Influence of Mechanical Properties in Carbon Black (CB) Filled Isotactic Polypropylene (iPP) and Propylene–Ethylene Block Copolymer

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SYNOPSIS

The mechanical properties of isotactic polypropylene (iPP) and propylene–ethylene block copolymer (Co-PP) with carbon black (CB) were added as a filler. By mixing appropriate amounts of the two components through melt-blending in a twin-screw extruder, the blended pellets were prepared to a series of test specimens by injection molding. A scanning electron microscopic study was performed of the morphologies of the impact fractured surfaces. The blending of CB in Co-PP not only improves the impact strength, but also improves the flexural modulus and tensile strength; however, the heat distortion temperature (HDT) of the Co-PP/CB blends decreased with greater filler content. Furthermore, the filler of CB improves the tensile yield strength only at low filler content in iPP/CB blends, and the heat distortion temperature (HDT) and flexural modulus of the iPP/CB blends increased with greater filler content. The impact behavior is not good for the iPP/CB blends. Overall, Co-PP/CB has better interaction of molecules than iPP/CB.

INTRODUCTION

Plastic is traditionally used as an electric and thermal insulation material which features ease of shaping, light weight, resistance to corrosion, etc. The modification from the blend of polymer with filler has already been widely practiced and become the current focus of materials development. The use of carbon black (CB) as a filler in thermoplastic polymers is not limited to use as a pigment but is also used to prolong the life of plastics when used outdoors. This is due to the features which can be found in modified materials, such as improved mechanical properties, thermal conductivity, and ultraviolet light absorption as generally seen in composite materials with CB filler.[1-9] The filling of CB in polyethylene resin has been extensively investigated in the following areas[1-6]: blends of polyethylene resin with various kinds of carbon black whose physical and chemical properties (such as particle size, degree of aggregation, chemical characteristics of the surface, content, etc.) affect the properties of polyethylene composite;[1] blends of polyethylene resin with electrically conductive CB to investigate the electrical[1,2] and the dielectric properties of the composite;[3,4] linear low density polyethylene resin filled with CB to study the electrical noise characteristics of the composite[5]; T-V characteristics of crystalline polyethylene resin filled with CB filler[6]; and others such as dynamical mechanical behavior of polymer containing CB by R. Salovery and K. Gandhi[7] and interaction between polypropylene and CB by Zoran S. Petrovic et al.[8]

The matrices used in this paper are propylene–ethylene block copolymer and isotatic polypropylene. The polypropylene is picked here due to its low price and easy machining, the CB was used as filler due to its stability, reinforcing effects as pigment in polypropylene, properties obtained from modification and finally absorption of ultraviolet light by carbon-filled composites.[9] In addition, since the properties of CB–polypropylene composite which go through melt-blending in a twin-screw extruder and then through injection molding were rarely studied,

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we will focus on the development of respective mechanical properties here.

EXPERIMENT

Materials

The matrices used here are isotatic polypropylene (iPP) by Yuan Chia Chemical Industries Co., with PP-1080, melt flow index: MFI = 8.0 g/min; and propylene-ethylene block copolymer (Co-PP) by Aristech Chemical Co., with TI-4070-GPP-3080 and MFI = 7.6 g/min. The filler used is CB by Cabot Co. with carbon black Vulcan-P whose major properties are nitrogen surface area absorption of 143 m^2/g; particle size of 20 nm; volatile content of 1.5%; pH = 9.5; and density = 0.337 g/cm^3.

Preparations

The polypropylene was first put into a vacuum oven with temperature set at 80°C for two days to remove the moisture. The CB filler was melt-blended with polypropylene resin, in various loadings, using a twin-screw extruder Model: Wending Engineers HT-0.8. The temperature settings for the extruding screws for each stage of the extrusion were 230°C, 240°C, 240°C and 230°C respectively, while the extruding screws rotated at a speed of 120 rpm. Once polypropylene resin and CB of various loadings were melt-blended in the twin-screw extruder, and then cut into chips, the blended pellets were then dried in a vacuum oven with temperature set at 80°C for two days, and finally prepared into test specimens by injection molding using Toshiba IS-55 EPN. The temperature settings for the extruding screws for each stage of injection molding were 220°C, 230°C, 240°C, and 230°C, respectively; the injection pressure, 1000 psi; and die temperature 60°C. Both iPP and Co-PP went through the same extrusion processes to give them a history identical to the blends.

Methods

The tensile strength testing was conducted using Hung Ta-8503 following ASTM-D638-Type I method with drawing speed: 10 mm/min and span length 25 mm. The flexural modulus was determined according to ASTM D790, method II, procedure B (4-point loading at $\frac{1}{4}$ points) on a universal testing machine (HUNG TA 8503) at 65 R.H. at room temperature; the cross-head speed, span length, and full scale load were 1.8 mm/min, 25 mm, and 40 kg, respectively. The Izod impact testing was conducted using Amityville TMI No. 43-1 following ASTM D-250 method. A temperature chamber adapted to an Izod impact testing machine (Amityville TMI No. 43-1) was used to provide a constant chamber temperature. The chamber was equipped with a resistance coil (heat), a liquid nitrogen coolant, an internal fan, and a digital multithermometer. The sample was held in the chamber at the testing temperature for more than 30 min before it was tested. The impact fractured surface was photographed using a scanning electron microscope: Cambridge S : 360. The impact fractured surface was first coated with gold using ION SPUTTER at 10 mÅ for 4 min and then photographed using 55 Polaroid to investigate its morphology. The dynamic mechanical testing was conducted using a rheometrics dynamic spectrometer: RDS by Rheometrics, INC. Model RDS II. The size of the specimen is 50 mm × 11 mm × 2 mm, testing frequency is 6.28 rad/sec, testing strain is 0.1%, and rate of heating is 3°C/min from −70°C up to 200°C. The heat distortion temperature (HDT) test was conducted using Ceast 6510 following ASTM D 648 with maximum stress 455 KPa and rate of heating 2°C/min.

RESULT AND DISCUSSION

Notched Izod Impact Strength

The Izod impact testing was conducted following ASTM D-256 method. Literature suggests a decrease in impact strength with an increase in CB concentration.[8,10] It is found that the increase in CB content generally leads to a decrease in impact strength. Figure 1 shows notched Izod impact strength of polypropylene and Co-PP vs. CB content. It is observed that the notched Izod impact strength of iPP with CB does not improve, but decreases. However, it is found that when CB content in Co-PP is less than 30 phr, the notched Izod impact strength of Co-PP increases dramatically. Such an increase is approximately three times that of the increase of notched Izod impact strength, which goes up from 12 Kg-cm/cm of the pure Co-PP to 45 Kg-cm/cm when the CB content is 30 phr. The study of the section fractured by impact testing for Co-PP/CB (30 phr) and iPP/CB (30 phr) as also shown in Figure 2, the CB remains an aggregate structure, in which cracks propagate through the interface between CB particles and CB particle/polymer particles. Such CB aggregate structures provide adhesive forces and cohesive forces[8] between polypro-

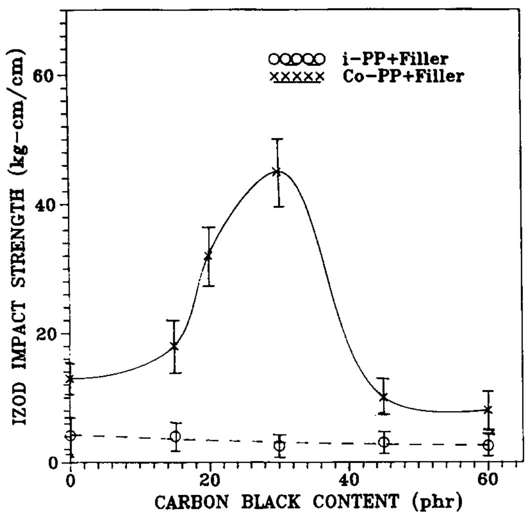


Figure 1 Izod impact strength as a function of filler loading in reinforced polypropylene ($\frac{1}{8}$ in thick, notched specimen) at room temperature.

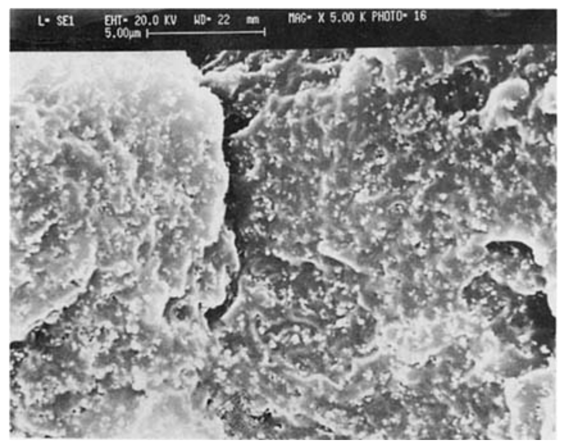
pylene and CB to prevent tearing propagation.[11] This feature is beneficial to improved impact behavior and other mechanical properties; however, the interaction between PP and CB particles must also be taken into consideration. On the other hand, the notched Izod impact strength at low temperature of polypropylene composite with CB was, however, not good. For instance, the impact strength of Co-PP/CB (30 phr) at −30°C was merely 1.3 Kg-cm/cm, therefore, it is concluded that the adding of CB can not efficiently improve the impact strength of carbon filled polypropylene at lower temperatures.

Other Mechanical Properties

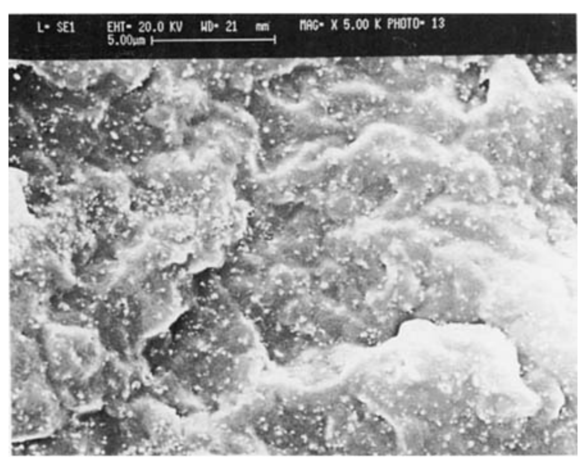
In Figure 4 is shown the change of tensile yield strength of polypropylene with respect to CB content. The tensile yield strength of CB filled propylene-ethylene block copolymer: Co-PP slightly increases with greater CB content. The tensile yield strength of CB filled isotatic polypropylene only at CB content 15 phr is slightly greater than the that of pure isotatic polypropylene; however, as CB content goes above 30 phr, iPP/CB has lower tensile yield strength than pure iPP.

In Figure 3 is shown the changes of the flexural strength and flexural modulus with respect to CB content. For both Co-PP or iPP, their flexural strength and flexural modulus increased with greater CB content. Such behavior in flexural strength and flexural modulus is similar to that of resin filled with inorganic matter.[12-14] Compare the relation between notched Izod impact strength and CB content to that of flexural modulus and CB content, which were shown in Figure 1 and Figure 5. When the CB content of Co-PP is lower than 30 phr, not only does the flexural modulus increase with greater CB content, but also the notched Izod impact strength increase is even more noticeable. In other words, the filling of CB in Co-PP improves not only the rigidity but the toughness as well. While in CB filled iPP, only the flexural modulus increases with greater CB content, the notched Izod impact strength decreases. That is to say, though the rigidity of CB filled iPP improves, the toughness is reduced.

In Figure 5 the relation between heat distortion temperature (HDT) and CB content is manifested. The HDT of CB filled iPP is higher than that of pure iPP; however, the HDT of CB filled Co-PP is lower than that of pure Co-PP, according to L. E.



(A)



(B)

Figure 2 Scanning electron micrograph of Izod impact fractured surfaces of (a) Co-PP/CB composite (30 phr) (b) iPP/CB composite (30 phr).

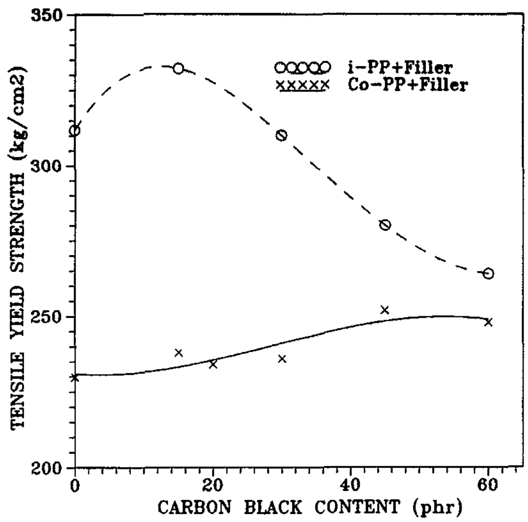


Figure 3 Comparison of the tensile yield strength of iPP, Co-PP/carbon black blends of different filler concentration at room temperature.

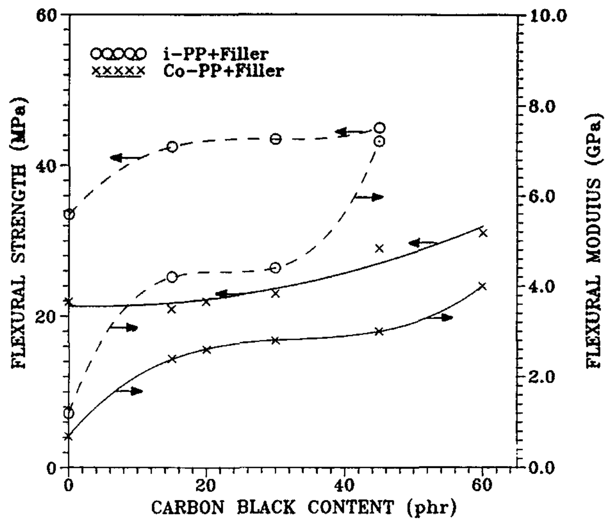


Figure 4 Comparison of the flexural strength and flexural modulus of iPP, Co-PP/CB blends of different filler concentration at room temperature.

Nielsen's prediction about the behavior of flexural modulus with filler.[15] It is said that such behavior is the same as that of HDT with filler. The increase of HDT is due to change in flexural modulus. In other words, the increase of flexural modulus leads to an increase of HDT. However, in Figure 4, it is seen that even though the flexural modulus of CB filled Co-PP increases with greater CB content (as shown in Fig. 5), its HDT, however, markedly decreases, which is contradictory to L. E. Nielsen's prediction. However, the behavior of HDT in the composite material as a result of the blend of CB and iPP conforms to L. E. Nielsen's. The flexural modulus increases with greater CB content, and likewise for the HDT.

Dynamic Mechanical Testing

The dynamic mechanical testing is conducted using rheometrics dynamic spectrometer: RDS, the results of the dynamic mechanical analyses are summarized in Table I. Figure 6 demonstrates changes of loss factors of CB filled Co-PP with respect to CB content and temperatures, it is observed clearly in this figure that there exist two secondary loss peaks in pure Co-PP. The first secondary loss peak occurs at 7°C which is also the first glass transition temperature, T_g1, and the second secondary loss peak at −53°C, which likewise becomes the second glass transition temperature, T_g2. It is found using transmission electron microscopy (TEM) that, in addition to the particles of polypropylene and polyethylene, there are still particles of polyethylene-polypropylene elastomer: EPR in pure Co-PP.[16] Therefore the first secondary loss peak occurs at 7°C due to the particles of polypropylene, and the second one occurs at −53°C due to particles of EPR. It is also found clearly in Figure 6 that there also exist two glass transition temperatures in Co-PP/CB. The first one is still 7°C, but the second one changes to −48°C. This proves that the interaction of molecules of CB with EPR plays a major role in Co-PP/CB. It can also be paraphrased that the particles of EPR existing in Co-PP enable efficient association of molecules necessary for the blend of CB and Co-PP.

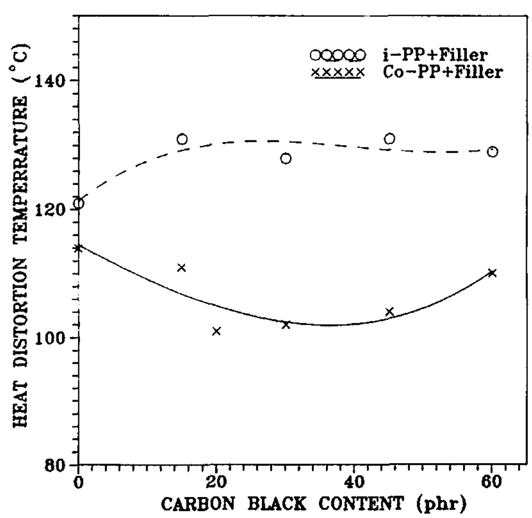


Figure 5 Comparison of the heat distortion temperature (HDT) of polypropylene/carbon black blends of different filler concentration.

Table I The Dynamical Properties of Polypropylene/Carbon Black Composites

Specimens	T_g1 (°C)[a]	tan δ[a]	T_g2 (°C)[b]	tan δ[b]
iPP	7	0.063	—	—
Co-PP/Carbon Black				
100/0	7	0.069	−53	0.037
100/15	7	0.071	−48	0.040
100/30	7	0.076	−48	0.041
100/45	7	0.062	−48	0.042
100/60	7	0.063	−48	0.034

[a] T_g2 is the glass transition temperature of the EPR (Co-PP).
[b] T_g1 is the glass transition temperature of Co-PP or i-PP.

Furthermore, from Figure 7 which it is also shows the change of loss factor of iPP/CB with respect to CB content and temperature, for pure isotatic polypropylene, there is only one occurrence of secondary loss peak at 7°C, i.e., one glass transition temperature at 7°C. The same thing also happens to iPP/CB. As shown in this figure, there is only one secondary loss peak at 7°C so the glass transition temperature remains at 7°C without being affected by change of CB content. Overall, the interaction of molecules in the blend of CB and Co-PP is better than that of the blend of carbon filled isotatic polypropylene. Perhaps, the interaction between Co-PP and CB leads Co-PP/CB to have greater impact strength and tensile yield strength than iPP/CB.

CONCLUSION

The mechanical properties of polypropylene matrix, isotatic polypropylene (iPP), and propylene-ethylene block copolymer (Co-PP) to which CB were added by mixing the appropriate amount of the two components through melt-blending in a twin-screw extruder. The blended pellets were prepared to a series of test specimens by injection molding and investigated. Overall, Co-PP/CB has better interaction of molecules than iPP/CB. The major conclusions are as follows:

1). For Co-PP/CB composite with CB content below 30 phr, not only its notched Izod impact strength increases markedly, but its flexural modulus

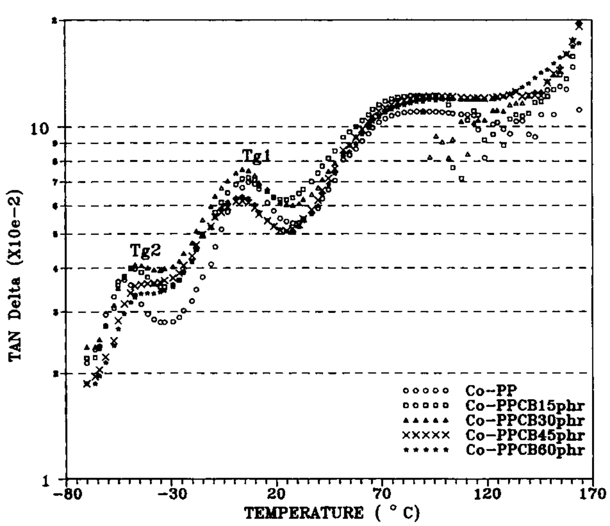


Figure 6 Dynamic mechanical curves of Co-PP/carbon black composites. Change of tan δ with temperature and concentration of carbon black.

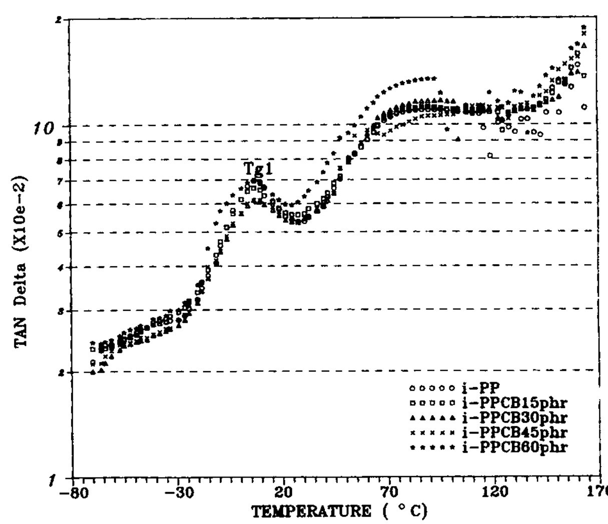


Figure 7 Dynamic mechanical curves of iPP/carbon black composites. Change of tan δ with temperature and concentration of carbon black.

also increases with greater CB content. That is to say, the filling of CB in Co-PP improves not only its rigidity but also its toughness. However, its HDT decreases slightly with greater CB content. The tensile yield strength also increases likewise.

2). For iPP/CB its flexural modulus increases with increasing CB content and likewise for heat distortion temperature (HDT). When CB content is lower than 15 phr, its tensile yield strength is greater than that of pure iPP. Whereas if the CB content is above 30 phr, the tensile yield strength is smaller than that of pure iPP. However, the blend of iPP and CB does not improve the notched Izod impact strength.

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