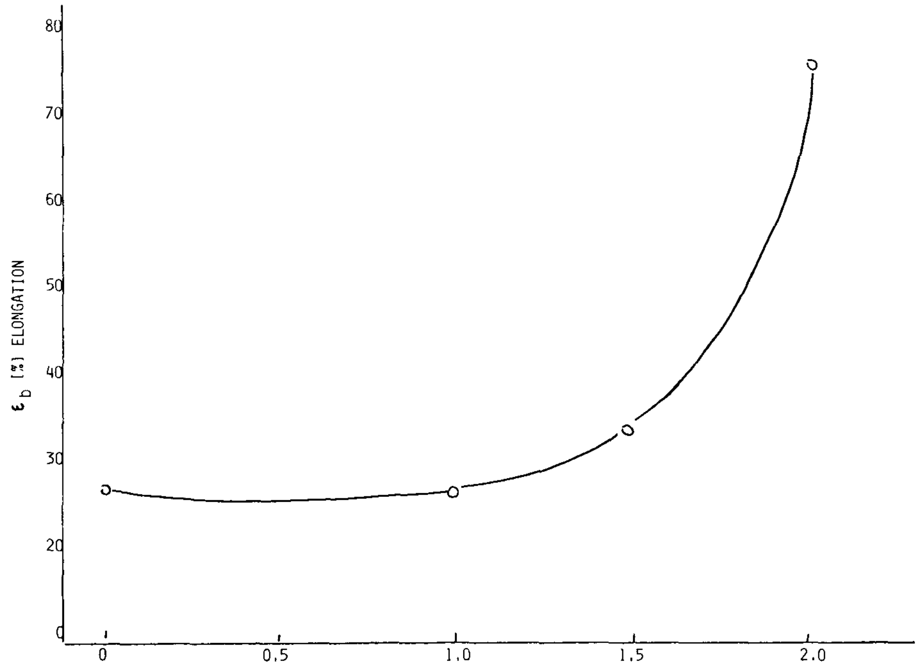

FIG. 4. Elongation (%) vs surface treatment level pp/$CaCO_3$ (50/50).

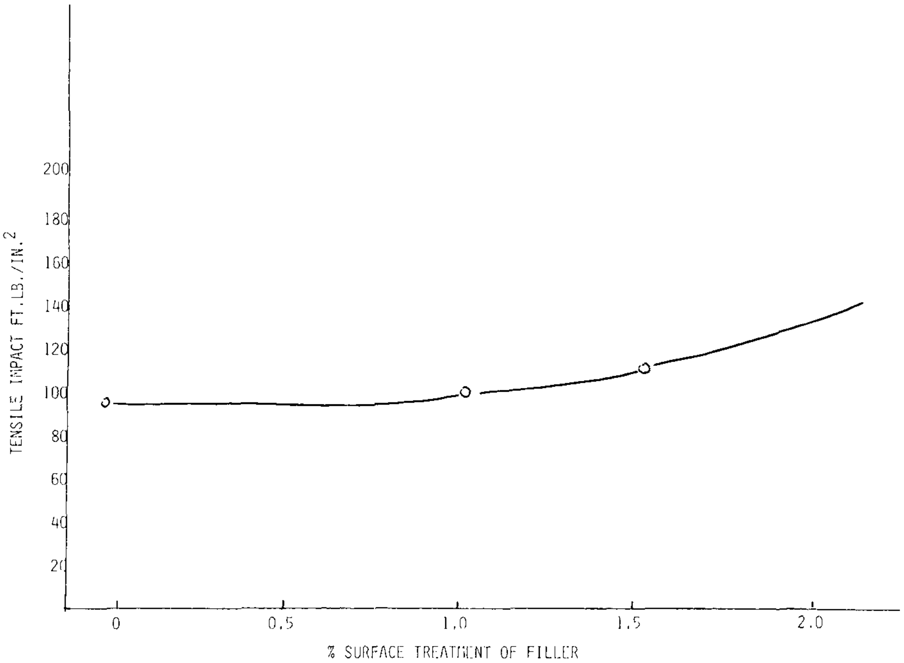

FIG. 5. Tensile impact strength pp/$CaCO_3$ (50/50).

surface treatment agent confirms the effectiveness of the treated composite to absorb higher amounts of mechanical energy than those containing untreated $CaCO_3$.

Figures 3-5 show the effect of surface treatment level on tensile strength, impact properties and elongation. At the 50% $CaCO_3$ concentration level, low concentration levels of the MAR improve the tensile strength, and the tensile impact strength of the composite was observed to increase with increasing levels of treatment.

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