Studies of the Effect of Titanate Coupling Agent on the Performance of Polypropylene–Calcium Carbonate Composite*

Y. N. SHARMA, R. D. PATEL, I. H. DHIMMAR, and I. S. BHARDWAJ,
Research Centre, Indian Petrochemicals Corporation, Ltd., Baroda-391 346, India

Synopsis

Composites of polypropylene—$CaCO_3$ coated with isopropoxy triisostearoyl titanate have been prepared on Buss Ko-Kneader. These composites have been evaluated for mechanical properties, melt index, dispersion, and adhesion of polymer to filler using the scanning electron microscope. Calcium carbonate being a platelike substance with low aspect ratio results in composites having inferior tensile properties but superior impact characteristics. Uniform dispersion of filler in the composite and long alkyl chains of the coupling agent provide additional advantages such as improved melt index, higher tensile elongation, and better optical properties.

INTRODUCTION

Mineral-filled polypropylene is a relatively low volume plastic, but there is currently more interest in using and developing fillers for use in it than any other thermoplastic, excepting polyvinyl chloride. This interest is primarily to widen its range of applications rather than to extend and cheapen it. Various kinds of thermoplastics have been compounded with fillers, and their properties and performances have been evaluated.[1–5] The major constraints in the development of highly filled polyolefin compounds have been nonuniform and poor dispersion of filler in the polymer matrix due to nonavailability of high shear continuous mixer and the coupling agents which increase the interfacial bonding energy at the polymer-filler interface. However, with the development of high shear continuous mixers a major headway has been made in this direction. The titanate type of coupling agents is gaining importance in the recent time, and lots of claims and counterclaims have been made about its efficacy. Han and coworkers[6] in their paper on the effect of titanate coupling agents on rheological and mechanical properties of filled polyolefins have shown about 100% improvements in impact properties of the PP/$CaCO_3$ system whereas the elongation of the composite arpoaches the unfilled PP homopolymer. In our study on the dispersion of titanate-coated and uncoated $CaCO_3$ in PP and evaluation of the mechanical properties of the composite, the maximum improvement in impact strength has been 20%, whereas tensile elongation is slightly less than the virgin PP.

Limestone-filled polypropylene has been virtually termed as a new engineering plastic with properties approaching to that of ABS and other high cost materials.[7,8] This approach to high cost plastics is mainly due to its unchanged ex-

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cellent chemical and environmental resistance, low water absorption, good electrical properties, and high service temperature above 100°C.

In this study we report our observations on the effect of the coupling agent on the dispersion of filler in the polymer matrix, the interfacial bonding energy using the scanning electron microscope, and the ultimate mechanical properties of the composite.

EXPERIMENTAL

Materials

Polypropylene-Koylene grade M5630 (IPCL, India) and commercial grade calcium carbonate (ground) of average particle size 5 μ have been used in this study. Isopropoxy triisostearoyl titanate (TTS) was imported from M/s. Kenrich Petrochemical, Inc., Bayonne, NJ.

Methods

The optimum amount of the coupling agent required is determined by plotting the fall in viscosity of a hydrocarbon oil–calcium carbonate mixture with increasing concentration of TTS as described by M/s. Kenrich Petrochemicals, Inc. Calcium carbonate was coated by the titanate dissolved in toluene (1:1) in a high speed mixer (Henschel type), and then was dry blended with polypropylene powder already stabilized with additives. This dry mixture was then melt blended in a Buss Ko-Kneader (Model No. PR-46). The single strand coming out of the extruder was quenched in cold water and pelletized.

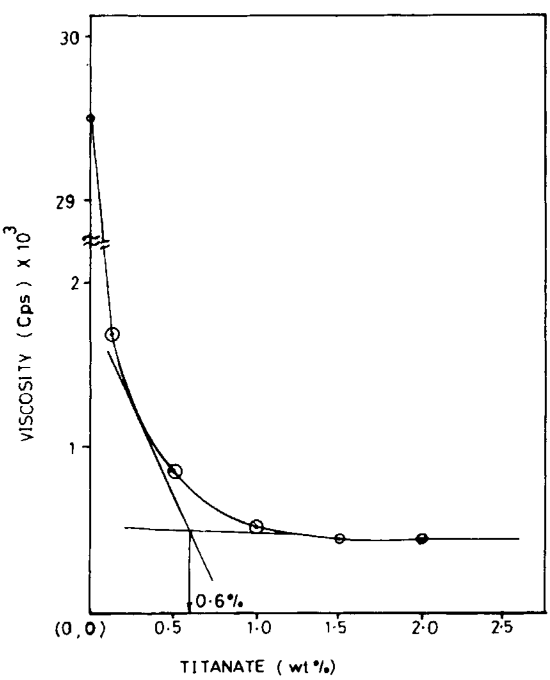


Fig. 1. Effect of TTS on viscosity of the composite.

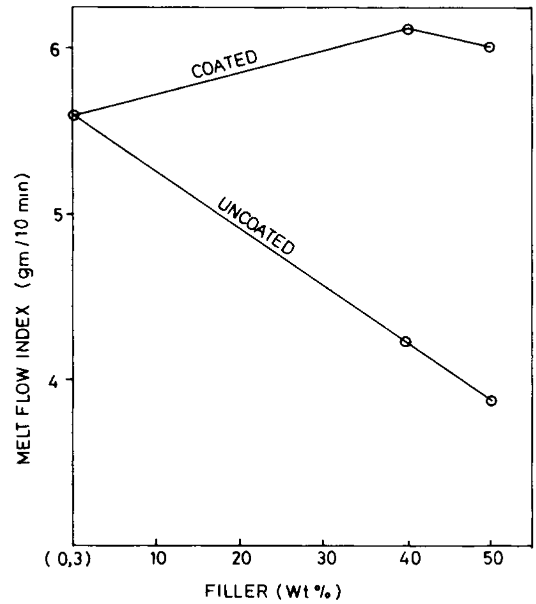


Fig. 2. Effect of TTS on MFI of PP/$CaCO_3$ composite.

Test specimens of the composite were made by either compression or injection moulding according to ASTM procedures, and were then subjected to various tests.

The effect of the coupling agent on the adhesion of filler and polymer phase and the dispersion of filler were investigated with the help of Scanning Electron Microscope, JSM-35C of M/s. JEOL, Japan. The fractured samples were sputter-coated with gold prior to observation in SEM.

RESULTS AND DISCUSSION

Determination of Optimum Amount of TTS for Coating

The efficiency of TTS coupling agent in improving the rheological and mechanical properties of the composite has been a subject of many publications.[4–6] There has been a wide variety of opinion about the properties improvement. In order to arrive at optimum concentration of this coating material for $CaCO_3$, Kenrich method of viscosity reduction of a hydrocarbon oil/$CaCO_3$ mixture was employed. The results are graphically represented in Figure 1. Although a concentration of 0.6% w/w of TTS was arrived by this method, higher concentrations up to 1.0% w/w were also investigated. However, it was observed that higher amount of TTS does not give any additional benefit to the characteristics of the composite.

Melt Flow Index

The addition of inorganic inert materials generally gives rise to the reduction of MFI of the composite because of the basic incompatibility of the two materials. Coating of the inorganic phase with compounds having easily hydrolyzable groups

TABLE I
Properties of Polypropylene and Its Composites

Serial no.	Property/sample	MFI	Tensile yield strength	Elongation at break	Brittle point	Izod impact strength notched	
	ASTM test method	D-1238	D-638	D-638	D-746	D-256	
	Unit	g/10 min	kg/cm^2	%	°C	kg·cm/cm	
1	Polypropylene (M-5630)	5.61	347	22	32	4.3	
2	PP + $CaCO_3$ (50:50)	3.87	193	14	−7	4.0	
3	PP + $CaCO_3$ + 0.6% TTS (50:50)	6.00	167	43	0	5.0	
4	PP + $CaCO_3$ + 0.6% TTS (60:40)	6.11	209	50	22.5	5.2	compression moulded
5	PP + $CaCO_3$ + 1% TTS (60:40)	7.20	231	30	21.5	5.2	
1	Polypropylene (M-5630)		366	99		5.1	
2	PP + $CaCO_3$ (50:50)		214	49		4.1	
3	PP + $CaCO_3$ + 0.6% TTS (50:50)		201	65		4.6	
4	PP + $CaCO_3$ + 0.6% TTS (60:40)		237	69		4.8	injection moulded
5	PP + $CaCO_3$ + 1% TTS (60:40)		243	61		5.3	

and long alkyl chains lead to the formation of bonds between the surface hydroxyl of inorganic molecule and easily hydrolyzable bonds of the coupling agent, whereas the long alkyl chains provide hydrophobicity of the mixture. This hydrophobicity has been estimated by the Filler Desorption Test devised by Rossen and Goddard.[9] Uncoated $CaCO_3$ immediately sinks to the bottom as it is spread on a still water layer whereas the coated filler floats on the surface

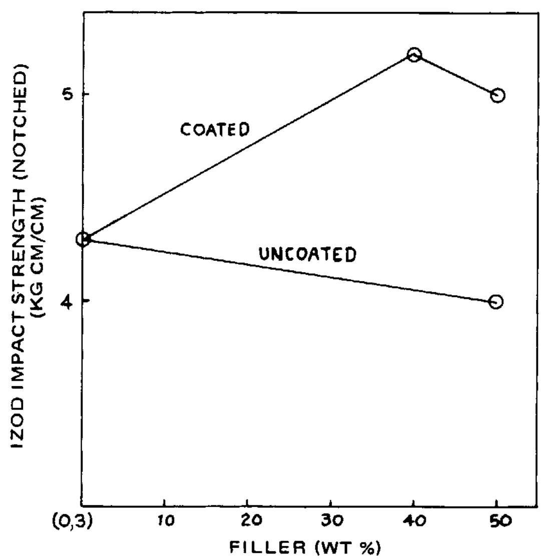


Fig. 3. Improvements in impact strength by the use of TTS coupling agent.

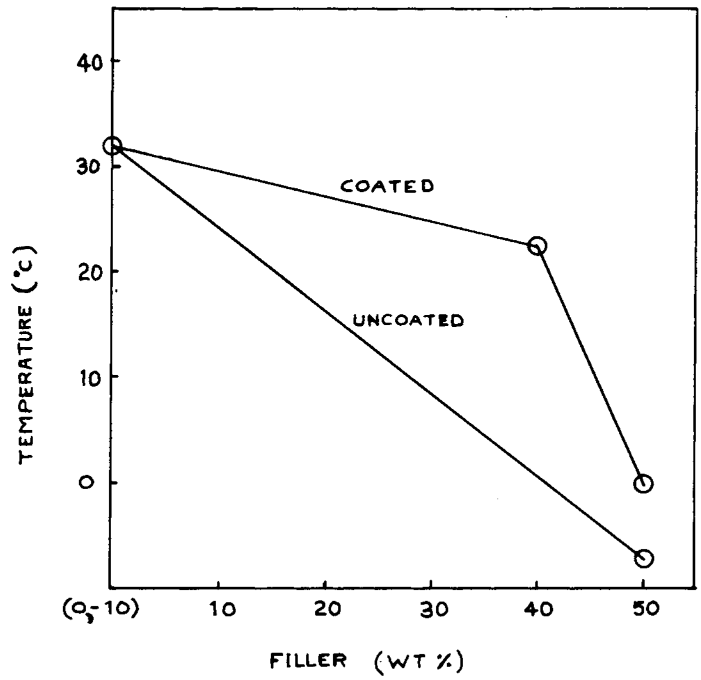
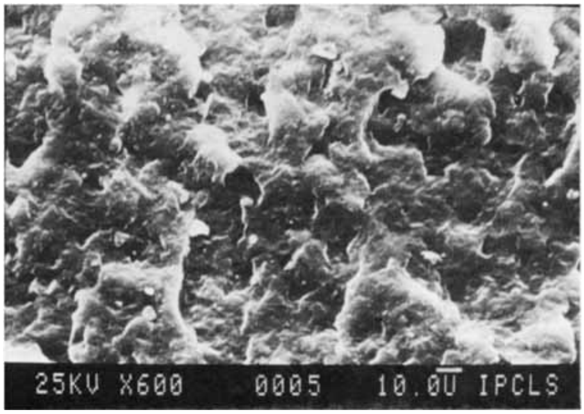


Fig. 4. Improvements in low temperature brittle point by use of fillers.

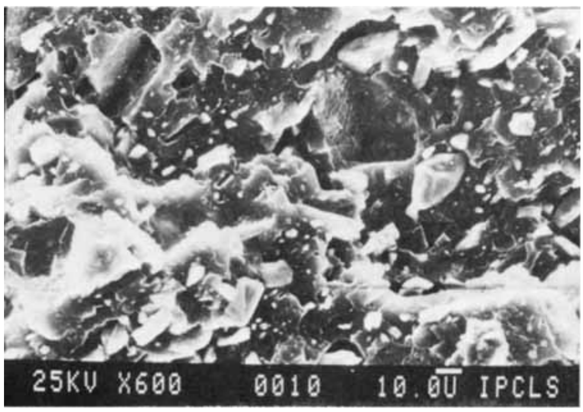
and the solution remains clear for weeks together. This suggests that the hydrophobicity can be a result of titanoxy bonds formed by the coupling agent. This helps in increasing the compatibility between the two phases, thereby affecting the flow properties only marginally. The long alkyl chains of the coupling agent also serve as lubricant and increase the MFI of the composite as depicted in Figure 2. Table I shows the MFI behavior with increasing filler content of the composite.

Mechanical Properties

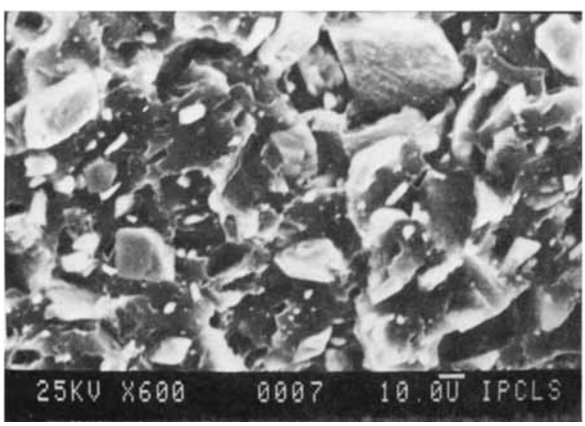
The effect of filler concentration on the mechanical properties of the composite is given in Table I. As is the general case, tensile strength falls with increasing loading of the filler in the composite. There is no improvement in tensile properties of the composite with or without addition of the coupling agents. However, the plasticizing effect of the alkyl chians of coupling agents help in improving ultimate elongation at the break of the composite. Since there is no interaction between the two phases of the matrix without coupling agent, it behaves just like a brittle material. As explained earlier, the coupling agent increases the interfacial bonding energy of the composite, and thus there is an improvement in the ultimate elongation of the composite by the use of the coupling agent.



(a)



(b)



(c)

Fig. 5. Scanning electron micrographs of fractured composite surfaces: (a) PP; (b) PP/uncoated $CaCO_3$ blend (50:50); (c) PP/coated $CaCO_3$ blend (50:50).

Impact Strength

A considerable improvement in the notched izod impact strength of the composite has been observed by the use of the coupling agent, graphically shown in Figure 3. Polypropylene is known to be a notch-sensitive material, and Izod impact strength results give only a relative value in terms of improvement. This improvement is again related to the plasticizing effect of the coupling agent and increase in the interfacial bonding force at the polymer/filler interface.

Low Temperature Brittleness

Low temperature properties of the composite are superior to the unfilled polypropylene as given in Figure 4. Since the low temperature characteristics of plastics are associated with the onset of crystallization, the addition of fillers lower this temperature. Hence, the composites prepared have much lower temperature brittleness as compared to virgin polypropylene.

Fracture Studies

Dispersion of filler and the adhesion between polymer and filler were studied with the help of the scanning electron microscopy of the fractured composite. Samples containing 50% of $CaCO_3$, with and without coupling agent, were used in this study. Our findings as shown in Figure 5 are very similar to those reported by $Mg(OH)_2$/PP composite.[10,11] This is mainly because of the similar nature of $Mg(OH)_2$ and $CaCO_3$ crystals; both these compounds have a low aspect ratio and are platelike in structure. It is well known that an increase in aspect ratio leads to improvement in tensile strength,[12] but notched impact strength is reduced. The composite made in our laboratory is poor in tensile properties whereas impact characteristics are superior, and this can be easily explained due to the low aspect ratio of the limestone filler.

In the fractured sample of virgin PP the spherulitelike texture has disappeared during fracture phenomenon as shown in Figure 5(a). The fracture is considered to be nearly circular voids of uniform diameter.

Figure 5(b) shows poor dispersion of $CaCO_3$ in the polymer matrix in the case of uncoated PP/$CaCO_3$ blend. This can be ascribed to small crystallite size and agglomeration of the filler particles.[13] The blend appears to be nonuniform with random fracture and uneven voids. The platey $CaCO_3$ is deshaped due to agglomeration, and very small polymer residue is adhering to the filler surface.

Figure 5(c) of the coated PP/$CaCO_3$ blend indicated better dispersion of the filler showing large crystallite size and low degree of agglomeration. The blend appears to be uniform with oriented fracture and rectangular-type voids. There is a uniform adhesion to the filler surface.

The major difference between uncoated and coated systems is the preservation of spherulitelike texture in uncoated system. In the uncoated system, there are some broken spherulitelike textures observed, which are completely absent in coated system.

Therefore, surface coating the TTS enhances the compatibility with PP but does not afford a chemical bonding between the filler and matrix. Orientation in the TTS-coated system is very good, which also indicates the increase in impact strength. The polarity is created because of the chemical interaction between filler and coupling agent which is effective for improvement of the mechanical and rheological properties of the composites.

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