High-Density Polyethylene Modified by Polydimethylsiloxane

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ABSTRACT: High-density polyethylene (HDPE) was modified by the grafting of polydimethylsiloxane (PDMS) through a free-radical process, in a melt-mixer chamber, using dicumyl peroxide (DCP) as an initiator. The influence of PDMS (0.2–0.8 mol %) and peroxide (0.03–0.08 mol %) concentrations on the grafting, final torque, and melt flow rate (MFR) of copolymers were investigated using factorial planning. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), MFR, and rheometry were used to characterize the copolymers obtained. Surface plots showed that higher degrees of grafted PDMS and higher final torques were obtained with increase in the PDMS amount at low DCP levels and with increase in the DCP amount at low PDMS levels. The peaks of fusion and crystallization of the copolymers showed no significant changes with respect to HDPE. Data of MFR and GPC suggested that crosslinking reactions and/or chain extension occurred concomitant with the grafting reactions. Copolymers with high grafting degrees showed high MFR and low dynamic shear viscosities in comparison with low grafting degree copolymers, which is probably due to the migration of the PDMS-containing copolymers on the surface. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3460–3467, 2001

Key words: polyethylethylene (PE); polysiloxane; graft copolymers; thermal properties; rheology

INTRODUCTION

Polyethylene is one of the most important polyolefins in terms of commercial production and technological applications. It has good mechanical and electrical properties, resistance to cold flow, ease of processing, and an excellent cost-performance relation. These characteristics of polyethylene have generated great interest in the development of polyethylene blends with other polymeric materials so as to improve some specific property or to enlarge its range of useful temperatures. In this way, blends of polyethylene with polyorganosiloxanes or silicones are of particular interest.

Polyorganosiloxanes have a number of outstanding properties, such as thermal and oxidative stability, a unique low glass transition temperature, which imparts mechanical resistance at low temperature, water and chemical resistance, water repellency, electric insulation property, high permeability to gases, biocompatibility, low surface tension, mold-release ability, and resistance to ultraviolet radiation.[1] The most widely used member of this class is polydimethylsiloxane (PDMS). Its structure is composed of highly flexible Si—O links in the main chain with methyl groups attached to silicon atoms.[1]

The major drawback of the use of PDMS in blends is its high immiscibility with carbon-based polymers; hence, it tends to be rejected from the matrix, causing fast deterioration of blend properties due to phase separation, diffusion of the polymer chains, etc. This difficulty can be overcome by forming copolymers of siloxanes with carbon-based polymers. In this way, an effective alternative is the modification of a carbon-based polymer with PDMS to form graft copolymers that will provide higher compatibility between the host polymer and the polysiloxane segments.

In the grafting process of polyethylene, or copolymers of polyethylene, with organosilicon compounds, the vinylsilane derivatives are one of the most commonly described grafting agents.[2–9] The role of the molecular structure and microstructure of polyethylene in the alkoxysilane grafting process and the network structure obtained upon moisture curing of this group have been studied.[5] Kinetics data of silane grafting and the moisture crosslinking process in the polyethylene chain and ethylene propylene rubber have been reported.[6,7] Hjertberg et al.[8] studied crosslinking reactions of ethylene vinyltrimethoxysilane (EVS) copolymers, and Palmlöf et al.[9] studied crosslinking reactions of these copolymers in different environments at various temperatures.

Although crosslinking reactions have been studied extensively, there is little research related to the product characterization and relationships between the silane grafting reaction and the properties of the grafted polyethylene.[10–13] Konar and Bhowmick[10] used contact-angle and contact-angle hysteresis techniques to characterize silane-grafted polyethylene and dibutyl maleate-grafted polyethylene. Fourier transform infrared spectroscopy (FTIR) data of low-density polyethylene (LDPE) modified by vinyltrimethoxysilane (VTMS) grafting demonstrated that, at a fixed amount of dicumyl perox-

ide (DCP), the extent of the silane grafting reaction increased with increase in the silane amount, reaction time, or temperature.[11] The thermal properties of both silane-grafted and silane-grafted water-crosslinking LDPE showed a decrease in the melting-point temperature and an increase in the decomposition temperature in relation to LDPE.[12]

Recent reports also showed the modification of polyethylene with other monomers. Chlorosilane-terminated polyethylenes were synthesized to be used as connecting molecules between a silica or glass surface and a polyethylene matrix.[13] Ghos et al.[14] studied the grafting of some acrylic monomers onto LDPE using DCP at 170°C. First-order reactions, with respect to the monomer concentration, were observed, with activation energy in the following order: acrylic acid > ethyl acrylate > butyl acrylate. The grafted products showed a much higher melt viscosity and low MFR compared to the parent polyethylene.

In this work, high-density polyethylene (HDPE) was modified with PDMS to obtain HDPE-*g*-PDMS, through a free-radical process, using DCP as an initiator in a melt-mixer chamber. The influence the amount of PDMS and of DCP on the properties of the products was investigated using factorial design. Reaction products were analyzed by FTIR, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), MFR, and rheometry.

EXPERIMENTAL

Materials

HDPE, without additives, density 0.953 g/cm^3 and MFR 2.3 g/10 min, was supplied by Ipiranga Petroquímica S.A. (Brazil) PDMS (DMS-R05 methacryloxypropyl-terminated PDMS), with a density of 0.98 g/cm^3 and molecular weight of 625 g/mol (ABCR Products), DCP 98% (Aldrich Chemical Co, USA), xylene, and THF (Merck Chemical Co), and commercial argon were used as received.

Grafting Reactions

The copolymers were prepared in a Haake Rheomix 600 internal mixer equipped with a pair of high-shear roller-type rotors. The mixer chamber was initially heated to 190°C and saturated with argon. HDPE (predried overnight) was introduced into the chamber and, after 2 min, a solu-

tion of PDMS and DCP was added. The rotor rate was set at 60 rpm and a time reaction of 12 min was previously selected. After mixing, the material was immediately pressed at room temperature and cut into small pieces. Unreacted PDMS and DCP were removed through extraction with boiling THF under an argon atmosphere for 16 h, with replacement of the solvent after each 6 h. Finally, the solution was filtered and the grafted products were dried in a vacuum oven at 40–50°C, for 48 h.

Analyses

The grafting degree of HDPE-*g*-PDMS copolymers was evaluated by infrared spectra recorded in an FTIR spectrometer BOMEN BM-102, using thin films (50–100 μm) molded at 190°C under 5 ton/cm^2 for 2 min. A calibration curve was constructed to determine the grafting degree of the copolymers. Xylene solutions of PDMS and HDPE of known composition were prepared at high temperature and cast films were produced from these solutions onto KBr crystals. The cast films were analyzed by FTIR to determine the peak areas of Si—O—Si absorption of PDMS in the 1095–1024 cm^{-1} range[15] (A_1) and the methylene group of the HDPE[15] (used as internal reference, A_2) at 720 cm^{-1}. The ratios A_1/A_2, obtained from the FTIR spectra, were plotted as a function of the PDMS content (mol %).

DSC was used to analyze the thermal behavior of the polymers. DSC TA Instruments 2920 and normal calibration procedures, involving standard material, were used. Five-to-ten milligram samples were encapsulated in aluminum pans and heated or cooled at 10°C/min, under nitrogen. Before any measurement, each sample was heated to 200°C and maintained at this temperature for 5 min to erase its thermal history. The degree of crystallinity of the copolymers was evaluated by the ratio between the enthalpy of fusion of the copolymer and the enthalpy of fusion of the perfectly crystalline HDPE ($\Delta H_f{}^0 = 64.5$ cal/g).[16]

The MFR of HDPE and HDPE-*g*-PDMS samples were measured using a plastometer under a load of 5.0 kg, at 190°C (ASTM D1238).

Molecular weights were determined by gel GPC in a Waters 150 ALC system equipped with four Toso Haas columns (13 μm) and a refractive index detector. Trichlorobenzene was used as a solvent at 140°C, and the molecular weights were calculated using a universal calibration curve constructed with polystyrene standards. The
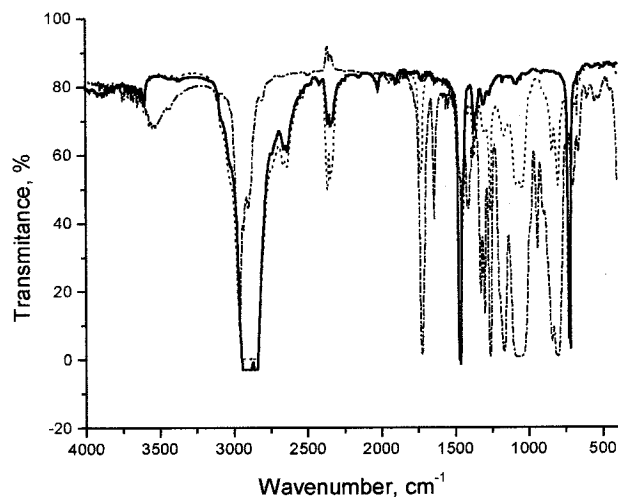

Figure 1 Infrared spectra of (—) HDPE, (— · ·) PDMS, and (· · · ·) HDPE-*g*-PDMS (PDMS 0.14 mol %).

shear viscosity of the HDPE and HDPE-*g*-PDMS copolymers were measured at 190°C, under nitrogen, in the frequency range of 1–300 rad/s using a Rheometric Scientific SR-5000 instrument and parallel-plate geometry.

RESULTS AND DISCUSSION

FTIR spectra of HDPE, PDMS, and HDPE-*g*-PDMS are shown in Figure 1. The absorption band of the HDPE-*g*-PDMS spectrum, in the 1095–1024-cm^{-1} range, demonstrated the occurrence of the grafting reaction, since this band is characteristic of the Si—O—Si groups of the PDMS main chain.

Grafted PDMS was monitored by FTIR measurements onto thin films obtained from samples after 8, 16, and 20 h of extraction. According to these measurements, there was no significant variation in the relative intensities of the Si—O—Si absorption after 16 and 20 h of extraction. An extraction time of 16 h was then chosen for the HDPE-*g*-PDMS purification.

The A_1/A_2 ratios of the cast films of HDPE/PDMS blends were plotted as a function of the concentration of PDMS. Good correlation ($R = 0.992$) among the data was obtained and the linear relation was used as the calibration curve (Fig. 2).

Grafting reactions of HDPE with 0.2% mol PDMS and 0.05% mol DCP, in relation to the repetitive unit of the HDPE chain, were carried out at 190 and 200°C with reaction times of 10
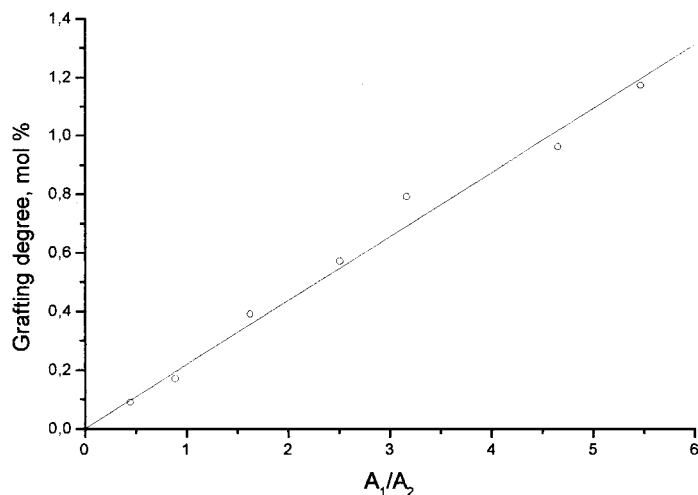
Figure 2 Calibration curve for the determination of grafting degree of PDMS onto HDPE.

and 20 min at 60 rpm. Figure 3 shows the torque–time behaviors and Table I reports the final torques and grafting degree values obtained.

The torque–time curve of pure HDPE (curve a) was characterized by an initial sharp peak due to the material loading, followed by a zone of decreasing torque, and, finally, a plateau region at nearly constant torque. Torque–time curves for the grafting reactions showed five characteristic zones: (1) initial sharp peak due to the material loading; (2) initial decrease of torque due to the material melting; (3) sharp decrease of torque due to the mixer opening (for the addition of the

PDMS and DCP mixture); (4) increase of torque attributed to the grafting reaction and, probably, to some chain coupling by a free radical (that could lead to microgel formation); and (5) a plateau region of nearly constant torque. The highest degree of grafting was obtained with 10 min of reaction at 190°C. On the other hand, the time required to reach the final plateau in the torque–time curves, which is related to the end of the reaction, was about 12 min. On the basis of these results, the grafting reactions were carried out at 190°C with a total reaction time of 12 min. After selection of the reaction temperature and time, a
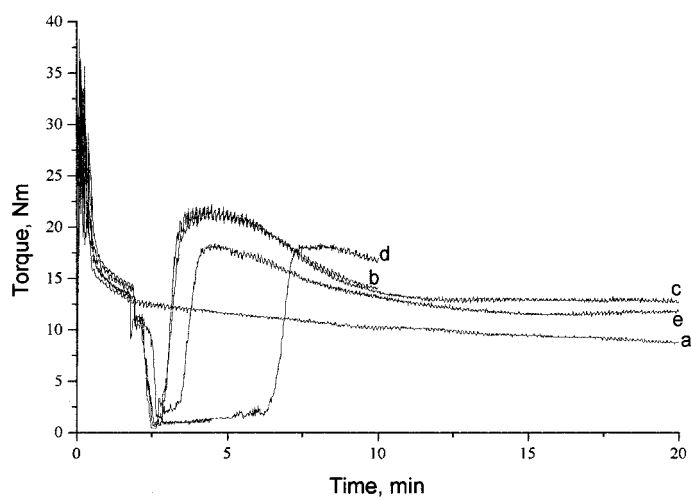

Figure 3 Torque–time curves for (a) pure HDPE and HDPE-*g*-PDMS copolymers: (b) 190°C and 10 min of reaction, (c) 190°C and 20 min of reaction, (d) 200°C and 10 min of reaction, and (e) 200°C and 20 min of reaction, using 0.2 mol % PDMS and 0.05 mol % DCP, at 60 rpm.

Table I HDPE Grafting Reaction with 0.2 mol % PDMS and 0.05 mol % DCP at 60 rpm

Reaction	Temperature (°C)	Time (min)	Final Torque (Nm)	Grafting Degree (mol %)
1	190	10	14.2	0.15
2	190	20	12.8	0.14
3	200	10	17.0	0.12
4	200	20	11.8	0.12
5[a]	200	20	8.7	—

[a] Pure HDPE processed.

factorial design[17,18] of two variables, PDMS and DCP contents, at three levels, was developed to study the effect of these variables on the following responses: grafting degree, MFR of the products, and final torque of the reaction. To reduce errors and increase the reproducibility of the model, all possible combinations of factors were run in random order with one replication. The results of factorial design are shown in Table II, and they are plotted as surface plots, to better visualize the effects of the variables on the responses. These surfaces are shown in Figure 4.

Higher grafting degrees [Fig. 4(a)] and final torques [Fig. 4(b)] were obtained with increase in the PDMS amount, keeping low to medium DCP levels. In reactions carried out at higher levels of one of the reagents (PDMS or DCP) and the increase of the other parameter led to a decrease in both the grafting degree and final torque. This latter behavior can be related to a low level of miscibility of PDMS at a high level. In addition, the HDPE-*g*-PDMS and PDMS can migrate to a sample surface, decreasing the surface tension of the material, which allows slippage of the polymer on the mixer chamber walls, leading to a low torque value and a low mixing level. This slip effect can be clearly seen in Figure 5, which shows torque–time behaviors for 0.5 mol % DCP and variable PDMS amounts (Reactions 7, 10, and 13).

Figure 6 shows the effect of DCP and PDMS compositions on the MFR values of the HDPE-*g*-PDMS copolymers. It shows that high values of the MFR were obtained with increase in the PDMS amount, keeping low DCP levels. This behavior can be related to the slip effect promoted by PDMS in the HDPE-*g*-PDMS copolymers in the pressing process. MFR values were observed in the range of 0.03–0.28 g/10 min (Tables II and III), all lower in relation to the pure HDPE (1.3 g/10 min). This decrease of the MFR after functionalization may be related to microgel formation due to chain coupling of HDPE induced by peroxide. It is important that, in this system, independently of the low MFR value obtained, the grafting process did not lead to detectable gel formation, since all the samples were soluble in xylene at elevated temperature.

These results point out that the best conditions to obtain major incorporation of PDMS are high

Table II Factorial Planning for HDPE Grafting Reaction with PDMS

Reaction	PDMS (mol %)	DCP (mol %)	Final Torque (Nm)	Grafting Degree (mol %)	MFR (g/10 min)
6	0.2	0.03	14.2	0.11	0.10
7	0.2	0.05	15.0	0.19	0.09
1	0.2	0.05	14.2	0.15	0.12
8	0.2	0.08	16.9	0.17	—
9	0.5	0.03	10.3	0.24	0.28
10	0.5	0.05	0.1	0.15	0.03
11	0.5	0.08	0.5	0.05	0.07
12	0.8	0.03	10.3	0.17	0.25
13	0.8	0.05	0.4	0.11	0.11
14	0.8	0.08	0.7	0.13	0.03
15	1	0.04	0.0	0.2	0.05
16	1.5	0.06	8.0	0.33	0.06
17[a]	—	—	10.5	—	1.3

Reaction time of 12 min, 60 rpm, 190°C.
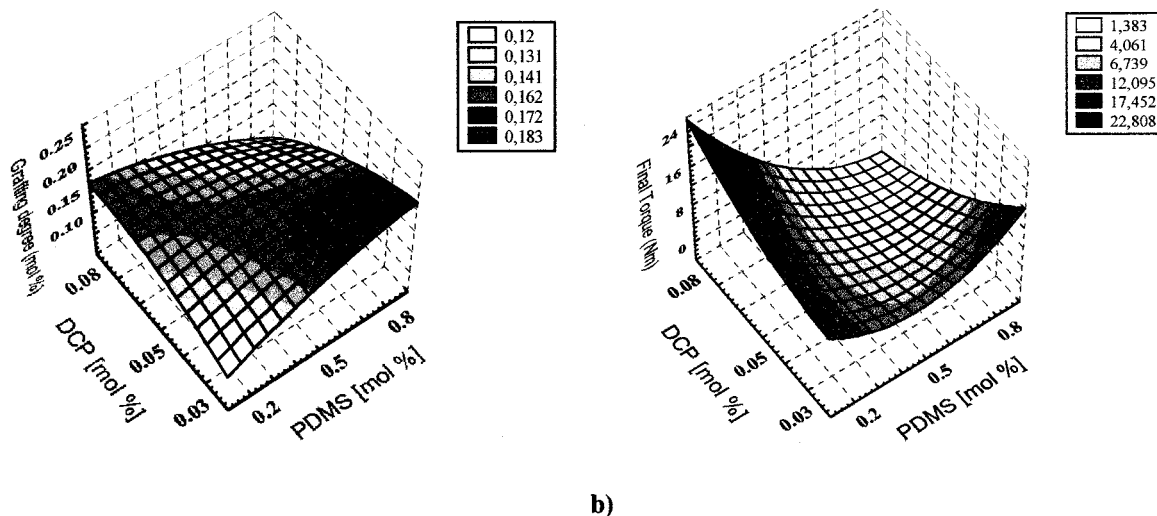[a] Pure processed HDPE.

Figure 4 Surface plots for the effect of [PDMS] and [DCP] in (a) grafting degree and (b) final torque.

PDMS and intermediate DCP levels. In this way, two final grafting reactions were carried out to obtain products with higher grafting degrees: 1.0 and 1.5 mol % of PDMS and 0.04 and 0.06 mol % of DCP. The data obtained are reported in the Table III (Reactions 15 and 16) and they confirm the tendency of increased PDMS incorporation with a high level of PDMS and an intermediate level of DCP since the highest grafting degree in this system (0.33 mol % of PDMS) was obtained with these levels.

Samples with higher grafting degrees (Reactions 16, 9, 7), and two samples with the same grafting degree, but different MFR (reactions 1 and 10), were analyzed by DSC, GPC, and rheometry. The data obtained are reported in Table III and Figure 7.

Table III shows no significant difference in the melting and crystallization temperatures for the HDPE-*g*-PDMS copolymers in relation to the processed pure HDPE. However, the crystallinity degree of HDPE-*g*-PDMS copolymers decreases
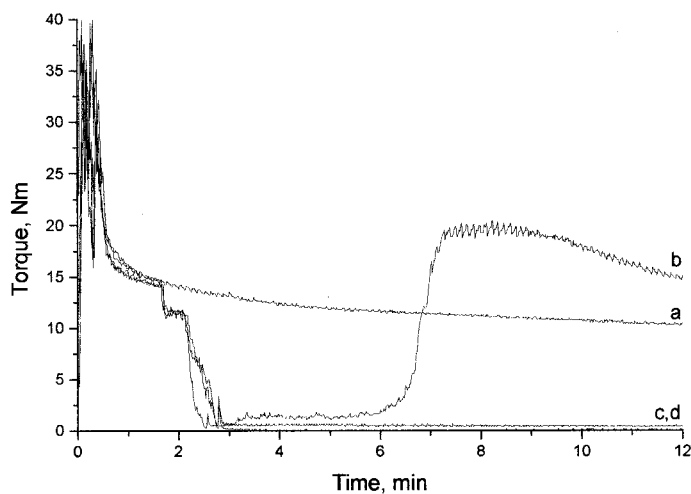

Figure 5 Torque versus time curves for (a) pure HDPE and grafting copolymers at 0.5 mol % DCP and PDMS (mol %): (b) 0.2; (c) 0.5; (d) 0.8.
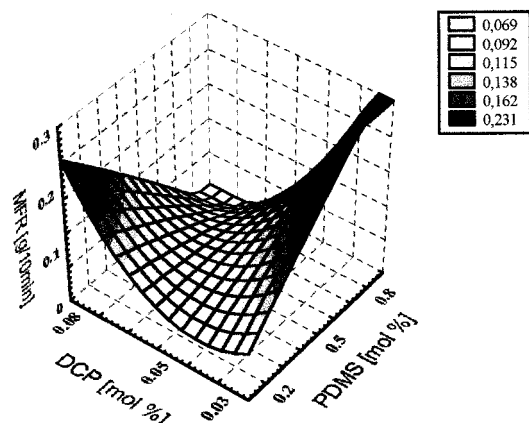
Figure 6 Effects of [PDMS] and [DCP] in the MFR of HDPE-*g*-PDMS copolymers.

with increase in the grafting degree. This behavior is probably related to the disturbance of the HDPE chain symmetry due to the presence of the grafted PDMS. The grafted copolymers showed a tendency to increase the M_z values in relation to pure processed HDPE. The sample with a higher M_z showed a lower MFR value (0.03 g/10 min) and low percentage of crystallinity (57.5%).

Dynamic shear viscosity changes of pure HDPE and HDPE-*g*-PDMS copolymers were investigated. Before trying to state a relation between the shear viscosity and grafting degrees, from curves shown in Figure 7, it is necessary to take into account the fact that the rheological behavior of the HDPE-*g*-PDMS samples is determined not only by the PDMS amount incorporated into the HDPE chain, but also by changes in the molecular weight distribution due to chain-extension reactions, by some microgel formation.

All HDPE-*g*-PDMS samples presented higher viscosity than that of the pure processed HDPE, which was another indication of these factors. On the other hand, comparing the curves obtained from Reactions 10, 1, 7, and 9, at low frequencies, a decrease in the shear viscosity with an increase in the grafting degree can be noted. The only deviation from this tendency is the one for the product of Reaction 16, which can probably be related to a higher microgel formation. This would also be the cause for the higher viscosity of Sample 10 when compared to Sample 1. On this basis, it can be suggested that HDPE-*g*-PDMS copolymers would have lower viscosity than that of the HDPE homopolymer in the absence of chain coupling during the grafting reactions. These results are in accordance with the MFR data.

CONCLUSIONS

HDPE could be modified by grafting PDMS onto the polymer backbone, using DCP as initiator in a melt-mixing process. The grafting degree was a function of both PDMS and DCP amounts. To obtain high grafting degrees, high PDMS and intermediate DCP levels must be used.

Significant effects of PDMS grafting on the melting and crystallization temperatures of the copolymers, in relation to HDPE, were not observed. However, the percentage of the crystallinity of the copolymers decreased slightly with increase of the grafting degree. The HDPE-*g*-PDMS copolymers showed higher melt viscosity (at low rate shear) and lower MFR flow rate, compared to pure HDPE, due to chain extension as revealed by the Mz values of the copolymers.

Table III   MFR, Viscosity, Thermal Behavior, and Molecular Weights of Pure HDPE and HDPE-*g*-PDMS Copolymers

Reaction	Grafting Degree (mol %)	MFR (g/10 min)	η^a (Pa s)	T_m (°C)	ΔH_f (J/g)	T_c (°C)	Crystallinity (%)	M_w/M_n	M_w (g/mol)	M_z (g/mol)
16	0.33	0.06	103,330	131.0	155.9	118.5	57.7	9	116,000	422,000
9	0.24	0.28	63,873	131.7	158.5	118.4	58.7	9	121,000	441,000
7	0.19	0.09	115,280	132.7	160.1	117.8	59.5	11	108,000	394,000
1	0.15	0.12	139,090	133.7	166.1	117.5	61.5	8	90,000	317,000
10	0.15	0.03	149,630	131.5	155.9	117.1	57.7	10	134,000	572,000
17[b]	—	1.3	49,310	132.4	166.7	118.7	61.7	9	111,000	394,000

[a] η at 0.1 rad/s.
[b] Pure processed HDPE.
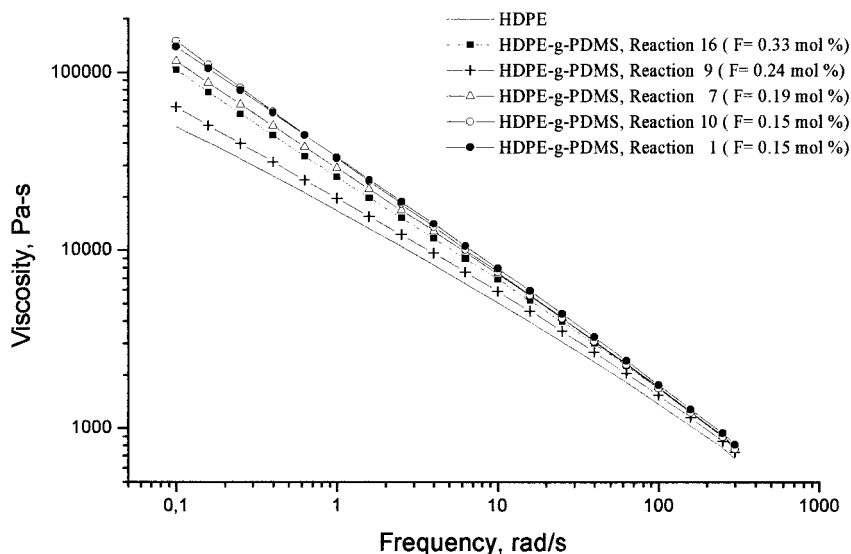
Figure 7 Viscosity of pure HDPE and HDPE-*g*-PDMS copolymers as a function of frequency.

REFERENCES

1. Hardan, B.; Torkelson, A. In Encyclopedia of Polymer Science and Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 15, p 204.
2. Cartasegna, S. Rubb Chem Technol 1986, 59, 722.
3. Dow Corning, Brit Patent 1 286 460, 1972.
4. BICC/Maillefer, Brit Patent 1 526 398, 1978.
5. Wong, W. K.; Varrall, D. C. Polymer 1994, 35, 5447.
6. Sen, A. K.; Mukherjee, B.; Bhattacharyya, A. S.; De, P. P.; Bhowmick, A. K. J Appl Polym Sci 1992, 44, 1153.
7. Sen, A. K.; Mukherjee, B.; Bhattacharyya, A. S.; De, P. P.; Bhowmick, A. K. J Therm Anal 1993, 39, 887.
8. Hjertberg, T.; Palmlöf, M.; Sultan, B. A. J Appl Polym Sci 1991, 42, 1185.
9. Palmlöf, M.; Hjertberg, T.; Sultan, B. A. J Appl Polym Sci 1991, 42, 1193.
10. Konar, J.; Bhowmick, A. K. J Appl Polym Sci 1993, 48, 1579.
11. Shieh, Y.-T.; Tsai, T.-H. J Appl Polym Sci 1998, 69, 255.
12. Shieh, Y.-T.; Tsai, T.-H. J Appl Polym Sci 1998, 70, 1075.
13. Duchet, J.; Chapel, J. P.; Chabert, B.; Sptiz, R.; Gerard, J. F. J Appl Polym Sci 1998, 70, 1075. 14, Ghos, P.; Chattopadhyay, B.; Sem, A. K. Polymer 1998, 39, 193.
15. Silverstein, R. M.; Bassler, G. C.; Morril, T. C. Spectrometric Identification of Organic Compounds, 5th ed.; Wiley: New York, 1991.
16. Beach, D. L.; Kissin, Y. V. In Encyclopedia of Polymer Science and Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 6, p 458.
17. Schimidt, S. R.; Launsby, R. G. Understanding Industrial Design of Experiments, 4th ed.; Air Academy: Colorado Springs, CO, 1994.
18. Montgomery, D. C. Design and Analysis of Experiments, 3rd ed.; Wiley: New York, 1991.