Toughened Polypropylene with Balanced Rigidity. III. Compositions and Mechanical Properties

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ABSTRACT: Toughened polypropylene with balanced rigidity (TRPP) was prepared by thermal mechanical blending of PP resin with a toughening master batch (TMB) in a twin screw extruder. The dependence of the mechanical properties of TRPPs on the ratio of ethylene-propylene to styrene-butadiene elastomers, the total elastomer content in the TRPP, and the amount of elastomers in the TMB were investigated. The TRPP with a total elastomer content of 14 wt %, which was made from a TMB with 32 wt % elastomer and a 80/20 (w/w) ratio of ethylene-propylene to styrene-butadiene elastomers, was found to have excellent balanced mechanical properties. The notched Izod impact strength at 23°C was 762 J/m (23 times that of PP), the flexural modulus was 1078 MPa (92% of that of PP), and the tensile strength at yield was 34.8 MPa (88% of that of PP). Moreover, its mechanical properties were much better than the simply blended sample with the same composition, demonstrating that dynamic vulcanization and polymer-bridge conjunction are excellent techniques to produce a high-impact, high-modulus PP. A sharp brittle–ductile transition was found at 14 wt % total elastomer content, which was assumed to be a percolation phenomenon. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1345–1350, 2001

Key words: toughened polypropylene; balanced rigidity; mechanical properties; compositions

INTRODUCTION

For polymers in engineering applications, the fracture toughness of a polymer becomes crucial in the material selection. Therefore, during the last two decades there was great interest in developing toughened polymers and polymer blends. Polypropylene (PP) has such properties as low price, good chemical resistance, and so forth, and was thus studied even more widely to improve its impact strength by blending it with elastomers. The toughness of PP blends is enhanced through the incorporation of elastomer, and the rigidity (i.e., the modulus and the tensile strength) is decreased because of the low miscibility of the added components. Inoue et al.[1–5] studied selective crosslinking in 80/20 PP/ethylene-propylene-diene monomer (EPDM) polymer blends. The notched Izod impact strength (NIIS) at 23°C exceeded 60 kg/cm^2 (about 12 times that of PP); the tensile yield stress (TYS) and flexural modulus (FM) were 225 and 11,500 kgf/cm^2, which are only 57 and 66% of those of PP, respectively. PP/EPDM binary blends and PP/high density polyethylene (HDPE)/EPDM ternary blends were also investigated by Choudhary et al.[6,7] The Izod impact strength of PP/HDPE/EPDM (90/10/20) was reported to be increased 12-fold from 25 to 316 J/m whereas the tensile strength and Young's modulus were retained at 213 and 3900 kg/cm^2, which are 67 and 60% of those of PP, respectively.

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To compensate for the above elastomer effect, three-component composites were reported by adding inorganic filler as a third component.[8–10] In such systems, the decrease in modulus and tensile strength were minimized while the improvement of toughness was not remarkable. Chiang and Yang[11,12] reported that a PP/PP-acrylic acid-EPDM/mica (80/20/20) system had balanced mechanical properties with an Izod impact strength of 2.4 kJ/m^2 (the same as that of PP), a tensile strength of 32 MPa (1.14 times that of PP), and a Young's modulus of 1.2 GPa (1.7 times that of PP), where acrylic acid grafted PP or EPDM was used as a compatibilizer.

In order to develop a high performance PP composite that possesses both excellent toughness and balanced rigidity at comparatively low cost, we developed a series of toughening master batches (TMBs) with different compositions by using dynamic vulcanization and polymer bridging techniques starting from PP as the matrix resin, EP or butadiene-styrene elastomer as the toughening agent, and a monomer containing a carbonate group as a bridging agent in the presence of a free-radical initiator.[13,14] The prepared TMBs consisted of unreacted PP, unreacted elastomers, a graft copolymer of PP and/or elastomers containing branched chains formed by a bridging agent, and a crosslinked copolymer of PP and/or elastomers in conjunction with polymer bridging chains also derived from the bridging agent. Moreover, the TMBs formed a special morphology through microphase separation with the PP component as the continuous phase and the elastomer component as the dispersed phase having a cellular structure containing some PP. Such morphological characteristics are essentially different from the packaged morphology[15–17] formed by flow encapsulation during the process of thermal mechanical blending.

In the present study we attempted to improve the impact properties of PP with a minimum decrease of rigidity by TMBs with various compositions. The effects of the ratio between the two elastomers, the total elastomer content in toughened PP with balanced rigidity (TRPP), and the elastomer amount in the TMB on the mechanical properties of PP were investigated.

EXPERIMENTAL

Materials

The antioxidant PKB-215 was purchased from Beijing Chemical Industry Factory. The other materials for the preparation of TMBs and TRPPs are described in Zhang et al.[13]

Preparation of TRPPs

A TE-34 twin screw extruder (Extrusion Machine Institute of Chemical Industry Ministry in China) was used for melt blending of the polymers. The granules of PP, TMB, and antioxidant were hand mixed in appropriate ratios prior to being added to the extruder.The temperatures of the six zones from the feed zone to the die zone of the extruder were successively 210, 220, 230, 240, 230, and 210°C. The main screw and feed screw speeds were adjusted to 90 and 70–80 rpm, respectively. The filaments obtained upon extrusion were immediately quenched in water and then chopped into small granules.

Various PP blends were prepared by varying the TMB type and the weight percent of the TMBs as shown in Table I. The TRPP samples 4G-I-1 to 4G-I-5 are a series made from TMBs I-1 to I-5 at the same composition ratio of PP to TMB. These five TMBs had the same elastomer amount of 32 wt % but different ratios of EP to styrene-butadiene (SB) elastomers of 20/80, 40/60, 60/40, 80/20, and 100/0 (w/w). The TRPP samples 1G-I-4 to 5G-I-4 were another group prepared from the same TMB I-4 (with elastomer content of 32 wt % and ratio of EP to SB elastomer of 80/20 w/w) at different amounts of TMB and thereby different individual elastomer contents of 8, 10, 12, 14, and 16 wt %. TRPPs 4G-I-4 to 4G-IV-4 were the third series prepared by the TMBs, which had the same 80/20 (w/w) ratio of EP to SB elastomer yet different respective amounts of elastomer of 32, 38, 44, and 50 wt % but at the same total elastomer content in the resulting TRPPs.

A control sample was prepared by blending PP with a control batch 0i[14] under the same extrusion process as above to obtain a similar thermal history with the samples of PP/TMB blends. The control batch 0i is described in Zhang et al.[14] and was prepared by simple blending of PP resin and elastomers in the same composition as that of 4G-I-4, instead of the dynamic vulcanization and polymer bridging techniques.

Mechanical Properties Testing

The samples in Table I were injection molded into specimens for testing with barrel temperatures of 210–230°C, an injection pressure of 1000 kgf/cm^2, and a mold temperature of 50°C.

Table I Compositions of TRPPs

	PP in TRPP (wt %)	M + N in TRPP (wt %)	TMB Used	PP in TMB (wt %)	M + N in TMB (wt %)	M/N (w/w) in TMB
PP	100	0	—	—	—	—
0G-0i	86	14	0i	68	32	80/20
4G-I-1	86	14	I-1	68	32	20/80
4G-I-2	86	14	I-2	68	32	40/60
4G-I-3	86	14	I-3	68	32	60/40
4G-I-4	86	14	I-4	68	32	80/20
4G-I-5	86	14	I-5	68	32	100/0
1G-I-4	92	8	I-4	68	32	80/20
2G-I-4	90	10	I-4	68	32	80/20
3G-I-4	88	12	I-4	68	32	80/20
4G-I-4	86	14	I-4	68	32	80/20
5G-I-4	84	16	I-4	68	32	80/20
4G-I-4	86	14	I-4	68	32	80/20
4G-II-4	86	14	II-4	62	38	80/20
4G-III-4	86	14	III-4	56	44	80/20
4G-IV-4	86	14	IV-4	50	50	80/20

In the TRPP the total weight of PP and elastomers is considered as 100 and the antioxidant is 0.05 wt % of the total resin. M, ethylene-propylene elastomer; N, styrene-butadiene elastomer. In the TMB the total weight of PP and elastomers is considered as 100, the bridging agent is 12 wt % of the total resin, and the initiator is 10 wt % of the bridging agent.

The TYS was measured on an Instron 1123 universal testing machine using dumbbell-shaped specimens at a crosshead speed of 50 mm/min based on ASTM D638M. The FM was tested on the same machine at a crosshead speed of 30 mm/min following GB 1042-88. The NIIS was determined on a Zwick 5101B pendulum impact tester with an impact rate of 3.15 m/s at a temperature of 23 ± 0.5°C following GB 1043-80. The average values of at least five tests are reported.

RESULTS AND DISCUSSION

Influence of Ratio Between Two Elastomers

The mechanical properties of TRPPs at the same elastomer content (14 wt %) made from TMBs with different EP to SB elastomer ratios are shown in Table II and Figure 1. The mechanical properties of pure PP and the control sample 0G-0i are also listed for comparison. From the toughness and rigidity (FM and TYS) viewpoints, which are the most important properties for engineering plastics, the mechanical properties of TRPP 4G-I-4 made from TMB I-4 was the most prominent. At 23°C the NIIS value reached 762 J/m (23 times that of pure PP); the FM was 1078 MPa and the TYS was 34.8 MPa, which are respective reductions of only 8 and 12% compared to pure PP.

In addition to the effect of small PP crystallites, TRPP 4G-I-4 had a typical chemical and morphological structure similar to acrylonitrile-butadiene-styrene or high-impact polystyrene, which caused the high performance of the PP composites and will be reported in the next article in this series. The introduction of the graft and crosslinked copolymer of PP and elastomers on the dispersed particle surfaces improved the affinity between the phases and also improved the dispersion state of the particles. Moreover, almost all of the dispersed particles incorporated PP during the polymerization and increased the elastomer apparent volume. On the other hand, the dispersed domain size was small, which would then cause more elastomer particles that function as stress concentrators under deformation. At the same time, the elastomer particles promote crazing or shear yielding in the matrix and suppress brittle fracture as a result. Considering the various composite models concerned with the relationship of the mechanical properties of the blends and the component,[18] the craze shearing band toughening theory, and the craze branching theory,[19] we decided that the above favorable structural characteristics would produce TRPP

Table II Notched Izod Impact Strength, Flexural Modulus, and Tensile Yield Strength of PP, Control Sample, and TRPPs

	Notched Izod Impact Strength		Flexural Modulus		Tensile Yield Strength	
	J/m	Increase (%)	MPa	Reduction (%)	MPa	Reduction (%)
PP	33	0	1177.9	0	39.7	0
0G-0i	111	236	942.3	20	31.6	20
4G-I-1	180	445	1125.3	4	35.2	11
4G-I-2	216	555	1081.6	8	34.1	14
4G-I-3	287	770	1075.9	9	33.5	16
4G-I-4	762	2209	1078.0	8	34.8	12
4G-I-5	557	1588	1008.3	14	30.2	24
1G-I-4	141	327	1156.3	2	38.1	4
2G-I-4	203	515	1101.8	6	38.4	3
3G-I-4	334	912	1095.4	7	36.8	7
4G-I-4	762	2209	1078.0	8	34.8	12
5G-I-4	821	2388	961.9	18	33.9	15
4G-I-4	762	2209	1078.0	8	34.8	12
4G-II-4	634	1821	1000.0	15	35.8	10
4G-III-4	331	903	969.0	18	35.7	10
4G-IV-4	282	755	958.9	19	31.5	21

The test was at 23°C.

4G-I-4 with balanced properties of excellent toughness and high rigidity.

Comparing TRPP 4G-I-4 to the simply blended control sample 0G-0i with the same composition, we found that the mechanical properties of 4G-I-4 were much better than those of 0G-0i. The NIIS of the former was sevenfold of the latter, the FM was 1.15 times more, and TYS was 1.1 times more. The results indicated that the prepared TMBs had effectively solved the problem of commonly toughened PP with remarkable rigidity loss.

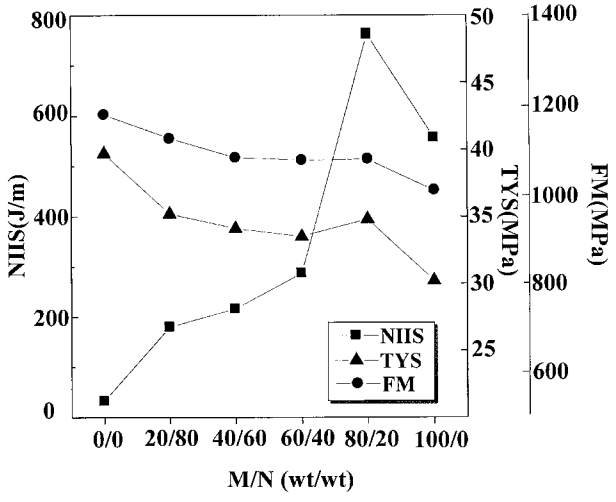

Figure 1 The notched Izod impact strength (NIIS), flexural modulus (FM), and tensile yield strength (TYS) of TRPPs versus the ratio of ethylene-propylene to styrene-butadiene elastomer (M/N).

Influence of Total Elastomer Content in TRPPs

The mechanical properties of the pure PP and those of TRPPs made from the same TMB I-4 with different total elastomer contents are shown in Table II and Figure 2. It can be observed that the NIIS increased, the FM and TYS gradually dropped, and the total elastomer content increased. These changes were not in a linear relationship. For instance, when the total elastomer content was increased from 8 to 12 wt %, the NIIS of TRPP was only enhanced from 4.3 to 10.1 times that of PP. However, when the total elastomer content was increased from 12 to 14 wt %, the NIIS was remarkably enhanced from 10.1 to 23.1 times that of PP. When the total elastomer content was increased from 14 to 16 wt %, the NIIS improved slowly from 23.1 to 24.9 times that of PP. Apparently, an onset exists on the curve of the NIIS versus the total elastomer content. Similar sharp changes were also found for the FM

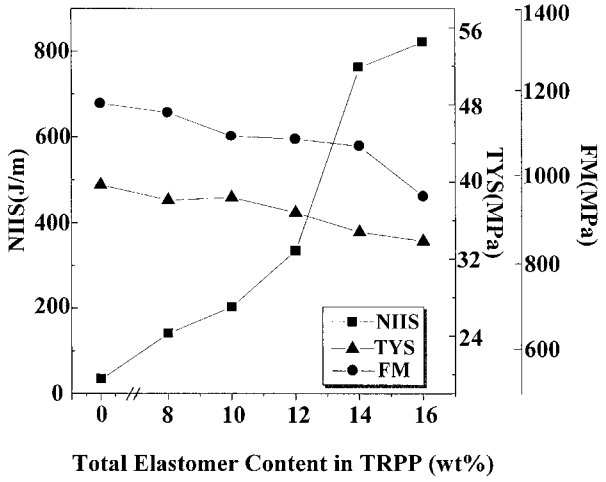

Figure 2 The notched Izod impact strength (NIIS), flexural modulus (FM), and tensile yield strength (TYS) of TRPPs versus the total elastomer content in the TRPP.

(with 14 wt % elastomer content) and the TYS (with 12 wt % elastomer content).

The above results may be due to the interparticle distance T in the dispersed phase being equal to or smaller than the critical interparticle distance Tc[20–26] for the brittle–ductile transition. Wu[23,24] proposed a concept of critical matrix thickness Tc (or critical matrix ligament thickness) for the toughening mechanism of polyamide (PA)-6/EPDM blends by which the toughness of the blends is determined by the matrix thickness T (or interparticle distance) between two particles. When the T between rubber particles is larger than the critical value (T > Tc), the blends exhibit brittle fracture and the toughness cannot be improved to a great extent with the T decreasing. When the T < Tc, the blends exhibit ductile failure when fractured by impact and the toughness cannot be remarkably improved. When T = Tc, a brittle–ductile transition can be observed, where the toughness was drastically increased. Margolina and Wu[25,26] also proposed that the brittle–ductile transition in PA/EPDM blends can be interpreted by a model based on the percolation theorem. We further expanded the concept from a single toughener to a complex toughener and proposed that the T in the elastomers dispersed phase in TRPP 4G-I-4 had reached the Tc value. Hence, the brittle–ductile transition of TRPP prepared from TMB I-4 appeared at a total elastomer content of 14 wt %.

Influence of TMBs with Different Elastomer Amounts

The mechanical properties of TRPPs with the same total elastomer content of 14 wt % made from TMBs with 32, 38, 44, and 50 wt % elastomer are shown in Table II and Figure 3. Note that the TRPPs made from TMBs with 32 and 38 wt % elastomer, especially the former, showed excellent balanced mechanical properties. These may have mainly resulted from the chemical structure and further morphological structure differences of the TMBs. Zhang and colleagues reported that in TMBs I-4 to IV-4 the elastomers existing in graft and crosslinked forms were 53.35, 50.73, 48.02, and 52.76 wt % and the PP existing in graft and crosslinked forms were successively 19.56, 17.69, 14.92, and 12.08 wt %.13 Therefore, the content of grafted and/or crosslinked elastomers in the resulting TRPPs were calculated as 6.8, 6.5, 6.1, and 6.6 wt %, respectively. However, the calculated content of grafted and/or crosslinked PP in the resulting TRPPs were 4.7, 3.7, 2.5, and 1.8 wt %, respectively. The decrease of elastomers and PP existing in graft and crosslinked forms in the TRPPs as a compatibilizer at the interface led to a coarse dispersion, unstable morphology, poor adhesion between the phases, and thus worse mechanical properties.[27]

CONCLUSIONS

This study revealed that the ratio of two different elastomers, the total elastomer content in the

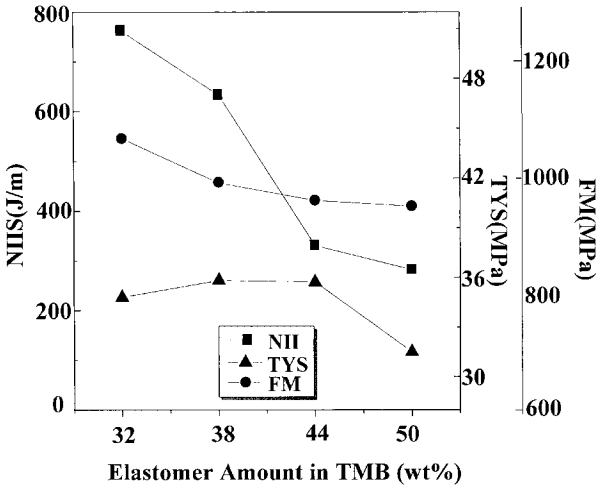

Figure 3 The notched Izod impact strength (NIIS), flexural modulus (FM), and tensile yield strength (TYS) of TRPPs versus the elastomer amount in the TMB.

TRPP, and the amount of elastomer in the TMB had significant influences on the mechanical properties of the TRPPs; and the mechanical properties of the PP ternary blend could be modified easily by varying the composition of TMBs and TRPPs. The TMB with an 80/20 (w/w) ratio of EP to SB elastomer and a 32 wt % elastomer content is preferred for preparing the resulting PP composites that possess not only highly improved toughness but also balanced rigidity. The TRPP with a total elastomer content of 14 wt % made from the TMB had excellent balanced mechanical properties with a NIIS of 762 J/m (23 times that of PP) at 23°C, an FM of 1078 MPa (92% of PP), and TYS of 34.8 MPa (88% of PP). A sharp brittle–ductile transition was found at 14 wt % total elastomer content when the other conditions were constant.

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