Modification of Polyolefins with Silicone Copolymers. II. Thermal, Mechanical, and Tribological Behavior of PP and HDPE Blended with Silicone Copolymers

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ABSTRACT: Thermoplastic polyolefin (TPO) films with permanent, silicone-rich, low-friction, low-abrasion surfaces were obtained by melt blending of high-density polyethylene (HDPE) and polypropylene (PP) with polydimethylsiloxane (PDMS)-containing block copolymers. Two different block copolymers, a siloxane–urea segmented copolymer and a polycaprolactone-*b*-PDMS triblock copolymer were used as modifiers at levels between 0.1 and 5.0% by weight. Blends were prepared in a twin-screw extruder. Modified films displayed surfaces with very low friction coefficients and high abrasion resistance, which depended on the type and the level of additive incorporated into the system. Bulk properties of these modified systems, such as crystallization and melting behavior or tensile properties, were not affected. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 535–540, 2002; DOI 10.1002/app.10279

Key words: polyolefins; polysiloxanes; additives; surfaces; modification

INTRODUCTION

After the discovery of metallocene catalyst systems, thermoplastic polyolefins (TPOs), such as high-density polyethylene (HDPE) and polypropylene (PP), have become the preferred plastic resins for many industrial applications. To increase the diffusion of these resins into a broader range of specific end-uses, it is desirable to optimize their bulk–surface properties and also processibility–performance relationships. As reported in the accompanying article,[1] incorporation of small amounts of silicone-containing block copolymers into PP and HDPE through blending resulted in substantial improvements in the extrusion rates of these materials. In addition, surface properties of the resins have also been permanently modified by the addition of these silicone copolymers. These modified TPOs with controlled bulk and surface properties may perform more like specialty plastics rather than like commodity resins for various applications, such as in release films, industrial and carpet fibers, and biomaterials. It is very important to achieve these improvements in the processing behavior of the resins and resultant surface properties without any sacrifice in the bulk properties of the modified materials, such as crystallinity, thermal behavior, or mechanical performance.

In this article, the thermal and mechanical properties of silicone-modified polyolefins are discussed. In addition, the tribological properties, such as the friction coefficient and wear resistance of PP and HDPE resins modified with small

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amounts of silicone copolymers, are provided. It is clearly demonstrated that improvements in the processibility and surface and tribological properties of PP and HDPE are achieved without any change in their thermal behavior or mechanical performance.

EXPERIMENTAL

Materials

PP (Profax 6523) was kindly supplied by Himont (Wilmington, DE). HDPE (4352 NT) was obtained from Dow Chemical (Midland, MI). A detailed description of silicone copolymer additives, polycaprolactone–polydimethylsiloxane (PCL–PDMS–PCL) triblock and polydimethylsiloxane–urea (PSU) segmented copolymers, processing conditions of the blends, and method of sample preparation for surface and bulk characterization tests were already provided.[1]

Characterization Techniques

Thermal analyses of the virgin polymers and the blends were obtained on a Polymer Laboratories PL-DSC Plus, under a nitrogen atmosphere, with a heating rate of 10°C per min. Temperature and enthalpy calibrations of the instrument were obtained using indium, lead, and zinc standards. Stress–strain tests were performed at room temperature, on an Instron Model 4411 tester with a crosshead speed of 10 mm/min. The tribological behavior of the materials was investigated by determining the coefficient of friction and the volume of the worn material. These tests were carried out on a Plint, Pin-on-Ring-type multipurpose tester according to the ASTM G 77 test method at various loadings. Used as the ring material was 100 Cr 6 steel with a hardness of 62 HCR, which was cylindrical with a diameter of 60 mm and a height of 2 mm. The roughness of the ring (Ra) was 0.2 μm. The sliding speed and sliding distance of the ring was 1.0 m/s and 950 m, respectively. Normal loads for PP- and HDPE-containing systems were 10 and 20 N, respectively. The volume of the worn material was determined by carefully measuring the dimensions of the wear track on the polymer film surface using a Mitutoyo microscope with 200× magnification and 0.005-mm accuracy.

RESULTS AND DISCUSSION

The preparation of polymers with controlled surface properties has been an important field of research both for academia and industry.[2–4] This is because most performance requirements for polymeric materials are related to the surface properties as much as to that of the bulk. These include environmental resistance (thermal, oxidative, and UV stability), adhesion (printability and paintability), fire and flame resistance, antistatic properties, friction, scratch and wear resistance, gloss, and biocompatibility. In general, polymers with the desired bulk properties for a specific application do not usually have the optimum surface properties. To achieve the desired surface properties, polymers are usually modified through the use of specific additives during processing or by various techniques after processing.[2–4] Important surface-modification techniques that are applied after production of the finished parts or products include corona or plasma treatment, chemical grafting onto the surface, and flame treatment. A simpler and cost-effective method of polymer-surface modification is the use of surface-active copolymers, which may be blended with the base polymer in small amounts before processing and which migrate to the polymer–air surface during and/or after processing.[5,6] Depending on the type, nature, overall molecular weight, and amount of the additive used, it is possible to obtain the desired surface properties in the finished product, including high-energy or hydrophilic surfaces.[7] Silicone-containing copolymers and fluoropolymers are frequently used for the surface modification of various polymers, especially in applications where hydrophobicity, low surface friction, and/or biocompatibility are required.[8] Major applications of silicone-modified polyolefin resins are in release films, industrial and textile fibers, and biomaterials.

Thermal Characterization of the Products

For many applications, it is important to obtain the desired surface modification without influencing the bulk properties of the base polymers. In this study, where surface modifications of PP and HDPE were achieved by blending with silicone copolymers, DSC and stress–strain tests were used to demonstrate that the thermal and mechanical behaviors of the base resins were not affected. The overall mechanical properties of PP and HDPE are directly related to their bulk crystallinity. Therefore, any factor that influences the bulk crystallinity will have a major effect on the properties of these resins. As a result, we first wanted to demonstrate that the incorporation of

Table I Influence of Silicone Additives on the Crystallinity of HDPE

Additive Type	Amount (% wt)	Peak Maxima (°C)	ΔH_{fus}(Expl) (mcal/g)	ΔH_{fus}(Norm) (mcal/g)
Virgin HDPE	—	133.7	35.9	35.9
Extruded HDPE	—	133.7	35.8	35.8
PCL–PDMS-PCL	0.10	133.5	35.6	35.6
PCL–PDMS-PCL	0.50	134.2	35.3	35.5
PCL–PDMS-PCL	1.00	135.7	34.4	34.8
PCL–PDMS-PCL	2.50	133.7	34.4	35.3
PCL–PDMS-PCL	5.00	134.1	32.8	34.5
PSU	0.25	133.5	35.3	35.4
PSU	1.00	133.7	34.6	34.9
PSU	2.50	132.4	34.2	35.1
PSU	5.00	132.6	30.8	32.4

silicone copolymers does not adversely affect the crystallization of PP or HDPE resins. For this purpose, DSC was used, where the melting point (T_m) and enthalpy of fusion (ΔH_{fus}) values of virgin materials and blends were determined. The melting points reported here are the temperatures corresponding to the maxima of the fusion peaks, whereas the enthalpy of fusion value is determined from the area under the curve.

Table I gives data on the melting points and enthalpy of fusion of HDPE and HDPE modified with PCL–PDMS–PCL and PSU copolymers. Virgin HDPE has a melting point of 133.7°C and an enthalpy of fusion of 150.1 mJ/g (35.9 mcal/g). As a control, virgin HDPE was extruded without any additive, and as shown in Table I, the T_m and ΔH_{fus} values were found to be identical to those of virgin HDPE, indicating no change in the resin properties during extrusion. Blends containing 0.1–5.0% by weight of the PCL–PDMS–PCL additive showed melting points within a very narrow range of 133.5–135.7°C, very similar to that of virgin HDPE. Similarly, there was also no change in the melting points of PSU-modified materials. As can be seen in Table I, HDPE containing small amounts of PCL–PDMS–PCL (0.1 and 0.5% by weight) showed no change in the enthalpy of fusion. When the amount of the modifier was increased to 2.5 and 5.0% by weight, respectively, a small decrease in the value of ΔH_{fus} was observed. However, when experimentally obtained ΔH_{fus}(Expl) values for the blends are normalized ΔH_{fus}(Norm) to take into account the presence of the additive in the system, very good agreement is observed, as shown in the final column of Table I. Very similar behavior was also observed in modified PP.

As shown in Table II, virgin and extruded PP show almost identical melting points. When small amounts of PCL–PDMS–PCL or PSU copolymers are added into the system, there is no noticeable change in the melting points. Similarly, there is no effect of these additives on the ΔH_{fus} values of PP. All these results clearly show that the crystallinities and thermal properties of HDPE or PP are not influenced by the addition of small amounts of the PCL–PDMS–PCL or PSU copolymers.

Tensile Properties of Silicone-modified Polyolefins

To determine the influence of silicone copolymer incorporation on the mechanical properties of polyolefin blends, the stress–strain behavior of these systems were studied. Detailed stress–strain data on virgin and modified HDPE systems are provided in Table III. When the results are examined, no noticeable differences are observed among the values of the tensile modulus, yield stress, yield strain, tensile strength, or ultimate elongation for virgin HDPE and its blends containing up to 2.5 wt % of the silicone additive. Stress–strain data on virgin, extruded, and PSU-modified PP are given in Table IV. Similar to the results obtained on modified HDPE, no major differences were observed in the overall stress–strain behavior of modified systems when compared with virgin PP.

Data obtained on the thermal characterization and stress–strain behavior of HDPE and PP blended with small amounts of silicone copolymers clearly show that there is no change in the bulk properties of the modified systems. However, as explained earlier,[1] the processing behavior and

Table II Influence of Silicone Additives on the Crystallinity of PP

Additive Type	Amount (% wt)	Peak Maxima (T_m; °C)	ΔH_{fus}(Expl) (mcal/g)	ΔH_{fus}(Norm) (mcal/g)
Virgin PP	—	167.4	17.1	17.1
Extruded PP	—	167.3	17.7	17.7
PCL–PDMS-PCL	0.10	167.5	17.6	17.6
PCL–PDMS-PCL	0.50	167.2	17.3	17.4
PCL–PDMS-PCL	1.00	166.6	17.4	17.6
PCL–PDMS-PCL	5.00	167.1	16.8	17.7
PSU	0.10	167.3	17.3	17.3
PSU	0.25	167.5	17.2	17.3
PSU	0.50	167.4	17.4	17.5
PSU	1.00	167.0	16.3	16.5
PSU	2.50	167.6	16.6	17.0

surface properties of the modified systems show substantial differences when compared with virgin resins. To further illustrate the major changes in the surface composition and properties of silicone-modified PP and HDPE resins, the tribological behavior of the modified systems were also studied and are discussed below.

Tribological Characterization of Silicone-modified Polyolefins

One of the major benefits of polymer-surface modification with silicones is the reduction in the coefficient of friction (μ).[9,10] It is interesting to note that there is a Gaussian-type relationship between the coefficient of friction and the water contact angles of surface-modified polymer films,[11] determined against a glass plate in water. For water contact angles of up to 40°, μ is very low (<0.1). Then, there is a sharp increase in μ up to a contact angle of 80°, where it reaches to about 1.0 (a tenfold increase). As the contact angle further increases from 80 to 120°, there is a sharp drop in μ to about 0.1 again. This interesting dependence of friction to the water contact angle was explained by the work of adhesion of polymers in water.[11] A reduction in the coefficient of friction is expected to lead to improvements of the abrasion resistance of modified surfaces. Such improvements play critical roles in many applications since they increase the durability and overall life of the polymeric materials.

Table III Tensile Properties of Silicone-modified HDPE

Additive	Amount (wt %)	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Tensile Strength (MPa)	Ultimate Elongation (%)
Virgin HDPE	—	95	18.5	13.7	26.3	1360
Extruded HDPE	—	100	19.0	13.6	26.1	1380
PCL–PDMS-PCL	0.10	103	23.0	13.3	27.8	1300
PCL–PDMS-PCL	0.25	107	22.6	15.3	28.1	1240
PCL–PDMS-PCL	1.00	110	23.7	13.2	29.8	1180
PCL–PDMS-PCL	2.50	108	18.5	12.8	24.7	1200
PCL–PDMS-PCL	5.00	105	17.9	12.2	24.2	1190
PSU	0.25	110	20.4	13.5	28.7	1380
PSU	0.50	114	20.7	13.6	26.1	1360
PSU	1.00	105	21.3	14.0	29.6	1390
PSU	2.50	104	18.0	12.8	24.8	1300
PSU	5.00	90	17.5	13.6	24.5	1250

Table IV Tensile Properties of Silicone-modified PP

Additive	Amount (wt %)	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Tensile Strength (MPa)	Ultimate Elongation (%)
Virgin PP	—	106	21.0	13.3	31.3	725
Extruded PP	—	115	23.1	13.2	29.8	700
PSU	0.25	129	23.9	13.5	33.1	745
PSU	0.50	150	26.1	13.0	31.9	700
PSU	1.00	144	24.5	12.8	28.9	675
PSU	2.50	134	25.5	12.2	31.7	630

Table V gives data on the coefficient of friction and abrasion resistance of silicone-modified HDPE surfaces. The tests were conducted under a load of 20 N for 4000 cycles at a speed of 650 rpm. Under these conditions, virgin HDPE showed a coefficient of friction of 0.32, which was modestly reduced to 0.24 with the addition of 5.0% by weight of the PCL–PDMS–PCL copolymer. On the other hand, when the volume of the worn material was examined, there was a drastic reduction in the abrasion of the silicone-modified systems. Under the experimental conditions used, virgin HDPE showed 0.34 mm^3 of wear. By the addition of 0.1% by weight of PCL–PDMS–PCL, the volume of the worn material decreased to 0.28 mm^3 (a reduction of 18%). As shown in Table V, as the amount of the silicone additive increased, the worn volume also decreased. At 5% PCL–PDMS–PCL addition, the volume of the worn material decreased to 0.05 mm^3, indicating a reduction of 85% or, in other terms, a very substantial, 7-fold improvement in the abrasion resistance. Similar behavior was also observed for PSU-containing HDPE, where abrasion was dramatically reduced by the addition of a silicone modifier as shown in Table V.

Table V Tribological Behavior of Silicone-modified HDPE Films (Normal Load 20 N, 4000 Cycles at 650 rpm)

Additive Type	Amount (% wt)	Coefficient of Friction	Worn Volume (mm^3)
Virgin HDPE	—	0.32	0.34
Extruded HDPE	—	0.32	0.34
PCL–PDMS-PCL	0.10	0.32	0.28
PCL–PDMS-PCL	0.25	0.31	0.20
PCL–PDMS-PCL	1.00	0.33	0.12
PCL–PDMS-PCL	2.50	0.26	0.08
PCL–PDMS-PCL	5.00	0.24	0.05
PSU	0.10	0.31	0.27
PSU	0.25	0.30	0.21
PSU	1.00	0.29	0.12
PSU	2.50	0.29	0.10
PSU	5.00	0.25	0.07

Abrasion tests for PP were performed under a load of 10 N at 650 rpm for 1200 cycles. The data on tribological behavior of PSU-modified PP are given in Table VI. For extruded PP, the coefficient of friction was determined to be 0.57. With the incorporation of PSU, a slight reduction to 0.50 was observed for the 2.5% by weight additive-containing system. This is similar behavior to that of HDPE, where only a small reduction in the coefficient of friction was observed. On the other hand, similar to modified HDPE systems, dramatic reductions in the abrasion resistance of PSU-modified PP were observed, as shown in Table VI. As the amount of PSU was increased in the blend, the volume of the worn material decreased

Table VI Tribological Behavior of Silicone-modified PP Films (Normal Load 10 N, 1200 Cycles at 650 rpm)

Additive Type	Amount (% wt)	Coefficient of Friction	Worn Volume (mm^3)
Virgin PP	—	0.56	0.60
Extruded PP	—	0.57	0.62
PSU	0.10	0.55	0.43
PSU	0.25	0.56	0.42
PSU	0.50	0.55	0.40
PSU	1.00	0.51	0.20
PSU	2.50	0.50	0.12

significantly. For the control extruded PP, the volume of the worn material was 0.62 mm^3. With the addition of 0.1% of PSU, the worn volume decreased to 0.43 mm^3, indicating a 30% improvement in the abrasion resistance. As the amount of PSU was increased to 2.5% by weight, the worn volume decreased to 0.12 mm^3, indicating a reduction of 80% or about a 5-fold improvement in the abrasion resistance. All these results clearly show the efficiency of silicone copolymer additives in improving the tribological performance of PP and HDPE dramatically.

CONCLUSIONS

The tribological properties of PP and HDPE were improved by blending these resins with small amounts of silicone-containing block copolymers. Depending on the type and the amount of the copolymer additive used, a significant reduction in the coefficient of friction and substantial improvement were observed in the abrasion resistance of the modified systems. Improvements in the tribological performance were achieved with no change in the bulk properties of these materials, as evidenced by DSC data on the level of crystallinity of the blends and their mechanical performance, determined by stress–strain tests.

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