

Aluminum Reinforcement of Some Polyethylenes

R. D. BÖHME, *Plastics Department, Research Laboratory,
Dow Chemical Company, Midland, Michigan 48640*

Synopsis

Filler reinforcement by aluminum powder was correlated to filler-matrix adhesion and was found to be a simple exponential function of the volume fraction for a series of polyethylenes.

INTRODUCTION

Polymer composites are potentially valuable structural materials, especially if, through the type of filler, some unusual improvement in properties can be realized. A filler which shows exceedingly large reinforcement would be of considerable importance. Synergistic reinforcement has been achieved in carbon black-filled rubbers where a high degree of dispersion and good chemical or physical interaction of the filler with the matrix has improved the matrix properties. In these systems the extent of dispersion of the filler particle and the strength of the filler-matrix bond affect the reinforcement obtained by the addition of filler.

A large variation in peel adhesion to aluminum has been observed between high-density polyethylene (henceforth abbreviated HDPE) and its copolymers, the high-density polyethylene-acrylic acid graft copolymer (HDPE-AA), and the random copolymer of ethylene and acrylic acid (PEAA).¹ Without prior treatment of the metal surface, HDPE will adhere to aluminum only very weakly, HDPE-AA will give about 6 lb./in. peel, while PEAA will show as much as 50 lb./in. peel, based on 8% acrylic acid in the copolymers. The reinforcement obtained by the filler will be compared to the reinforcement obtained by noninteracting fillers in an amorphous matrix as described by accepted equations.

Since good adhesion of matrix to filler is realized in the random copolymer of ethylene and acrylic acid filled with aluminum powder, a synergistic reinforcement might be observed.

EXPERIMENTAL

Materials

Materials used were a high-density polyethylene (HDPE), density 0.95 g./cc.; a high-density ethylene-acrylic acid graft copolymer (HDPE-

AA), density of 0.95 g./cc., graft level 8%; and an ethylene-acrylic acid random copolymer (PEAA), density 0.925 g./cc., acrylic acid content 8%.

Aluminum powder was Alcoa 101 aluminum powder, 100 mesh or 19 μ average particle size. The shape of the individual particles varied from spherical to oblong.

Procedure

Composites of HDPE, HDPE-AA, and PEAA with aluminum were prepared by blending on a roll mill with roll temperatures of 165–185°C. and milling times of 10 min. The composites were then compression-molded in a window mold at 180°C. and 20,000 psig to $1/8$ in. thickness.

From the molding rectangular bars of 0.7 cm. width and 10 cm. length were cut for the evaluation of the dynamic properties on a torsion pendulum. Test rate varied from 0.1 to 2.0 cps over the test range of -150 to $+150^\circ\text{C}.$ ²

The 10-sec. shear modulus,³ $G(10)$, was determined on a specially constructed apparatus in which the angular deflection of a horizontally mounted, rectangular bar could be measured under constant torque as a function of time. The method was based on ASTM D1043-51, but the horizontal placements of the specimens in a constant temperature air bath permitted the simultaneous measurement of four samples. Temperature control and air circulation were obtained by a Tenney temperature controller. $G(10)$ in dynes/square centimeter was derived from the torque (T in inch-pounds) and the angle of deflection (x in degrees) by eq. (1):

$$G(10) = (6.33 \times 10^8 TL)/(ab^3 \mu x) \quad (1)$$

where a , b , and L are sample width, thickness, and length in inches; μ is a shape factor based on a/b and tabulated in Table IV of ASTM D1053-54T. A temperature range of -20 to $+110^\circ\text{C}.$ was covered.

RESULTS AND DISCUSSION

Shear Properties

The measured dynamic shear modulus G' and 10-sec. shear modulus $G(10)$ are summarized in Table I for the filled polyethylenes at 25°C. G' as listed here should correspond to the shear modulus, G , within 1% for HDPE and HDPE-AA. The maximum difference between G' and G for PEAA is 4%, based on the value Δ , the logarithmic decrement.

Equations (2) and (3) express these relations:

$$\tan \delta = \Delta/\pi = G''/G' \quad (2)$$

$$G' = G \cos \delta \quad (3)$$

where G'' is the loss modulus and G' the dynamic shear modulus. $G(10)$ also should be close to the actual shear modulus, since creep in this temperature range and for this time interval is quite negligible. The values

TABLE I
Shear Moduli of Composites at 25°C.

Sample	Aluminum, vol.-%	Dynamic shear modulus $G' \times 10^{-10}$, dyne/cm. ²	Logarithmic decrement at 25°C.	Shear modulus $G(10) \times 10^{-10}$, dyne/cm. ²
HDPE	0	0.74	0.29	0.53
	5	0.85	0.28	0.48
	10	0.95	0.26	—
	20	1.20	0.25	—
	35	1.99	0.25	1.72
	50	2.68	0.35	3.22
	65	3.38	0.42	6.43
HDPE-AA	0	0.80	0.28	0.59
	5	0.90	0.27	0.59
	10	1.05	0.24	—
	20	1.50	0.26	—
	35	2.15	0.27	2.15
	50	2.80	0.31	3.70
	65	4.0	0.34	4.80
PEAA	0	0.108	0.66	0.05
	5	0.137	0.69	0.05
	10	0.15	0.70	—
	20	0.22	0.74	—
	35	0.41	0.78	0.19
	50	0.80	0.83	0.42
	65	1.30	0.87	0.95

of $G(10)$ and G' should therefore be very close and seem to be within a factor of two or better.

Figures 1-3 show the dependence of G' on the temperature from -150 to $+150^\circ\text{C}$. for the three matrix polymers and various filler contents. Similarly Figure 4 depicts $G(10)$ as a function of temperature for the polymers and filler contents of 5, 35, 50, and 65 vol.-% aluminum from -20°C . to about 100°C . Both sets of data show that an inflection temperature³ exists for all composites in the vicinity of 0°C . and from then on the materials traverse the region from glassy (modulus $> 10^{10}$ dyne/cm.²) to rubbery (modulus $\sim 10^6$ dyne/cm.²) behavior. HDPE and HDPE-AA behave in the typical fashion of a crystalline polymer—a very gradual decrease in modulus up to the melting point, while the much less crystalline PEAA shows a steeper decline in modulus. Breakdown of the modulus occurs at the crystalline melting point which is relatively unaffected by filler content. HDPE-AA filled with 65 vol.-% aluminum does, however, seem to melt at 145°C ., according to the temperature dependence of G' , although, differential thermal analysis showed a normal melting point at 132.5°C ., somewhat lower than the 136.5°C . melting point measured on the unfilled sample.

The aluminum filler, as Figures 1-4 show, has no other effect on the modulus-temperature curve than to shift it vertically at all temperatures

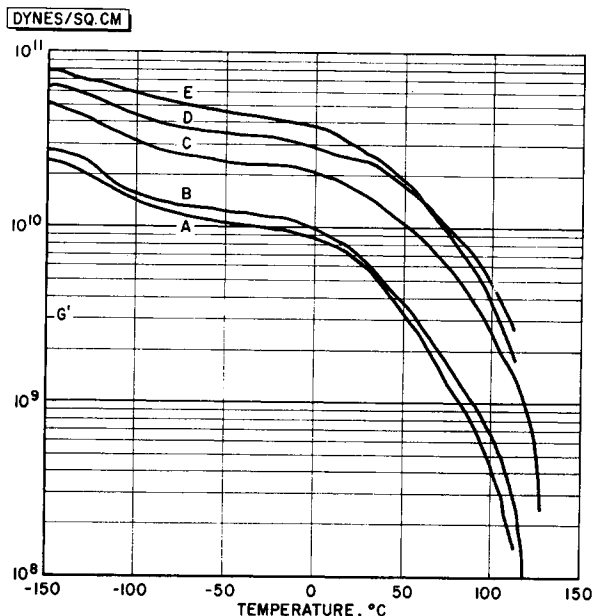


Fig. 1. Dynamic shear modulus of HDPE filled with aluminum powder: (A) unfilled polymer; (B) 5 vol.-% Al; (C) 35 vol.-% Al; (D) 50 vol.-% Al; (E): 65 vol.-% Al.

up to the melting point of the crystalline fraction in the matrix. The shift is to higher moduli with filler, contrary to the shift to lower moduli over the same temperature range, when HDPE is chemically crosslinked.⁴ Accordingly, the filler has only a minimal disrupting effect on the crystalline properties of the matrix, except perhaps at the 5% filler level, where a decrease in $G(10)$ was observed for HDPE-AA and for HDPE; G' and $G(10)$ were virtually unchanged for PEAA.

Evaluation of Composites in Terms of a Non-Interacting Filler

There exist several equations,⁵⁻⁹ theoretical as well as semiempirical, which predict the increase in tensile modulus with filler concentration. Most of these are particle size dependent, and apply to an amorphous matrix in thorough contact with a well-dispersed inclusion.

The polyethylenes under study have, in contrast to the above, a semi-crystalline continuous phase. In a first approximation, the crystallites in the polymers represent one type of crosslink, which contributes to the strength of the material. If the filler were to interfere by reducing the crystalline fraction, a modulus less than predicted should be observed. Initially, at low filler levels, an actual decrease in modulus may take place. The aluminum particle, however, replaces to some extent the lost crystalline crosslinks by strong adsorption of ethylene to its surface. The extent of this adsorption should be related to the peel strength of the respective

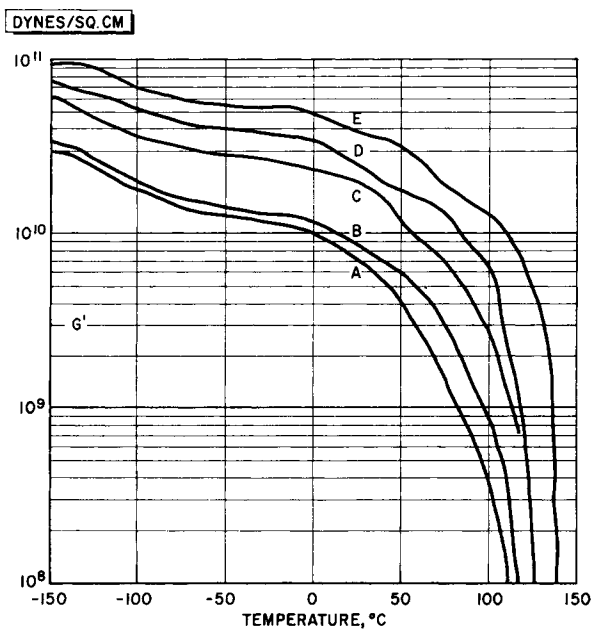


Fig. 2. Dynamic shear modulus of HDPE-AA filled with aluminum powder: (A) unfilled polymer; (B) 5 vol.-% Al; (C) 35 vol.-% Al; (D) 50 vol.-% Al; (E) 65 vol.-% Al.

matrix material. With acrylic acid in the polymer, hydrogen bonding between carboxyls of two chains represent another potential crosslink. In addition, the acid chemisorbs to the aluminum particles. However, the predominant strength-giving factor in the polyethylenes is still the crystallinity, as evidenced by the breakdown of the modulus at the melting point, and, if filler were to interfere with it, a reinforcement less than the expected should be observed. A comparison then to the predictive equations may reflect the extent of filler-particle interaction.

The simplest expression,⁶ based on a similar equation for viscosity dependence on volume fraction c of filler,⁷ describes the effect of a non-interacting filler on Young's modulus E of a composite:

$$E = E_0(1 + 2.5c) \quad (4)$$

where the subscript zero refers to the matrix. Equation (4) has been found applicable only to $c = 0.1$. To extend the applicability of this equation to higher filler level, an additional term was introduced:⁵

$$E = E_0(1 + 2.5c + 14.1c^2)$$

$$\text{For } c \leq 0.3 \quad (5)$$

More recently the shear modulus of a composite of a hard filler in a rubbery matrix has been described by Kerner⁷ and verified¹⁰ for a poly-

urethane rubber filled with NaCl. According to Kerner, shear modulus is given by:

$$G = G_0 \frac{\frac{G_1 c_1}{(7 - 5\sigma_0)G_0 + (8 - 10\sigma_0)G_1} + \frac{c_0}{15(1 - \sigma_0)}}{\frac{G_0 c_1}{(7 - 5\sigma_0)G_0 + (8 - 10\sigma_0)G_1} + \frac{c_0}{15(1 - \sigma_0)}} \quad (6)$$

where subscripts zero and one (0, 1) refer to matrix and inclusion, respectively, and σ is the Poisson's ratio. The shape of the inclusion has been accounted for theoretically⁸ by eq. (7):

$$\frac{1}{G} = \frac{1}{G_0} \left[1 + \frac{c}{1 + (2 + 4R/3)(A/5)} \left(\frac{G_0 - G_1}{G} \right) \right] \quad (7)$$

where

$$R = 3G/3K + 4G \quad (8)$$

and

$$A = (G_1/G_0) - 1 \quad (9)$$

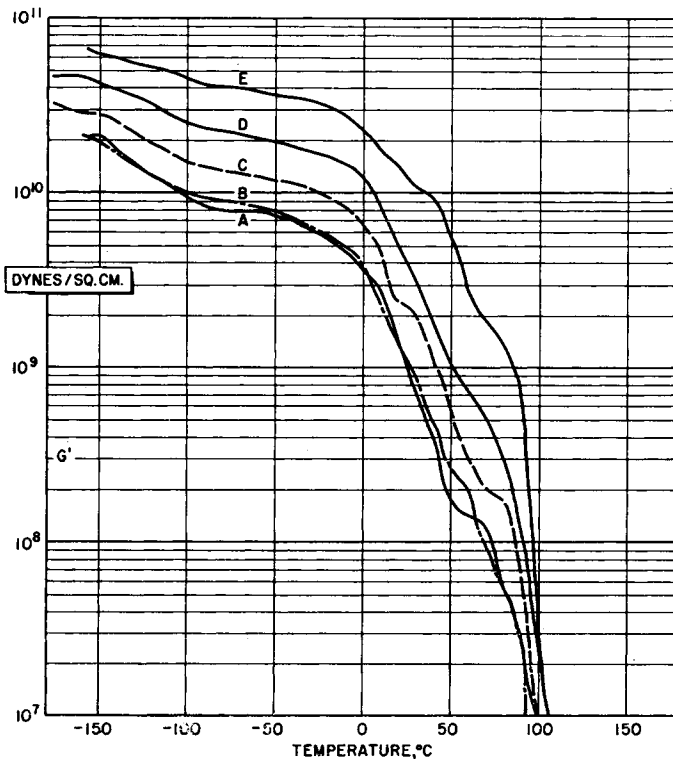


Fig. 3. Dynamic shear modulus of PEAA filled with aluminum powder: (A) unfilled polymer; (B) 5 vol.-% Al; (C) 20 vol.-% Al; (D) 35 vol.-% Al; (E) 65 vol.-% Al.

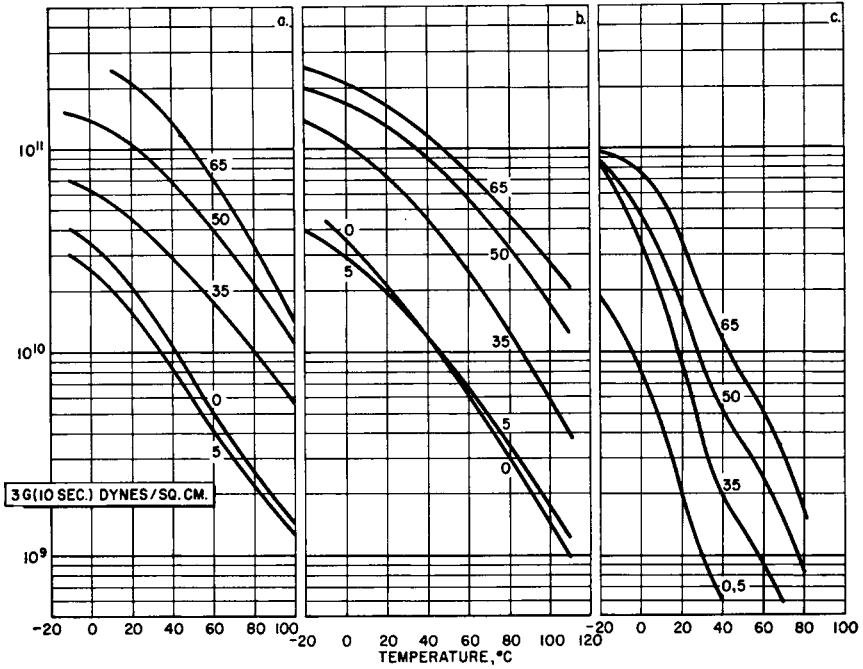


Fig. 4. The 10-sec. shear modulus for aluminum-filled ethylene polymers: (a) HDPE; (b) HDPE-AA; (c) PEAA. Numbers indicate volume-per cent of aluminum filler.

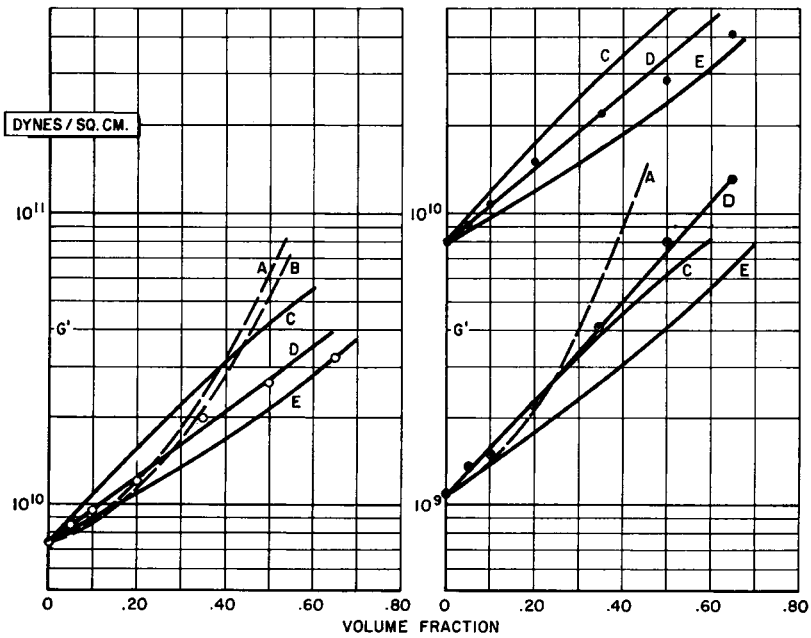


Fig. 5. Comparison of dynamic shear modulus at 25°C.: (A) eq. (7), σ ; (B) eq. (7), σ_0 ; (C) eq. (5); (D) eq. (11); (E) eq. (6); for (O) HDPE, (●) HDPE-AA, (○) PEAA.

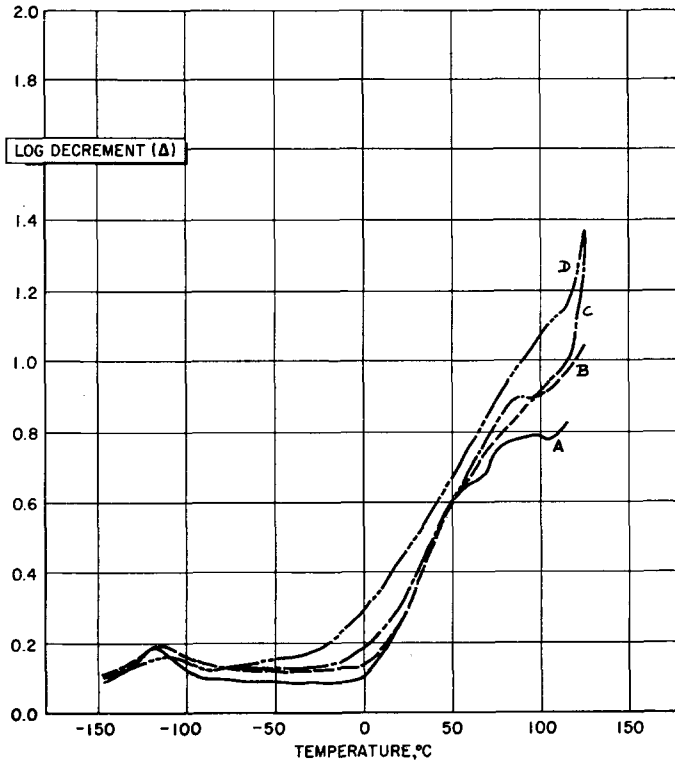


Fig. 6. Logarithmic decrement Δ of HDPE filled with aluminum powder: (A) unfilled polymer; (B) 35 vol.-% Al; (C) 50 vol.-% Al; (D) 65 vol.-% Al.

where the subscripts have the usual meaning and K is the bulk modulus, relating to G by the expression:

$$E = 2G(1 + \sigma) = 3K(1 - 2\sigma) \quad (10)$$

Figure 5 compares G' to the above expressions for the ethylene-aluminum composites, eq. (7), being evaluated for both $\sigma = \sigma_0$ and σ_1 , since the Poisson's ratio of the composite, though unknown, would be expected to fall between the above extremes. As can be seen from Figure 5, the choice of σ does not overly affect eq. (7). Figure 5 indicates quite clearly that eq. (5) gives the best overall fit and actually holds for PEAA up to a 40% filler level. The HDPE and HDPE-AA composites, however, fall below the value predicted by eq. (5) at 20 vol.-% for HDPE-AA and even lower for HDPE. Experimental data are quite well represented over a higher concentration range, by an equation of the type:

$$G = G_0 e^{Kc} \quad (11)$$

presumably as long as $G_1 \gg G_0$. It covers the entire composition range for PEAA and is a good average for the other polymers. Further-

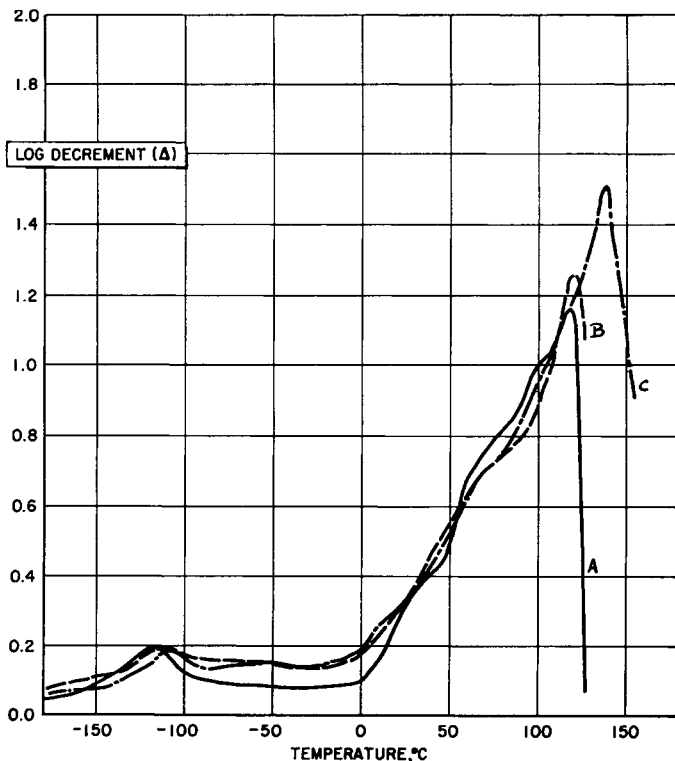


Fig. 7. Logarithmic decrement Δ of HDPE-AA filled with aluminum powder: (A) unfilled polymer; (B) 50 vol.-% Al; (C) 65 vol.-% Al.

more, eq. (11) can be readily approximated by a series solution of the form

$$G = G_0(1 + Kc + (Kc)^2/2! + \dots)$$

which immediately resembles eq. (5) and in a first-term approximation simplifies to Smallwood's equation [eq. (4)].

Examination of the present data allows us to assign some physical significance to the exponent K in eq. (11). Theoretically⁶ K should be 2.5 for a truly noninteracting filler. By experiment, K for HDPE is 2.6, for HDPE-AA 3.0, and for PEAA 3.8, in direct correspondence with the increased metal-polymer adhesion from approximately 1 lb./in. peel for HDPE to about 50 lb./in. peel for PEAA. From this point of view, K reflects the reinforcement that a filler brings to the composite and is also a measure of filler-matrix interaction. Thus the high-adhesion material, PEAA, is proportionately more reinforced by an aluminum filler than HDPE, in spite of the lower modulus of the former.

Loss Factor as a Function of Filler

The logarithmic decrement Δ as a function of filler concentration indicates that energy loss per cycle increases with filler, since the magnitude

of Δ reflects energy loss.¹¹ Figures 6-8 depict this variable for the three composite systems. The highly crystalline HDPE and HDPE-AA show only small increases in Δ below their melting point, while a loss peak around 25°C. in PEAA is considerably enhanced. The latter peak relates to the amorphous β relaxation of low-density polyethylene¹² and may thus reflect an increasingly more amorphous material as a larger percentage of the acrylic acid in the polymer is tied to aluminum particles. High filler concentrations have an additional effect: they seem to raise the energy loss

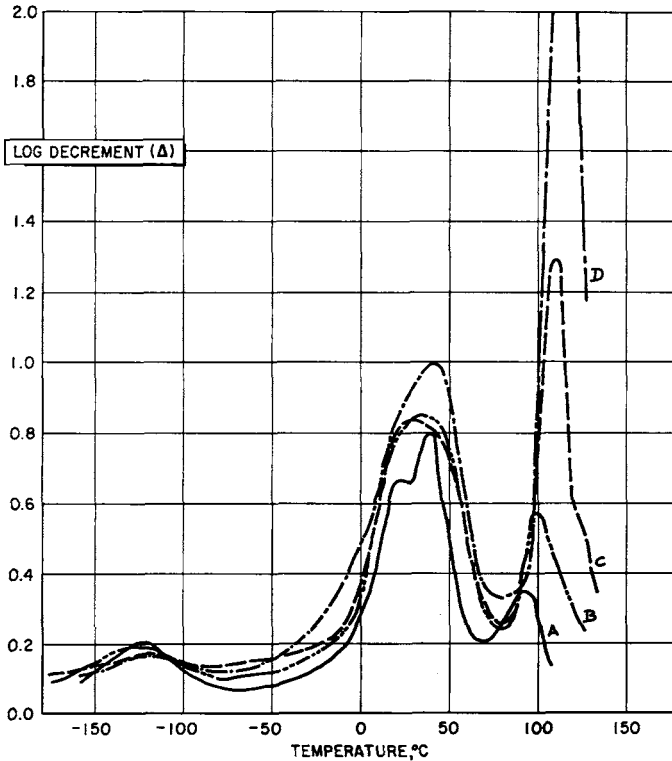


Fig. 8. Logarithmic decrement Δ of PEAA filled with aluminum powder: (A) unfilled polymer; (B) 35 vol.-% Al powder; (C) 50 vol.-% Al powder; (D) 65 vol.-% Al.

associated with melting. It can only clearly be observed in HDPE-AA, where a shift of the peak from 132 to 140°C., is noted, and in PEAA, where a shift from 95°C. to 120°C. is observed for the 65% by volume aluminum composite. For the same systems, the DTA showed a slight melting point decrease; for HDPE-AA a drop from 136.5 to 132°C., and for PEAA a drop of 2°C. from 103°C. was observed with the corresponding filler level. The energy loss is thus protracted over a larger temperature range and is increased in magnitude by the filler. Work or energy loss per

vibration depends on the Young's modulus and the relaxation time³ in a Voigt model:

$$\frac{\text{work}}{\text{cycle}} = \frac{\pi S_0^2(\omega\tau)}{E(1 + \omega^2\tau^2)} \quad (12)$$

where the retardation time τ is given by $\tau = \eta/E$, η is the viscosity, ω the frequency of vibration and S_0 the applied stress. Since a relation similar to eq. (12) should hold for the polymeric composite, E and τ are the determining variables. We know that E drops precipitously at the melting point, automatically giving rise to an increased energy expenditure as long as τ changes less rapidly during the transition from the crystalline to the amorphous state.

In highly filled composites and above the melting point of the crystalline phase, the filler particles can be expected to contribute more to the viscosity of the composite, due to particle-particle interactions, than to the elastic modulus.

The net effect of such action is a smaller decrease in τ , and correspondingly a shift in the energy dissipation maximum to higher temperatures should be observed. Better adhesion of the matrix to the filler should also contribute to the viscosity of the composite by increasing the effective radius of the filler particle. Accordingly, HDPE-AA shows a shift to higher temperatures of 8 and PEAA of 25 degrees.

CONCLUSION

The dynamic shear modulus G' of aluminum-polyethylene composites was measured, and a simple exponential dependence of the modulus on volume fraction was found to hold up to a filler volume fraction of 0.65. As metal-polymer adhesion increased, the metal proved to be a more efficient reinforcing filler and this fact was reflected in a larger exponent in the equation:

$$G' = G_0' e^{Kc}$$

where c is the volume fraction and K depends on the extent of filler-matrix interaction.

It was observed that high filler levels interfered with the net crystallinity in the polymers and that energy dissipation in the amorphous phase increased.

The author wishes to thank S. G. Turley for the measurement of G' and Δ as well as C. B. Arends for some very helpful discussions.

References

1. G. G. Vincent, private communication.
2. S. G. Turley, in *First Biannual American Chemical Society Polymer Symposium* (*J. Polymer Sci. C*, **1**), H. W. Starkweather, Jr., Ed., Interscience, New York, 1963, p. 101.

3. A. V. Tobolsky, *Properties and Structure of High Polymers*, Wiley, New York, 1960.
4. S. Bonotto, *J. Appl. Polymer Sci.*, **9**, 3819 (1965).
5. E. Guth, *Proc. Rubber Technol. 2nd Conf.*, **1948**, p. 353.
6. H. M. Smallwood, *J. Appl. Phys.*, **15**, 758 (1944).
7. E. H. Kerner, *Proc. Phys. Soc.*, **B69**, 808 (1956).
8. Tai Te Wu, *Int. J. Solids Structures*, **2**, 1 (1966).
9. R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).
10. C. W. VanderWal, H. W. Bree, and F. R. Schwarzl, *J. Appl. Polymer Sci.*, **9**, 2143 (1965).
11. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
12. R. D. Böhme and S. G. Turley, to be published.

Received September 14, 1967