Composition-Dependent Properties of Polyethylene/Kaolin Composites. I. Degree of Crystallinity and Melting Behavior of Polyethylene

E. G. PRIVALKO,¹ A. V. PEDOSENKO,¹ V. P. PRIVALKO,¹ R. WALTER,² K. FRIEDRICH²

¹ Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv, Ukraine

² Institute of Composite Materials Ltd., University of Kaiserslautern, D-67663, Kaiserslautern, Germany

Received 5 August 1997; accepted 10 December 1998

ABSTRACT: Injection-molding and blow-molding grades of high-density polyethylene composites containing up to 30 vol. % of calcinated Kaolin were characterized by measurements of melting temperatures (T_m) , heats of fusion (ΔH_m) and room-temperature densities. Both T_m and the degree of crystallinity of a polymer matrix proved essentially unchanged regardless of filler content and/or presence of a custom coupling agent. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1267–1271, 1999

Key words: polyethylene/Kaolin composites; degree of crystallinity; melting temperature; density

INTRODUCTION

The original purpose of adding mineral fillers to polymers was primarily the one of cost reduction. However, in recent years fillers have come to play an increasingly functional role. Addition of mineral fillers was a common practice for improving the cost/performance balance of polyolefins, with particular reference to the increase of stiffness and temperature resistance, and to the reduction of creep, shrinkage, warpage, and thermal expansion. In general, it can be stated that the mechanical properties, and in particular impact strength and toughness, can be drastically varied, depending on matrix characteristics, type, and content of filler, and the adhesion between filler and matrix.¹⁻⁷ For a fundamental understanding of the material properties as well as for an optimized processing, the melting behavior and the crystallinity of a matrix in a filled system is of high importance.

The present investigation deals with a Kaolin-filled high-density polyethylene (HDPE), which might be an alternative to polypropylene for injection molding and for mica-filled HDPE in blow-molded parts.^{8,9} In this first article of the present series, it was of particular interest to study the effect of filler particles on the final crystallinity and melting behavior of the HDPE-matrix.

EXPERIMENTAL

Materials

The materials used as a matrix were HDPE for injection molding (I) applications and HDPE for blow molding (B). For blow molding, a higher viscosity is necessary. Reinforcement was obtained by Kaolin particulates [China clay of the formula $Al_2O_3(SiO_2(2H_2O)]$ with a density of 2.63 g/cm³ and two different particle sizes (the equivalent spherical diameters and matrix data are given in Table I). The crystal structure of the filler was essentially destroyed by calcination above 400°C, so that the hydrated water was removed and, therefore, the surface catalytic activity was

Correspondence to: R. Walter.

Contract grant sponsor: BMBF; contract grant number: UKR-031-96.

Journal of Applied Polymer Science, Vol. 73, 1267-1271 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/071267-05

| Matrix | | + Filler + Coupling Agent | | | | |
|---------------------|--------|---------------------------|------|-------|-----|----|
| | Kaolin | | | | | |
| | Con | tent | Si | ze | | |
| HDPE | vol % | wt % | [ESD | , μm] | | |
| Injection molding | 10 | 23 | 0.80 | 1.40 | yes | no |
| | 15 | 33 | 0.80 | 1.40 | yes | no |
| Density 0.953 | 20 | 41 | 0.80 | 1.40 | yes | no |
| MFI [g/10 min] 4.00 | 30 | 54 | 0.80 | 1.40 | yes | no |
| Blow molding | 10 | 23 | 0.80 | | yes | |
| _ | 15 | 33 | 0.80 | | yes | |
| Density 0.944 | 20 | 41 | 0.80 | | yes | |
| MFI [g/10 min] 0.27 | 30 | 54 | 0.80 | | yes | |

Table I Sample Composition

improved.¹⁰ Of all mineral fillers except mica, Kaolin has the highest surface area.¹¹ The filler weight content (W) was varied from 0.235 to 0.542

(i.e., from 0.10 to 0.30 in volume content). Compounding, with (Y) and without (N), a custom coupling agent, was carried out by the manufac-

Table IIDensities of Composites, Melting Temperatures, and MeltingHeats of PE Matrix

| Series | W | $ ho / { m g} \cdot { m cm}^{-3}$ | $T_m/{ m K}$ | $\Delta H_m/{ m J}\cdot{ m g}^{-1}$ |
|--------|-------|-----------------------------------|--------------|-------------------------------------|
| INS | 0 | 0.949 | 402.0 | 175.0 |
| | | 0.956 | | |
| | 0.235 | 1.096 | 401.0 | 159.2 |
| | | 1.109 | | |
| | 0.327 | 1.189 | 402.5 | 138.6 |
| | | 1.212 | | |
| | 0.408 | 1.263 | 401.5 | 132.3 |
| | | 1.266 | | |
| | 0.542 | 1.468 | 401.5 | 102.3 |
| | | 1.501 | | |
| IYS | 0 | 0.949 | 402.0 | 175.0 |
| | | 0.956 | | |
| | 0.235 | 1.097 | 402.0 | 149.9 |
| | 0.327 | 1.098 | 402.5 | 118.2 |
| | | 1.125 | | |
| | 0.408 | 1.238 | 401.5 | 114.5 |
| | | 1.269 | | |
| | 0.542 | 1.436 | 403.0 | 81.8 |
| | | 1.508 | | |
| BYS | 0 | 0.940 | 403.0 | 183.1 |
| | | 0.948 | | |
| | 0.235 | 1.101 | 400.5 | 141.7 |
| | | 1.121 | | |
| | 0.327 | 1.186 | 401.0 | 124.9 |
| | | 1.161 | | |
| | 0.408 | 1.272 | 403.0 | 119.6 |
| | 0.542 | 1.412 | 402.0 | 96.0 |
| | | 1.428 | | |



Figure 1 Composition dependence of the melting heats of HDPE matrix.

turer (Enichem, Italy) on a twin-screw extruder. To demonstrate the influence of the matrix material, the samples made of either the injectionmolding type or the blow-molding type of matrix were compared on the basis of various filler volume fractions in the presence of a coupling agent. As an example, the sample coding INS means: Injection molded, without coupling agent (No); Short particles; BYS means: Blow molded, with coupling agent (Yes), Short particles.

Methods

Melting heats (ΔH_m) and melting temperatures (T_m) of HDPE were measured with the custommade differential calorimeter with diathermal shells^{12,13} (sample weight: 0.1 g; heating rate: 2°/min; mean errors of ΔH_m and T_m measurements: 1 J/g and 0.5 K, respectively).

Room-temperature densities ρ were measured by a hydrostatic weighing technique in ethyl alcohol with the Mettler AT 261 microbalance (estimated mean error: 0.001 g/cm³); the data re-



Figure 2 Composition dependence of the specific volumes of composites.



Figure 3 Distribution of Kaolin particles with a 0.8- μ m equivalent spherical diameter and a filler content of (a) 10 vol %, (b) 30 vol % in HDPE for injection molding.

ported below are the averages of at least four to five independent measurements.

RESULTS AND DISCUSSION

As can be seen from Table II, the melting temperatures $T_{\boldsymbol{m}}$ of the HDPE are composition independent, and fluctuate around the mean value $T_m = 402$ \pm 1.5 K. This result implies that the mean dimensions of lamellar HDPE crystals in the composites are not appreciably affected by Kaolin particles. In contrast, the values of the melting heats ΔH_m of the HDPE crystals in composites estimated by a linear extrapolation of the best fits to the experimental data down to W = 0 (Fig. 1) are higher than the measured values of ΔH_m for the neat polyethylenes. In quantitative terms, the degree of crystallinity of HDPE matrix $X = \Delta H_m / \Delta H_m^{\circ}$ (where $\Delta H_m^{\circ} = 290$ J/g is the melting heat of a hypothetical perfect HDPE macrocrystal¹⁴) increased from X = 0.60 in the unfilled HDPE up to X = 0.64 in the series IYS and BYS, and up to X = 0.76 in the series INS.

Apparently, the observed phenomenon should be attributed to nucleating effects of the Kaolin particles on melt crystallization of HDPE, thus promoting higher crystallinities of the HDPE matrix. The somewhat smaller nucleating effect of Kaolin in the series IYS and BYS can be tentatively explained by the migration of a coupling agent at the HDPE melt/ filler interface (i.e., by weaker interfacial interactions).

The best-fit straight lines on the specific volume $v = 1/\rho$ vs. W plots (Fig. 2) reasonably account for the experimental data over the whole composition interval for all composite series. These data can be regarded as an indirect evidence that the procedure used for melt processing of composites ensures homogeneous dispersion of individual Kaolin particles in the HDPE matrix (Fig. 3);⁶ otherwise (i.e., if the Kaolin particles agglomerate into loosely packed, polymer-free clusters), the best-fit lines would have passed well above the point for specific volume of pure kaolin at W = 1.0. A similar conclusion can be inferred from the electron microscopy studies of fracture surfaces of HDPE/Kaolin composites.⁶

An equally good fit of the straight lines to the experimental data over the whole composition interval is observed for the ΔH_m vs. v plots for series IYS and BYS (Fig. 4); in the series INS; however, the measured ΔH_m value of the neat HDPE is considerably lower than that expected from the best fit to the specific volumes of the corresponding HDPE composites ($\Delta H_m = 207$ J/g). Incidentally, this latter value yields almost the same crystallinity of the HDPE matrix in composite series INS (X = 207/290 = 0.71) as that estimated earlier from the ΔH_m vs. W plots (Fig. 1). Thus, the earlier claim about a stronger ability of Kaolin particles to nucleate HDPE crystallization in INS composite series (i.e., those without a coupling agent) could be confirmed.

CONCLUSIONS

- 1. Both the present data, as well as our earlier electron microscopy studies, confirm that the procedure used for melt processing of composites ensures homogeneous dispersion of individual Kaolin particles in the HDPE matrix.
- 2. The melting temperatures of the HDPE matrices in different HDPE/Kaolin composites are not affected by the filler particles.
- 3. The ability of Kaolin particles to promote a higher degree of crystallization of the HDPE matrix is somewhat reduced by the use of a coupling agent.



Fig. 4 (a-c) Dependence of the melting heats of HDPE matrix on the specific vlumes of composites.

This work was supported by the BMBF through the project UKR-031-96.

REFERENCES

- Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites; Marcel Dekker Inc.: New York, 1993.
- 2. Jancar, J.; Dianselmo, A.; Dibenedetto, A. T. Polym Eng Sci 1992, 32, 1394.
- Bohse, J.; Grellmann, W.; Seidler, S. J Mater Sci 1991, 26, 6715.
- 4. Fu, Q.; Wang, G. Polym Int 1993, 30, 309.
- Dolkov, H.; Hudecek, F. J Macromol Sci Phys B 1978, 15, 337.
- Walter, R.; Friedrich, K.; Privalko, V.; Savadori, A. J Adhes 1997, 64, 87.
- Gähde, J.; Müller, V.; Lebedev, Ye. V.; Lipatov, Yu. S. Polym Sci USSR 1997, 10, 1446 (from Vysokomol soyed 1977, A19, 1254).

- Savadori, X.; Scapin, M.; Walter, R. EUROFILLERS '95, Mulhouse (September 11–15, 1995) In Macromolecular Symposia; Höcker, H., Ed.; Hthig & Wepf Verlag: Zug: Heidelberg, Oxford, CT/USA, 1996, p. 183, vol. 108.
- Allen, D.; Peters, D.; Rathman, J.; Kowalski, D. In Ann. of 51st Tech. Conf. of the Society of Plastics Engineers, 1993, p. 2467.
- Howard, E. G.; Lipscomb, R. D.; MacDonald, R. N.; Glazar, B. L.; Tullock, C. W.; Collette, J. W. Ind Eng Chem Prod Res Dev 1981, 20, 421.
- Katz, H. S.; Milewski, J. V. Handbook of Fillers For Plastics; Van Nostrand Reinhold: New York, 1987.
- Godovsky, Yu. K. Thermophysical Methods of Polymer Characterization; Khimia: Moscow, 1977 (in Russian).
- Privalko, V. P.; Titov, G. V. Vysokomol Soed Ser A 1979, 21, 348.
- Wunderlich, B. Macromolecular Physics; Academic Press: New York, 1978, vol. 3.