

Toughening and Reinforcing of Polypropylene

Z. WANG

Polymer Department, Beijing Research Institute of Chemical Industry, Beijing 100013, People's Republic of China

SYNOPSIS

To improve the mechanical properties of polypropylene (PP), some elastomers and fillers are used. The impact properties and tensile strength are affected by both the mineral additives and the polymer additives. There are also some changes in the thermal properties. To improve the interfacial adhesion, some low molecular polymers are added to assist the dispersion of the fillers and the uniformity of the various polymers with PP. The addition of low-density polyethylene (LDPE), high-density polyethylene (HDPE), or the styrene-butylene-styrene block copolymer (SBS) can improve the impact properties of PP. The propylene-ethylene copolymer has a more pronounced effect than does the physical blending of PP with PE. Calcium carbonate can reinforce PP resin. The ethylene-vinyl acetate copolymer (EVA) has an effect on the printing properties of the PP. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) has been widely used in the form of molded articles, films, or sheets, since it is excellent in molding processibility, water resistance, gasoline resistance, and chemical resistance. It has low specific or gravity density and it is inexpensive.¹ It generally has good mechanical properties. However, as its low-temperature impact property is very poor, some elastomers and other polymers have to be added into it for special applications. Different polymers have different effects on the toughening efficiency. For example, the ethylene-propylene-diene terpolymer (EPDM) can significantly increase the impact property of PP while modification with the butadiene-diene-styrene terpolymer (BDS) has only a modest effect.² The blends of PP/*trans*-polyoctenamer elastomer (TOR) were found to have a higher notched impact strength than that of unmodified PP.³

In blending PP with other polymers, the compatibility is an important factor. Some low molecular polymers can provide good compatibility for different polymers. The most favored situation is that the

propylene has some chemical relation with the monomers of other polymers. Although PP can be toughened by polyethylene (PE), the properties of the PP copolymer are better than those of the physical blended PP-PE mixture. The reason is that the copolymer achieved a chain-chain link. It is easy to obtain a material with excellent properties by subtracting the PP homopolymer with the PP copolymer.

The application of the PP can also be widened by the addition of various fillers. The commonly used fillers include talc, calcium carbonate, titanate oxide, magnesium hydroxide, and glass beads. The incorporation of inorganic fillers can reinforce PP materials. Mutual miscibility and adhesion of the fillers with the PP matrix are the crucial factors influencing the structure and properties of the filled PP. Any modification changing these relationships will lead to significant microstructural changes and, thus, to changes of mechanical properties.⁴ Surface treatment of the filler can improve the filler/PP interaction. There are usually three groups of treating agents: (1) fatty acids, both saturated and unsaturated, and their derivatives; (2) surface active compounds, like cation active, anion active, and nonionic active agents; and (3) coupling agents, especially the titanate coupling agents.

Table I Composition of the PP Mixture

No.	PP	LDPE	EVA	SBS	LMPP	LMPE
1	100					
2	100	20				
3	100	20	6.4		2.5	
4	100	20	6.4	3.6	2.5	
5	100	20	6.4	3.6		2.5

Much work has been done on the calcium carbonate-PP system.⁵⁻¹⁰

In this article, we discussed the effect of the PP composite with fillers and elastomers. There exists a balance between the modulus and the toughness. In toughening the PP, it seems that the styrene-butylene-styrene block copolymer (SBS) has a greater effect than does the ethylene-vinyl acetate copolymer (EVA). Also, the calcium carbonate treated with the titanate coupling agent can effectively improve the modulus of the PP resin.

EXPERIMENTAL

Materials

The PP used has a melt index of 5 g/10 min, and the PE copolymer, a melt index of 3 g/10 min. The calcium carbonate used was of a particle size no less than 10 μm . The low molecular PE (LMPE) with a molecular weight about 5000 and a low molecular weight PP (LMPP) with a molecular weight about 6500 are produced by the heat-cracking method. The SBS block copolymer used has a line structure with a molecular weight about 90,000 (the butylene content is about 35%), and the EVA, a molecular weight about 28,000 (VA content of 26%). The PS used is a general-grade product with a molecular weight about 40,000. (See Table I.)

Sample Preparation

The calcium carbonate was first heated in a mixer (fixed with mechanical stirrer) to 100°C for about 5 min to rid it of water. Then, the titanate coupling agent was blended with the calcium carbonate to make the coated filler. After that, PP was added, then other polymers. Finally, the composite was melt-mixed in a twin-screw extruder at about 210°C. The samples for mechanical measurements were prepared by injection molding.

Measurement of Mechanical Properties

Tensile properties were measured with an XL-100 tensile tester, according to ASTM D638. Testing was done at a speed of 50 mm/min. The notched Izod impact strength was measured using an Izod UJ-40 impact tester, according to ASTM 256. Flexural strength was measured on an LJ-500 tensile tester, according to ASTM D790, and heat deflection was measured according to ASTM D648. In all experiments, the temperature was set to 23°C, and the mean value of five measurements was taken.

RESULTS AND DISCUSSION

From Table II, we can see that various polymers have different effects on the properties of PP. The combination of SBS and LDPE gives the highest impact strength while the EVA does not have the same effect on the impact properties. The reason may be that LDPE is a highly branched polymer which makes it very flexible and ductile and SBS is a very good elastomer that gives it very high impact resistance. It also seems that the interaction among PP, SBS, and LDPE is much stronger than that between PP and EVA. However, the tensile strength suffered very much from these materials as LDPE has a relatively low tensile strength. Since stress transfer depends on the size of the interface and on

Table II Properties of PP Blended with Some Other Polymers

	Tensile Strength (MPa)	Flexural Modulus (MPa)	Heat Deflection (°C)	Impact Strength (J/m)
1	37.4	1683	117.5	24.9
2	25.6	1005	91.3	400
3	29.2	1168	105.3	36.9
4	23.6	588	86.9	456
5	23.3	806	82.0	600

Table III Mechanical Properties of the PP Composite

Samples	Tensile Strength (MPa)	Flexural Modulus (MPa)	Heat Deflection (°C)	Impact Strength (J/m)
1	28.2	1490	110	40
2	31.1	1570	112	43
3	29.5	1300	97	32

the thickness of the interface on the boundary of the different phases, tensile yield stress proved to be an excellent property to predict interfacial interaction in heterogeneous polymer systems. In this system, yield stress is determined by the decrease of effective load-bearing cross section and by the load carried by the dispersed phase. These results reflect again the differences in the structure of the blends prepared with the different types of polymers and also prove that adhesion of PP to them differs significantly. The thermal properties have also been decreased by the blending with other polymers. The addition of the LMPP and LMPE has some effect on the thermal properties. They made the twin-screw extruder work perfectly, but their effects on the mechanical properties are not very distinctive. The decrease of the flexible strength may be due to the fact that all the added polymers have very low flexible properties.

These results show that effective impact modification of PP can be achieved by LDPE. But the LDPE seems to decrease other properties sharply. So, further experiments were carried out with same amount of HDPE instead of LDPE. To compensate for the tensile and flexible strength, about 30 weight parts calcium carbonate were added into the system. As the results showed that the LMPE did not influence the mechanical properties as seriously as did LMPP, the LMPE was chosen for the further experiments with the same weight parts. EVA was also used in the same weight parts. In all the experiments, PP was 100 weight parts. The samples were (1) PP

+ CaCO₃ + HDPE + EVA, (2) PP + CaCO₃ + HDPE + EVA + LMPE, and (3) PP + CaCO₃ + HDPE + EVA + LMPE + SBS. The results are shown in Table III.

There are several simultaneous and synergistic phenomena which can toughen the filled PP⁵: (1) recovery of chain mobility of interfacial layers, (2) change in morphology of interfacial layers, (3) removal of additional relaxation process which follow the bonding of filler particles to polymer, (4) change in the localization of zones of plastic deformation, (5) formation of pores, which contributes to the macroscopic strain of the samples, (6) fibrillation of pore walls, (7) reorientation of anisotropy filler particles, (8) better heat subtraction, and (9) better physical contact between filler particles and polymer. The results showed that the calcium carbonate really increased the strength of the PP composites due to the good conditions at the interfacial layers which is achieved by the coating of the filler with a titanate coupling agent. But the tensile properties and thermal properties are still lower than those the pure PP as result of the addition of SBS and EVA. The EVA, SBS, and HDPE all improved the impact of the filled PP. However, as there is no chemical reaction between the different polymers, even with HDPE, the properties of homo-PP is not so easy to be promoted. To examine the chain-link effect on the properties of the composites, the PP copolymer was used in another series of experiments. The PS is also employed to see the effect of the styrene monomer on the propylene monomer. The compo-

Table IV Composition of PP Copolymer Samples

Materials (Wt)	Composition 1	Composition 2	Composition 3	Composition 4
PP copolymer	100	100	100	100
PS		30	30	30
HDPE	30			
SBS		5	5	
CaCO ₃	50		50	
Ti-coupling agent	0.5		0.5	

Table V Properties of PP Copolymer Samples

Samples	Tensile Strength (MPa)	Flexural Modulus (MPa)	Heat Deflection (°C)	Impact Strength (J/m)
PP copolymer	28	1870	104	60
Composition 1	28.2	2160	115.7	327.9
Composition 2	28.1	1600	88.8	87.5
Composition 3	28.2	1820	94.6	75.4
Composition 4	28.6	1840	95.5	49.04

sitions are listed in Table IV. The results are listed in Table V.

It is clear that the composites have a higher impact strength than that of homo-PP because the copolymer has higher impact properties than those of the PP homopolymer. By comparing compositions 2 and 4, we can see that a small amount of SBS improved the impact properties due to the good interfacial reaction between the SBS and the PS. The HDPE improved the impact strength five times over that of the original resin because there is an ethylene monomer in the PP copolymer. In general, the system has good coadhesion among various polymers and the filler. But the styrene in PS cannot give the same influence as does the styrene in SBS, which is shown by the decrease of impact properties in composition 4.

As with tensile strength, the HDPE enclosed in the system has a higher tensile strength than that of LDPE and improved the whole tensile property. On the other hand, PS can also give a higher tensile strength. Nevertheless, it did not provide the same result as did the HDPE, meaning that it may not mix with other polymers uniformly.

The calcium carbonate contributed to the increase of the flexible properties as shown by compositions 1 and 3. Composition 1 has obtained higher thermal properties as well. This means that the calcium carbonate is very effective in improving the antiheat properties and in enforcing the PP materials. It further confirms that the uniformity and compatibility are more important than are any other factors.

CONCLUSION

The properties of PP composites are the key factors which will determine the future of the PP materials. The studies on the relationship between properties and compatibility are successful for PP homopoly-

mer and PP copolymer composite materials. They showed that various polymers having different properties can donate their properties to the composite.

The blending of PS and SBS into PP showed that SBS can improve the impact properties of the PP materials while PS cannot, meaning that the structure of a polymer is the crucial factor affecting its properties. However, the balanced properties of a composite are determined mostly by the coadhesion among the different parts. The physical mixing of LDPE and HDPE into PP improved the impact properties to some really higher degree, just like the SBS. But the composite with higher impact strength, higher tensile properties, and higher flexible modulus is achieved only with the chemical-bonded PP copolymer which contains ethylene blocks. The LMPE and LMPP can increase the melt flow index of the composite materials, but the mechanical properties may suffer from their low strength.

The EVA does not contribute much to the mechanical properties. But the adhesion tape test showed that the composite with it has more adhesion to printing materials such as acrylic resin. The calcium carbonate can reduce the product cost and improve the thermal properties and strength. Its use is encouraged by the fact that it can blend with PP very well after being treated with a titanate coupling agent. The calcium carbonate-filled PP system has been a research point for a long time. The factors affecting the dispersion state and therefore the mechanical properties are mainly the conditions at the interfacial layer. The treating agent is the key method to improve the adhesion between the filler and the polymers. The titanate coupling agent is proved to be an efficient coating material. The properties of the blended PP can reach an optimum one if the optimum situation among the polymers and the fillers can be achieved.

REFERENCES

1. F. Takeshi and Y. Masashi, EP 443,346 (1991).
2. W.-Y. Ching, W.-D. Yang, and B. Pukanszky, *Polym. Eng. Sci.*, **32**, 642 (1992).
3. F. H. Axtell, D. Autsawasatarn, and K. Rujiranontapong, *Plast. Rubb. Compos. Process. Appl.*, **18**, 47 (1992).
4. N. Tamashima, K. Ueno, T. Akagawa, S. Hinenoya, and S. Katsui, U.S. Pat. 5,039,525 (1991).
5. A. Galeski, M. Kryszewski, and T. Kowalewski, *Polym. Engin. Sci.*, **32**, 1217 (1992).
6. J. Chou, K. Vijayan, D. Kirby, A. Hiltner, and E. Baer, *J. of Mater. Sci.*, **23**, 2521 (1988).
7. K. C. Dao, *J. of Appl. Polym. Sci.*, **27**, 4799 (1982).
8. Y. Suetsugu, *Int. Polym. Process.*, **5**, 184 (1990).
9. J. Chou, K. Vijayan, D. Kirby, A. Hiltner, and E. Baer, *J. of Mater. Sci.*, **23**, 2533 (1988).
10. R. Herzig and W. E. Baker, *J. of Mater. Sci.*, **28**, 6531 (1993).

Received July 11, 1995

Accepted November 25, 1995