

Preparation and Characterization of Perlite-Filled High-Density Polyethylenes. II. Thermal and Flow Properties

G. AKIN-ÖKTEM¹ and T. TİNÇER^{2,*}

¹Abant İzzet Baysal University, Department of Chemistry, 14100 Bolu, Turkey, and

²Middle East Technical University, Chemistry Department, 06531 Ankara, Turkey

SYNOPSIS

Thermal and flow properties of perlite-filled high-density polyethylenes (HDPE), studied in the first part of the paper, are discussed. Maximum peak temperatures of endotherms (T_{mp}) and the corresponding relative peak heights were examined by differential scanning calorimetry (DSC). The data obtained from a Brabender torque rheometer were evaluated to find the melt viscosities at low shear rate during preparation of perlite-HDPE composites. The filler concentration, types of HDPEs, and the use of γ -APS are found to be effective and influential factors on the thermal and flow properties of these composites. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The presence of fillers affects the thermal properties of polymer, especially when the polymer undergoes a phase transition such as crystallization after the introduction of fillers.¹⁻³ Among the thermal properties, the melting temperature for crystalline polymers is largely unaffected by the presence of fillers since crystalline material normally remains the same unless the filler can affect the crystal habit.¹ The filler may act as a nucleating and/or antinucleating agent. In these cases, crystallite size or perfection may be affected and this can influence not only the melting but also the mechanical properties dependent on the morphology.^{1,2}

It is reported that crystallinity of polymers decreases as the filler content increases, since volume occupied by the filler presents a discontinuous space for crystallization.²⁻⁶ Surface treatment usually is found to increase the degree of crystallinity if there is good adhesion between the filler and the polymer.^{7,8}

By compounding polymers with fillers, the rheological (flow) properties are also changed. The most significant parameters affecting the flow properties

of the composites are molecular parameters of polymers (molecular weight, molecular weight distribution, degree of branching), shape of the filler, volume loading, degree of particle agglomeration, and the polymer-filler interaction.^{9,10} In general, fillers tend to increase the melt viscosity and reduce the melt elasticity since the mobility of the chains is restricted by the presence of fillers.⁹⁻¹³

In the presence of a coupling agent, two different behaviors are observed in the melt viscosity. Depending on the chemical structure and the nature of the filler, coupling agents may act as adhesion promoters, thereby increasing melt viscosity,^{12,13} and, second, they may behave as lubricating agents, thereby decreasing melt viscosity.¹¹⁻¹³

In the previous paper, Part I, on the perlite-filled HDPEs, the mechanical properties were discussed.¹⁵ This second paper considers mainly the thermal and flow behavior of perlite-filled HDPE composites. The composites prepared in Part I were studied by differential scanning calorimetry (DSC) and the results were discussed in correlation with the mechanical properties and the inherent thermal properties of polyethylenes. Melt viscosity data for the composites were also evaluated and the influence of γ -APS on the flow behavior was examined. It was observed that γ -APS increased the melt viscosity values for perlite-filled HDPE composites, demonstrating that γ -APS acts as an adhesion promoter for our system.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials used, sample preparation, and application of a silane coupling agent were already provided in our previous paper: Part I.¹⁵ The irregular flake filler, perlite, was used for making HDPE composites. To provide the same thermal history, and also for other property measurements, for all composites, great care was taken during the compression-molding process. All composites were compression-molded at 200°C and 1400 kg/cm² between steel plates, after mixing in a Brabender torque rheometer. The temperature was allowed to decrease to 175°C at the

same pressure. Then, the mold was cooled by circulating tap water to room temperature. This routine cooling procedure—slow cooling followed by fast cooling—took about 30 min.

Thermal Properties

Thermal analysis data of the perlite-filled HDPE composites were obtained from DSC with a Perkin-Elmer DSC-4. Measurements were carried out by using about 5 mg of the samples with a heating rate of 20°C/min under nitrogen atmosphere.

Maximum peak temperatures were read directly

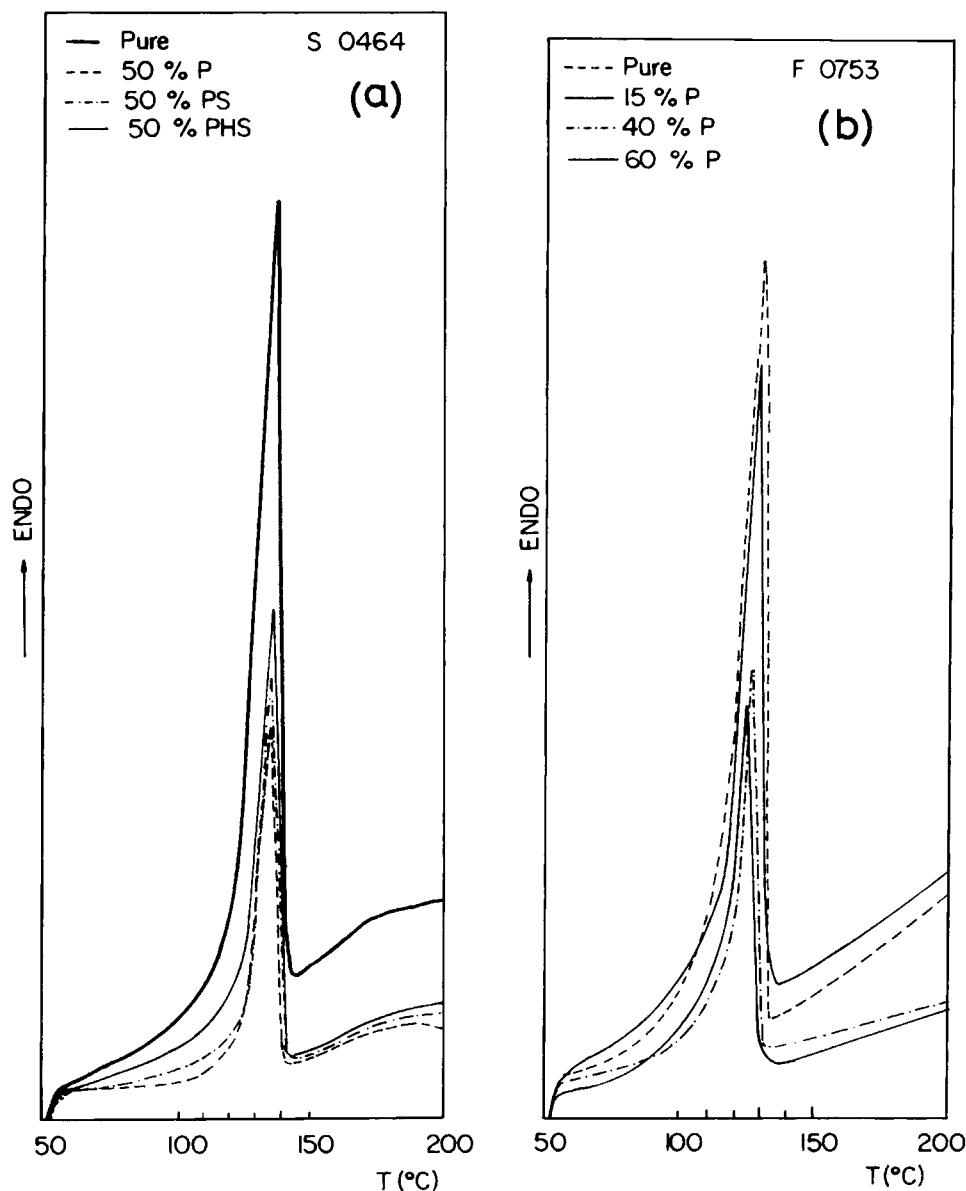


Figure 1 DSC Thermograms of (a) SO464 and (b) FO753 polyethylenes. P, S, and SH stand for untreated, dry silane-treated, and hydrolyzed silane-treated perlite, respectively.

from the calorimeter and the relative peak heights of melting curves were examined. For the calculation of relative peak heights, corrections due to the weight difference of the samples and the concentration of perlite in the composites were considered. DSC thermograms of FO753 at different compositions of untreated perlite and of SO464 at 50% perlite composition, untreated and dry and hydrolyzed silane-treated, are shown in Figure 1(a) and (b) with pure polyethylenes.

Flow Properties—Brabender Torque Data Evaluation

The recordings obtained from a Brabender torque rheometer were evaluated at the point of 10 min mixing. The viscosities are represented according to the low shear rate from the equation

$$\eta \text{ (poise)} = 360M \text{ (m-g)} / S \text{ (rpm)}$$

where M is the torque in meter-grams and S is the speed of rotation in rounds per minute. Care should

be taken in using the melt viscosity values since this is an approximate approach in evaluating the Brabender data, as noted by Goodrich and Porter.¹⁶

RESULTS AND DISCUSSION

Thermal Properties

In Figure 2(a)–(d), the variation of maximum peak temperatures of the melting curves (T_{mp}) as a function of the amount of perlite are presented. The effect of filler on melting peak temperatures of HDPEs was small, but distinguishable. The values range from 138.0 to 134.0°C for H02054P, from 130.6 to 127.2°C for F0753, from 137.5 to 134.6°C for 00660P, and from 138.0 to 137.6°C for S0464 untreated perlite composites. T_{mp} was depressed suddenly for high molecular weight, highly viscous polyethylene, H02054P, just after the initial filler loading [Fig. 1(a)]. On the other hand, for other polyethylenes [Figure 2(b)–(d)], a slight increase in T_{mp} was observed, followed by a maximum at around 10–15% compositions containing untreated and treated per-

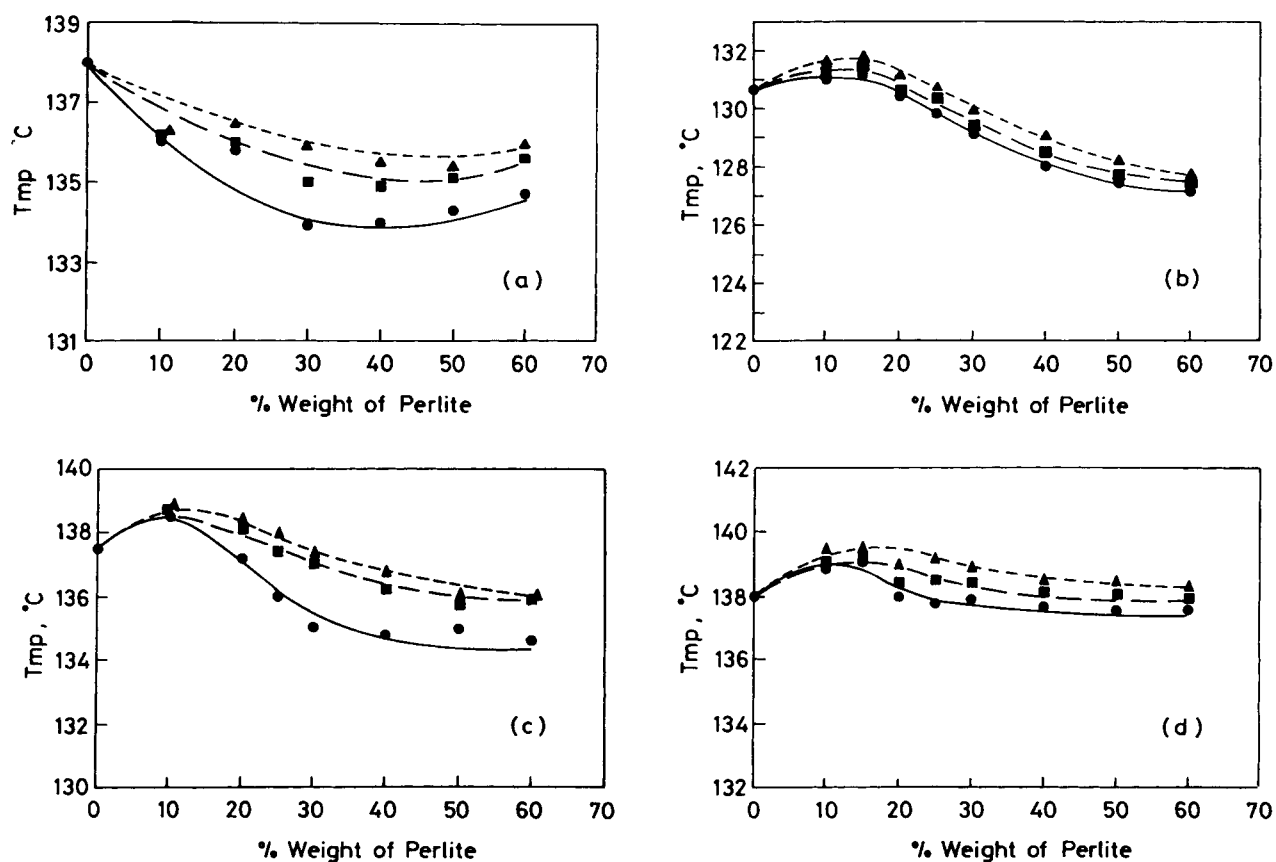


Figure 2 The variation of T_{mp} with the perlite concentration for HDPE composites: (a) H02054P; (b) F0753; (c) 00660P; (d) S0464. (●) Untreated perlite; (■) dry silane-treated perlite; (▲) hydrolyzed silane-treated perlite.

lite. T_{mp} decreased gradually, reaching a constant value after that increase. This maximum in T_{mp} was possibly caused by the restriction of mobility of polymer chains. Although the restriction of chain mobility increases with the perlite content, HDPE matrices lose their closed-packed structure and discontinuous space for crystallization increases; hence, T_{mp} and the degree of crystallinity decrease. The decrease in T_{mp} , which was also related to crystallite size and/or perfection, was affected by the presence of filler.² The decrease in T_{mp} without a maximum for H02054P composites can be explained by the long chains of this polyethylene. The long chains in the presence of perlite particles in H02054P create more discontinuous space for crystallization, which leads to an instantaneous reduction in T_{mp} values and degree of crystallinity [Fig. 2(a) and 3(a)].

Regarding the low molecular weight polyethylene S0464, we observed almost no change in T_{mp} after the mentioned maximum at 10 and 15% filler concentration; hence, any discontinuity for the crys-

tallization for the low molecular weight S0464 is not effective. In other words, S0464 appears to be at the critical limit of crystallization, free from the effect of the presence of filler.

In Figure 2(a) and (b), the relative peak heights of endotherms (i.e., the ratio of the peak height of the composites to the peak height of pure polyethylenes) are plotted against the perlite concentration. The area under the peak in DSC measurements is directly proportional to the total amount of energy transferred. Therefore, it is also related to the amount of crystallinity. Figure 2 gives a clear observation about the variation of the relative amount of crystallinity compared to pure polyethylenes with respect to the filler concentration in the composites. The degree of crystallinity decreased as the amount of perlite increased. This is expected for all composites, since the amount of filler with respect to the amount of polymer matrix (mass ratio of filler to polymer) and the discontinuous space for crystallinity increases with the concentration of filler.

γ -APS treatment augments T_{mp} and improves crystallinity, indicating that interfacial adhesion is increased by using this silane coupling agent. The effect of hydrolyzed γ -APS is more pronounced than for the unhydrolyzed case.

It was observed that, although vinylsilanes grafted to the HDPE matrix, the methacrylate silane was more effective in increasing crystallinity at the interface.^{7,8} In addition, methacrylate and aminoalkyl silanes form interpenetrating polymer networks with polyethylenes at the interface, and the improved mechanical properties of kaolin-filled HDPE composites were attributed to the polymer structure at the interface. A similar conclusion can be made for perlite/ γ -APS/HDPE systems. The degree of crystallinity is found to increase and the improved properties such as yield stress¹⁴ and other properties discussed in Parts I, II, and III may be attributed to the enhancement of morphology of polyethylenes at the interface in the presence of γ -APS.

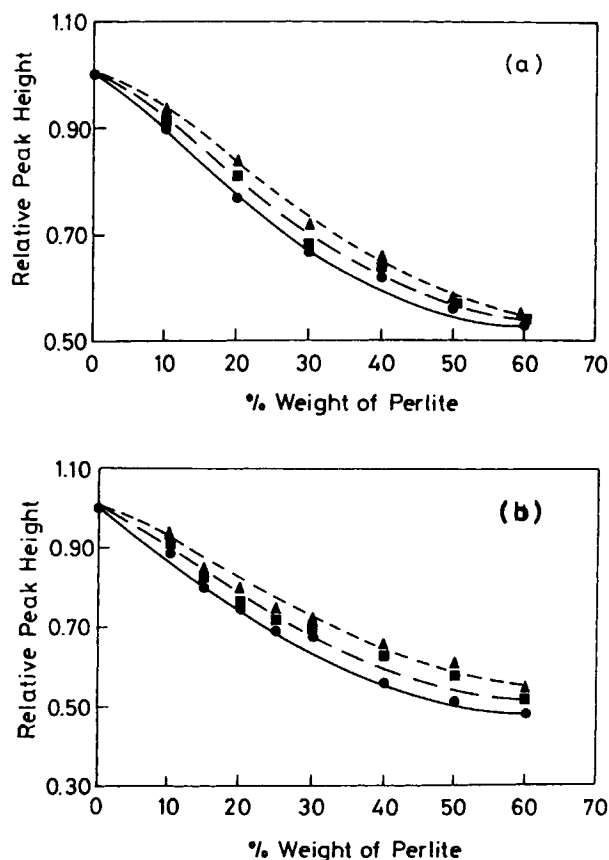


Figure 3 The variation of relative peak heights with the amount of perlite in HDPE composites: (a) H02054; (b) S0464. Symbols used for perlite treatment are the same as used in Figure 2.

Flow Properties of HDPE Composites

The variations of melt viscosity with respect to percent perlite at 10 min mixing are given in Figure 4(a) and (b) for H02054P and F0753 composites, respectively. Melt viscosity shows a maximum at 10% composition and then reduces with increasing perlite concentration for H02054P. This decrease in melt viscosity of this composite may be attributed to poor mixing of perlite and high-viscosity polyethylene, H02054P, especially at higher concentrations of perlite. Yet, it is difficult to assess the main

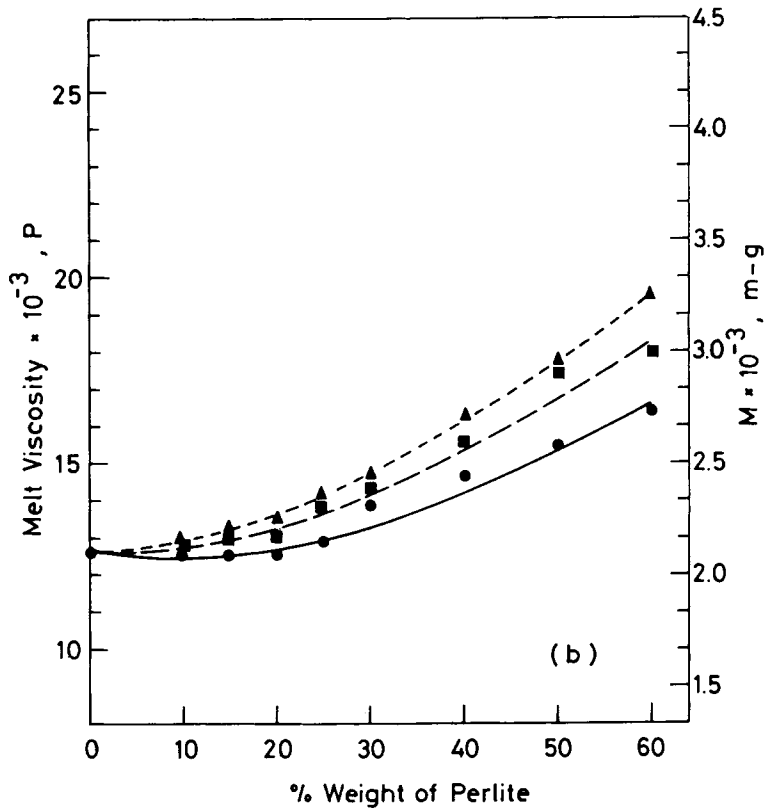
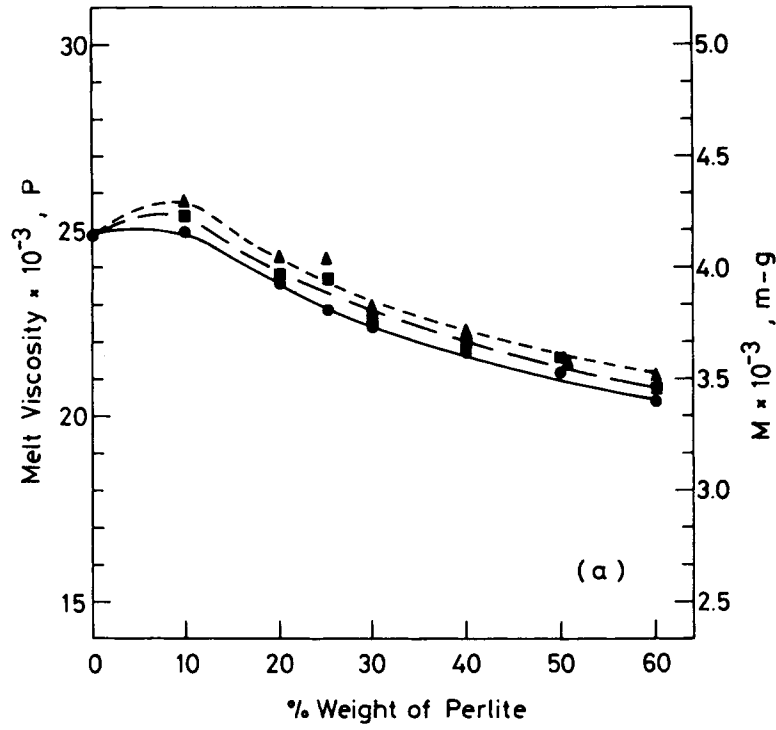


Figure 4 The variation of melt viscosity with the perlite loading for HDPE composites: (a) H02054P; (b) F0753.

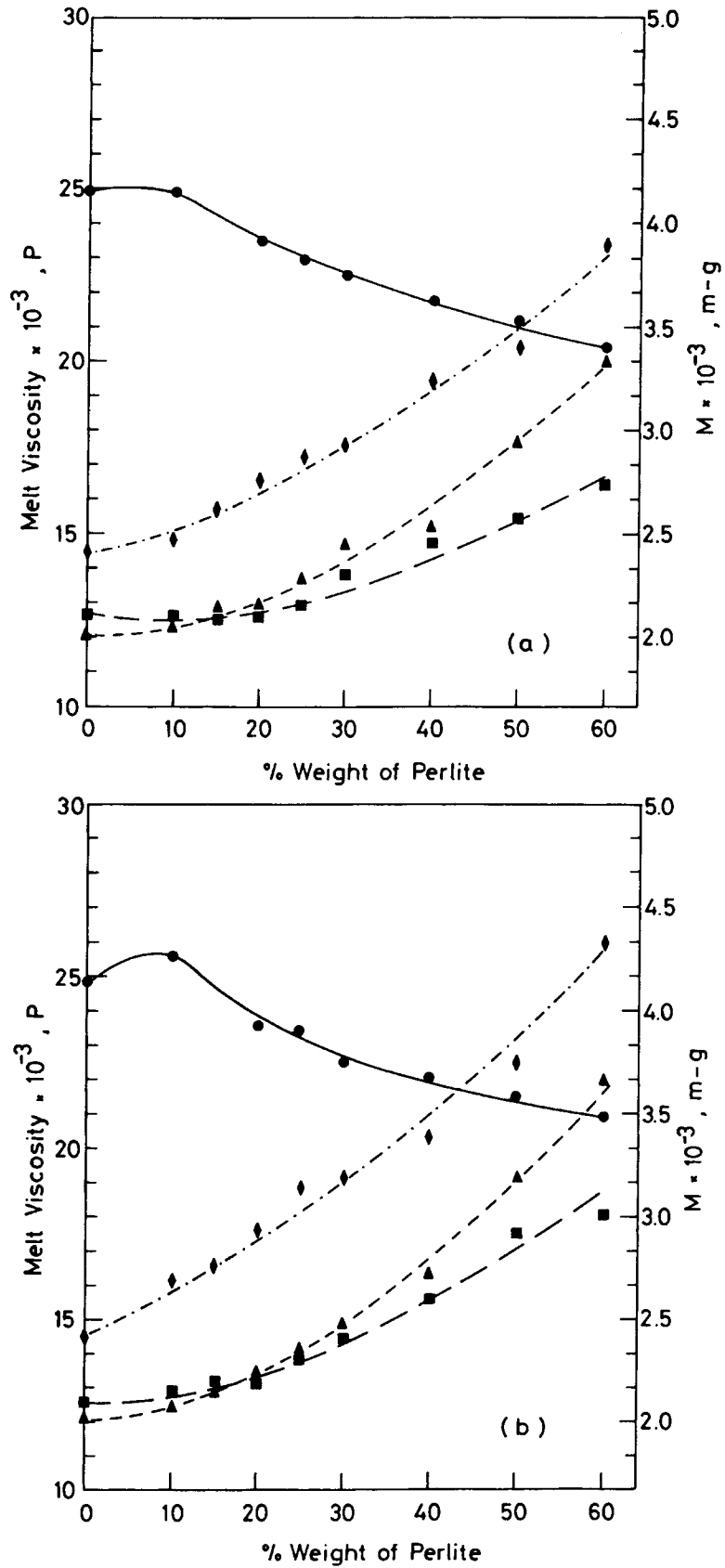


Figure 5 The comparison of the melt viscosities of perlite-HDPE composites: (a) untreated perlite composites; (b) dry silane-treated perlite composites; (c) hydrolyzed silane-treated perlite composites: (●) H02054P; (■) F0753; (▲) 00660P; (◆) S0464.

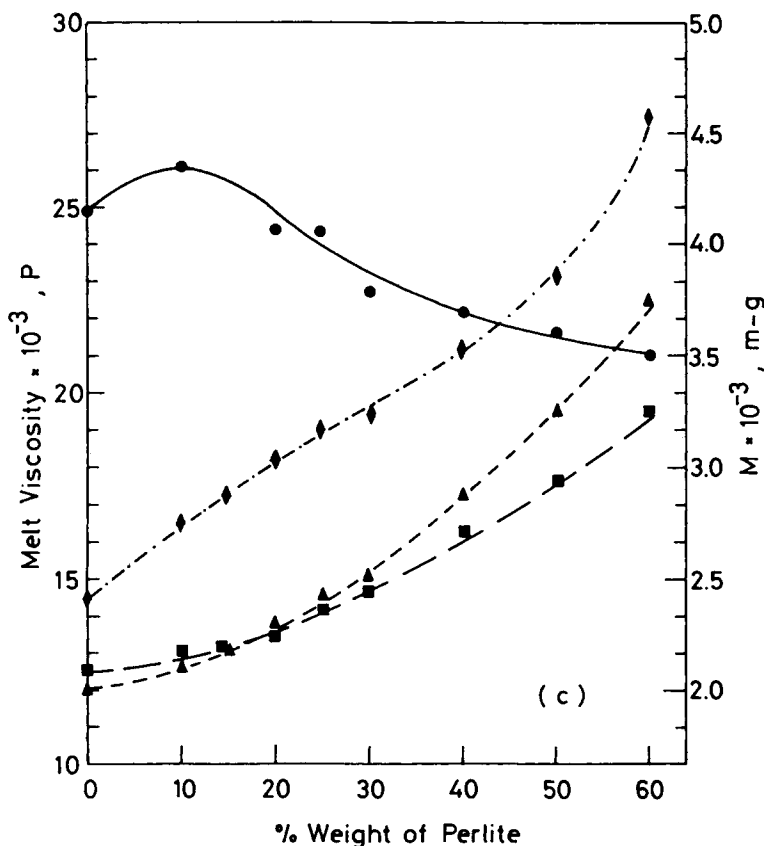


Figure 5 (Continued from the previous page)

reason because this behavior is rather unexpected, since, for the untreated compositions of H02054P, as discussed in the previous part, we did not encounter any contrary behavior in the mechanical properties due to mixing difficulties. The unusual melt viscosity variation in H02054P may be explained by its high molecular weight compared to that of the others. H02054P had a rather nonsticky character from the beginning to the end of mixing, whereas the others stuck to the walls of the mixing cavity. It should also be noted that the interfacial adhesion between H02054P polyethylene and hydrolyzed silane-treated perlite was apparently as strong as that of the others.

The melt viscosity variation of F0753 composites containing untreated and treated perlite are nearly the same as that of pure F0753 up to 20% perlite [Fig. 3(b)]. After this concentration of perlite, as expected, melt viscosity increases with the amount of perlite. For the other polyethylenes studied, melt viscosity increased as the concentration of perlite increased, as it did for F0753. The effect of molecular weight and other inherent properties of HDPEs on the variation of melt viscosities at 10 min mixing

time, with respect to treated and untreated perlite concentration, are plotted in Figure 5(a)–(c).

Silane treatment increases melt viscosities of polyethylene composites. The change in melt viscosity by the silane treatment showed no big differences in H02054P, F0753, and 00660P composites compared to the untreated samples, especially at low filler concentrations. The effect of the silane coupling agent was observed particularly at high loadings of perlite. The highest increase in melt viscosity by the treatment of γ -APS was seen in highly crystalline, low molecular weight polyethylene, S0464 composites. Upon hydrolysis of the silane coupling agent, the melt viscosity increased further compared to the unhydrolyzed one, in all cases. Hence, it can be concluded that the silane coupling agent's action as an adhesion promoter starts during melt blending.

CONCLUSIONS

Maximum peak temperatures and relative peak heights of melting curves decreased as the amount of filler increased. The slight increase in T_{mp} at lower

concentrations of perlite may be attributed to the restriction of mobility of polymer chains, for F0753, 00660P, and S0464. However, there is no increase of T_{mp} in high molecular weight polyethylene, H02054P, since the long chains of this polymer may form more discontinuous space for crystallization. For highly crystalline polyethylene, S0464, the addition of filler does not affect the T_{mp} values after a certain filler concentration: T_{mp} remains almost constant.

γ -APS treatment increases T_{mp} values slightly and augments relative peak heights that are proportional to the degree of crystallinity, indicating that the interfacial adhesion is improved by using the silane coupling agent.

Melt viscosities of polyethylene composites increased as the perlite content increased, with the exception of H02054P. H02054P showed a reduction in melt viscosity with the amounts of perlite due to its "nonsticky" property. This particular unusual behavior will be studied in more detail in the future. γ -APS increased melt viscosity in all cases, especially at high concentrations of perlite, and this demonstrates that this silane coupling agent acts as an adhesion promoter for perlite-filled HDPE systems rather than as a plasticizer.

REFERENCES

1. R. P. Sheldon, *Composite Polymeric Materials*, Applied Science, London, 1982.
2. V. P. Chacko, F. E. Karasz, and R. J. Farris, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 2177 (1982).
3. S. N. Maiti and P. K. Mahapatro, *Int. J. Polym. Mater.*, **14**, 205 (1990).
4. W. Y. Chiang and W. D. Yang, *J. Appl. Polym. Sci.*, **35**, 807 (1988).
5. C. G. Ek, J. Kubat, and M. Rigdahl, *Rheol. Acta*, **26**, 55 (1987).
6. S. F. Xavier and Y. N. Sharma, *Polym. Compos.*, **7**, 42 (1986).
7. E. P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
8. J. Gaehde, *Plast. Kautschuk*, **22**(8), 626 (1975).
9. A. V. Shenoy, D. R. Saini, and V. M. Madkarni, *Polym. Compos.*, **4**, 53 (1983).
10. D. M. Bigg, *Polym. Eng. Sci.*, **17**, 745 (1977).
11. C. D. Han, C. Sandfort, and J. H. Yoo, *Polym. Eng. Sci.*, **18**, 11 (1978).
12. C. D. Han, T. Van Ten Weche, P. Shete, and J. R. Haw, *Polym. Eng. Sci.*, **21**, 196 (1981).
13. T. M. Malik, M. I. Farooqi, and C. Vachet, *Polym. Compos.*, **13**, 174 (1992).
14. G. Akin Öktem and T. Tinçer, *J. Mater. Sci.*, **28**, 6313 (1993).
15. G. Akin Öktem and T. Tinçer, *J. Appl. Polym. Sci.*, to appear.
16. J. E. Goodrich and R. S. Porter, *Polym. Eng. Sci.*, **7**, 45 (1967).

Received September 14, 1993

Accepted January 13, 1994