

Effect of the Molecular Weight of Poly(ethylene Glycol), Used for the Surface Treatment of Calcium Carbonate, on the Tensile Modulus of Filled Oriented Polypropylene

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Synopsis

A relation between tensile modulus of oriented polypropylene filled with calcium carbonate, and modified with poly(ethylene glycol) (PEG) or alkyl phenyl ether derivatives (APED) of different molecular weights was investigated. Upon stressing, voids appear in the composites material. For systems prepared with unmodified CaCO_3 , the void volume increases with an increase of filler content. For systems containing modified CaCO_3 , the void volume is smaller than the one of the reference material and decreases with an increase of PEG or APED molecular weights (which range from 400 to 4000 for PEG). Moreover, the relative modulus of oriented composites, E_c^d/E_r^d , are reasonably accounted by the void volume irrespective of filler content and modifier molecular weight, wherein E_c^d , E_r^d are respectively the modulus of oriented composites and the modulus of oriented polymer matrix.

INTRODUCTION

The influence of the degree of filler dispersion on the mechanical properties of polymeric composites has been studied by many authors.¹⁻⁵ Inorganic fillers are commonly added to commercial thermoplastics and rubber matrices to achieve economy as well as to favorably improve their properties such as Young's modulus and heat dissipation. However, properties such as impact strength, elongation at break, and melt viscosity are usually deteriorated. In order to overcome these disadvantages, many methods have been developed based on an improvement of the adhesion between the filler and the polymer matrix.^{6,7} In the composites filled with particles, the mechanical properties are generally studied as a function of filler content, filler type, filler aspect ratio, filler/matrix adhesion, and properties of polymer matrix.⁸ Among these factors, the filler/polymer matrix interface determines largely the bulk mechanical properties of particle-filled composites. In the previous paper, we reported the properties of polypropylene filled with calcium carbonate, surface modified with phosphate esters,⁹ and titanate and poly(ethylene glycol) derivatives.¹⁰

This paper is concerned with the influence of the molecular weight of the surface treating agents, essentially, on the tensile modulus of oriented polypropylene filled with poly(ethylene glycol)-modified calcium carbonate.

EXPERIMENTAL

Materials

Polypropylene (PP, $[\eta] = 1.78$ in tetralin at 135°C) from Showa Denko Co. was used as the polymer matrix. Calcium carbonate samples (CaCO_3 , density = 2.7 g/cm³) from Bifoku Funka Co. were used as fillers. Their mean size, surface area, and size distribution are shown in Table I. Mainly F4.5 was used in this instance.

SAMPLE PREPARATION

Poly(ethylene glycol) (PEGX) and alkyl phenyl ether derivatives (APEDN) were tested as modifiers for CaCO_3 , where X is the molecular weight (MW) of PEGX, and N corresponds to the repeating unit of APEDN, as indicated in Table II. Firstly, CaCO_3 was air-dried at 105°C for 2 h. Next, 500 mL of ethanol, 100 g of CaCO_3 , and 2 g of the modifiers were introduced into a round flask to carry out the modification of CaCO_3 . CaCO_3 impregnated with PEGX or APEDN in an ethanol suspension was modified in a rotary evaporator at $50 \pm 2^\circ\text{C}$. Then, the modified CaCO_3 was dried thoroughly at 105°C for 4 h. Polymer material and modified filler samples were mixed on a two-roll mill from Kansai Roll Co. at $180 \pm 5^\circ\text{C}$ for 8 min. Filler volume fractions of 1.6, 3.2, 6.4, 9.0, 14.5, 21.0 were used. Films, 0.3 mm in thickness, were prepared by compressing of the mixed samples at $230 \pm 2^\circ\text{C}$ under a pressure of 14.7 MPa during 5 min after a preheating stage of 5 min. The molded plate was quenched by a cold press.

TABLE I
The Characteristics of CaCO_3 Particles

Filler	Average mean size (μm)	Surface area (m^2/g)	Size distribution (μm)
F1	1.0	6.1	< 3
F4.5	4.5	3.0	< 8
F15.1	15.1	1.5	5-30
F30	30.0	1.0	10-80

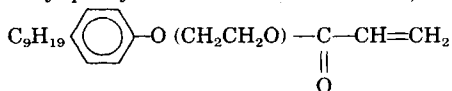
TABLE II
Modifiers for CaCO_3

Poly(ethylene glycol) (PEGX, X = molecular weight)

$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

X = 400, 600, 1000, 1540, 4000, 20,000

Alkyl phenyl ether derivatives (APEDN, N = repeating unit)



$n = 13, 16, 33, 40$

METHODS

Dumbbell-shaped samples (Japanese Industrial Standard K 6301) were cut from the films for uniaxial tensile tests. They were strained to a 600% elongation in hot water at $80 \pm 1^\circ\text{C}$ in order to prepare uniaxially oriented composites. Void volume (ΔV) is calculated from

$$\Delta V = V_1/V_0 - 1 = (h'l'w'/hlw) - 1$$

where V_1 = the volume of composites after drawing, V_0 = the volume of composites before drawing, h' , l' , w' are the length, width, and height of composites after drawing, respectively, and h , l , w , the length, width, and height of composites before drawing, respectively. The storage modulus (E') and loss tangent ($\tan \delta$) of the composites were measured, at 25°C , under a frequency of 50 Hz, using a viscoelastic spectrometer (Iwamoto Seisakusho Co.). The surface of the specimen was observed by scanning electron microscopy (SEM, Nihon Denshi Co.) in order to examine the adhesive state between the polymer matrix and the fillers.

RESULTS AND DISCUSSION

Void Volume

Figure 1 displays the variation of the void volume (ΔV) with the fillers volume fraction (ϕ). Fillers of various particle size, modified or not with PEGX or APEDN, were used. ΔV of oriented PP composites increases with an increase of filler content and filler size for unmodified CaCO_3 -filled PP. It is reasonable to expect that the filler/polymer matrix separation is smaller for F1 than that for F30. Namely, the smaller the filler size in the PP composites, the smaller the value of ΔV is. This shows that the void

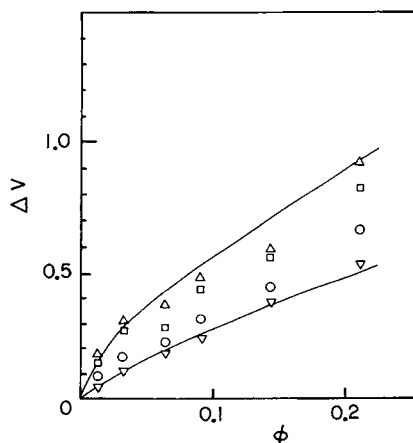


Fig. 1. Relation between void volume (ΔV) and various filler volume fractions. Unmodified systems: (∇) F1; (\circ) F4.5; (\square) F15.1; (\triangle) F30.

volume is apparently concerned with the filler content and filler size. Figure 2 shows the relationship between ΔV and ϕ for composites containing PEGX-modified CaCO_3 samples. As reported in the previous paper,⁹ the better dispersion achieved with phosphate ester $[\text{CH}_2=\text{CHOCO}(\text{CH}_2\text{CH}_2\text{O})_5\text{—OPO}(\text{OH})\text{O}—(\text{CH}_2\text{CH}_2\text{O})_5\text{OCOCH}=\text{CH}_2]$ -modified CaCO_3 leads to a greater reduction of the void volume at the filler/polymer matrix interface. ΔV of modified systems increased with an increase of filler content irrespective of the MW of the PEGX modifiers. However, the larger the MW of PEGX, the smaller ΔV is, except for PEG20000. Especially, in the case of PEG4000, the variation of ΔV with ϕ is minimum. Figure 3 gives plots of ΔV ($\phi = 0.145$) vs. MW of PEGX or APEDN. ΔV of the composites containing modified CaCO_3 decreased with an increase of the MW with range 400–4000, ΔV being minimum for PEG4000. It is seen that for all systems tested, the fillers modified with PEGX or APEDN modifiers produce a plasticizing effect, perhaps due to the improvement of the compatibility of inorganic fillers with the polymer matrix.

Consequently, the presence of PEGX or APEDN modifiers at the interface of filler/polymer matrix could decrease the void volume and could inhibit crack initiation and propagation.¹¹ This is attributed to the existence of a thin liquid layer causing the reduction of stress concentration at the interface, as indicated also by the values of the loss tangent, which increased with an increase of PEGX or APEDN MW (see Fig. 9). As far as chain length effect is concerned, the conformation of poly(ethylene glycol) chains grafted on silica, studied by Hommel et al.,^{12,13} may be indicated. Then they have shown that the polymer chain do interact more with each other in a manner consistent with the "random walk model" than do poly(ethylene glycol) oligomer chains.

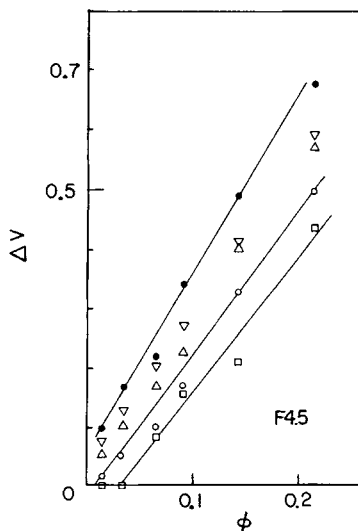


Fig. 2. Relation between void volume (ΔV) and filler volume fraction (ϕ) for various modifiers: (●) unmodified; (▽) PEG400; (○) PEG1000; (□) PEG 4000; (△) PEG20000.

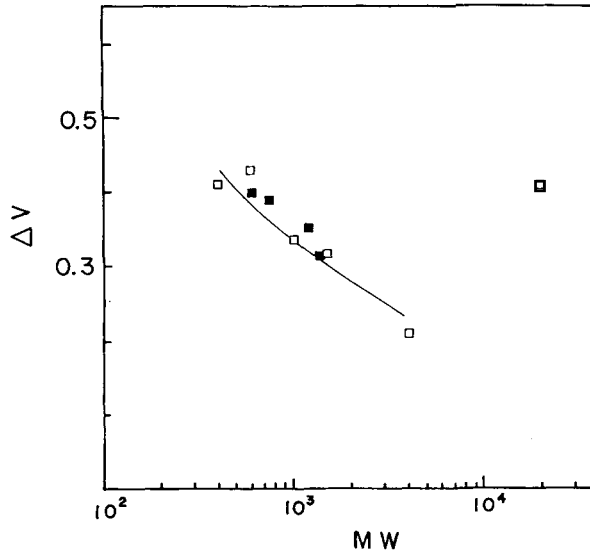


Fig. 3. Void volume (ΔV) vs. molecular weight of PEGX or APEDN: (□) PEGX; (■) APEDN ($\phi = 0.145$).

MODULUS OF ORIENTED COMPOSITES

The influence of fillers upon mechanical properties (tensile strength, Young's modulus) of polymeric composites has been investigated by many authors.¹⁴⁻¹⁶ According to Sumita et al.,¹⁷ the modulus of oriented composites is determined by three factors: (1) orientation of the matrix polymer, (2) filler volume fraction and filler size, and (3) void volume fraction upon elongation. Sumita's equation applies quite well up to $\phi = 0.075$ for silica-filled polypropylene. In order to extend the applicability to higher filler contents, the simple expression based on the theory of Sumita and Kerner's equation,¹⁸ for modulus dependence on the filler content, filler size, void volume fraction, and orientation of polymer matrix, was modified as follows. The relative modulus of oriented composites is determined by the three factors:¹⁹

1. The relative modulus is expected by Kerner's equation for undrawn and drawn samples.
2. The filler size effect is taken into account by means of a K value.
3. The orientation of composites is calculated from the orientation factor of the crystalline phase.

First, it is assumed that the filler is spherical and that the dispersion of the filler is optimum. If we assume further that the void at filler/polymer matrix interface in oriented PP composites is negligible, we may write:

$$\frac{E^d}{E_r^d} = \frac{x\phi/(7-5v^d) + (8-10v^d)x + (1-\phi)/15(1-v^d)}{\phi/(7-5v^d) + (8-10v^d)x + (1-\phi)/15(1-v^d)} = Md \quad (1)$$

When voids exist,

$$\frac{E_c^d}{E^d} = \frac{1}{1 + 15(1 - v^d) \phi v / (7 - 5v^d) (1 - \phi v)} \quad (2)$$

From eqs. (1) and (2), we obtain the following expression for the variation of the relative modulus ϕ :

$$\frac{E_c^d}{E_r^d} = \frac{Md}{1 + 15(1 - v^d) \phi v / (7 - 5v^d) (1 - \phi v)} \quad (3)$$

$$x = E_f K / E_r^d \quad (0 \leq K \leq 1) \quad (4)$$

where K value is zero, when the filler/polymer matrix interaction is negligible. When K is 1, eq. (4) is identical with Kerner's equation. In the equations, E_c^d , E_r^d , v^d , ϕv , and K are respectively the modulus of the oriented PP composites, the modulus of oriented PP, Poisson's ratio of oriented PP, the void volume fraction, and the parameter depending on filler size. For undrawn samples, when we would apply the Kerner's equation to the measuring data for ϕ , the values of K are: 0.41, 0.30, 0.27, and 0.20 for F1, F4.5, F15.1, and F30, respectively. These K values applied to the drawn samples. The overall orientation function, $Fc = (3 \langle \cos^2\theta \rangle - 1)/2$, of the polymer matrix, where θ is the orientation angle between the stretching direction and the molecular chain of the specimens, is measured and elongated specimens from the (110) and (040) X-ray ($\text{CuK}\alpha$) diffraction pattern of PP. The degree of crystallization is 0.71 according to density measurement. The behavior of the amorphous region is not considered in this paper. Figure 7 shows the relation between Fc and MW of PEGX. The larger filler content the smaller value of Fc is. Further Fc is not really dependent on MW of PEGX. Figure 4 shows the relative modulus E_c^d/E_r^d as a function of ϕ for oriented PP composites filled with unmodified and PEGX modified F4.5. For unmodified systems, E_c^d/E_r^d decreased with an increase of filler content, but E_c^d/E_r^d of PEGX-modified systems are larger than that of unmodified ones. The full lines in Figure 4 are calculated by using eq. (3), as reported earlier, which applies to higher filler contents. Figure 4 indicates quite clearly that eq. (3) gives the best overall fit. The dotted line in Figure 4 is calculated by using Sumita's equation. Figure 5 shows the relative values E_c^d/E_r^d plotted against ΔV for oriented PP composites comprising 1.6–14.5 volume fraction of F4.5 filler. The value of E_c^d/E_r^d decreases with ΔV irrespective of MW of the modifiers. Kowaleski et al.¹¹ reported that the improvement of impact strength of ethylene-oxide-oligomer-modified chalk-filled polyolefins was considered to the affinity of polymer/filler interface according to ethylene oxide oligomer layer causing the reduction of stress concentration at interface. Therefore, maybe this investigation is because of the damping effect of filler/polymer matrix interface according to the difference of MW of PEGX. Figure 6 shows the relative values E_c^d/E_r^d plotted against MW of PEGX. In the case of $\phi = 0.032$, the dependence on the E_c^d/E_r^d is not obvious, but, beyond $\phi = 0.032$, the high molecular weights of

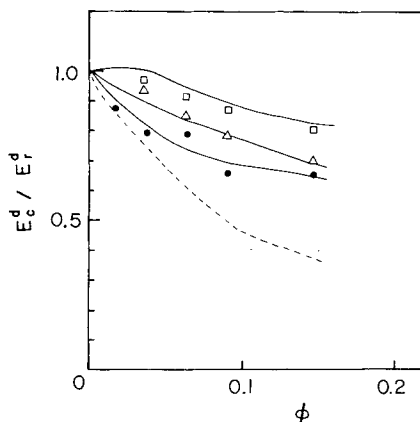


Fig. 4. Relative modulus E_c^d/E_r^d against filler volume fraction (ϕ) for F4.5 filled PP composites: (●) unmodified; (□) PEG4000; (△) PEG20000; (—) calculated from eq. (3); (---) calculated from Sumita equation.

the modifier lead to larger values of E_c^d/E_r^d , except for PEG20000. It is also seen that this fact is in relation with the reduction of void volume. Finally, Figure 8 shows the SEM photographs of the surface of oriented PP composites. The difference of filler adhesion to the polymer matrix, depending on the MW of PEGX, is clearly observed. These observations support the variation of the adhesive state between the polymer matrix and the filler with MW of PEGX.

In conclusion, the filler/polymer matrix interface plays an important role for the precision of the mechanical properties of particle-filled composites. In particular, we demonstrated the effect of the molecular weight of the

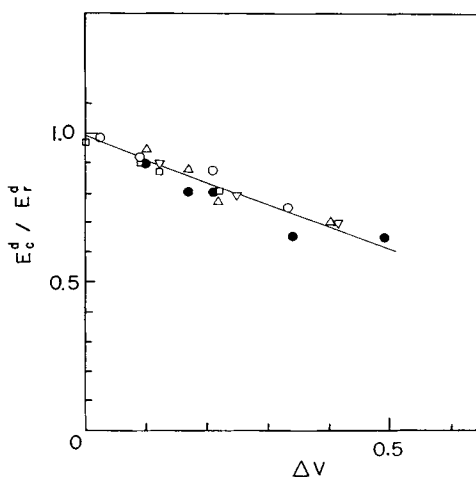


Fig. 5. Relation between relative modulus E_c^d/E_r^d and void volume (ΔV) for PP filled with modified CaCO_3 . (●) unmodified; (▽) PEG400; (○) PEG1000; (□) PEG4000; (△) PEG20000.

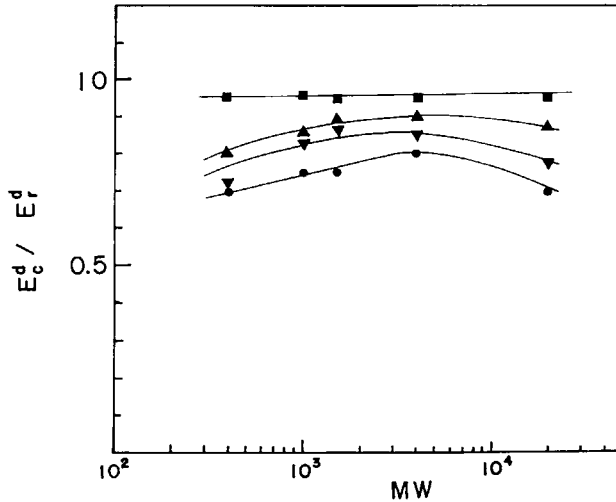


Fig. 6. Relative modulus E_c^d/E_t^d against molecular weight of PEGX for several filler content: (■) 0.032; (▲) 0.064; (▼) 0.09; (●) 0.145 (volume fraction).

modifier on the tensile modulus of oriented polypropylene, filled with poly(ethylene glycol)-modified calcium carbonate. The void volume of the filler/polymer matrix interface is smaller than that of unmodified systems. Moreover, void volume decreases with an increase of PEGX or APEDN molecular weights. Finally, the relative modulus of oriented composites are reasonably accounted for by the void volume irrespective of molecular weights of modifiers.

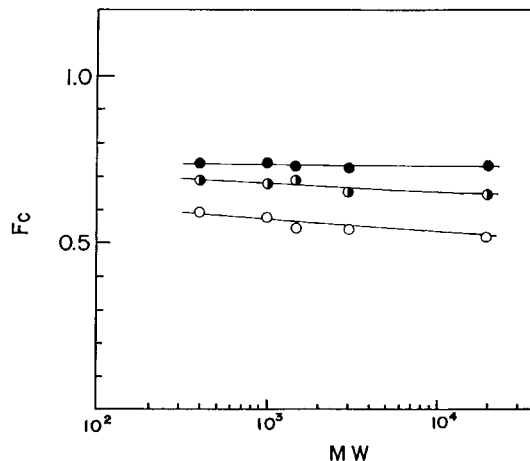


Fig. 7. Orientation factor (F_c) vs. molecular weight of PEGX. For filler content: (●) 0.032; (●) 0.145; (○) 0.21 (volume fraction).

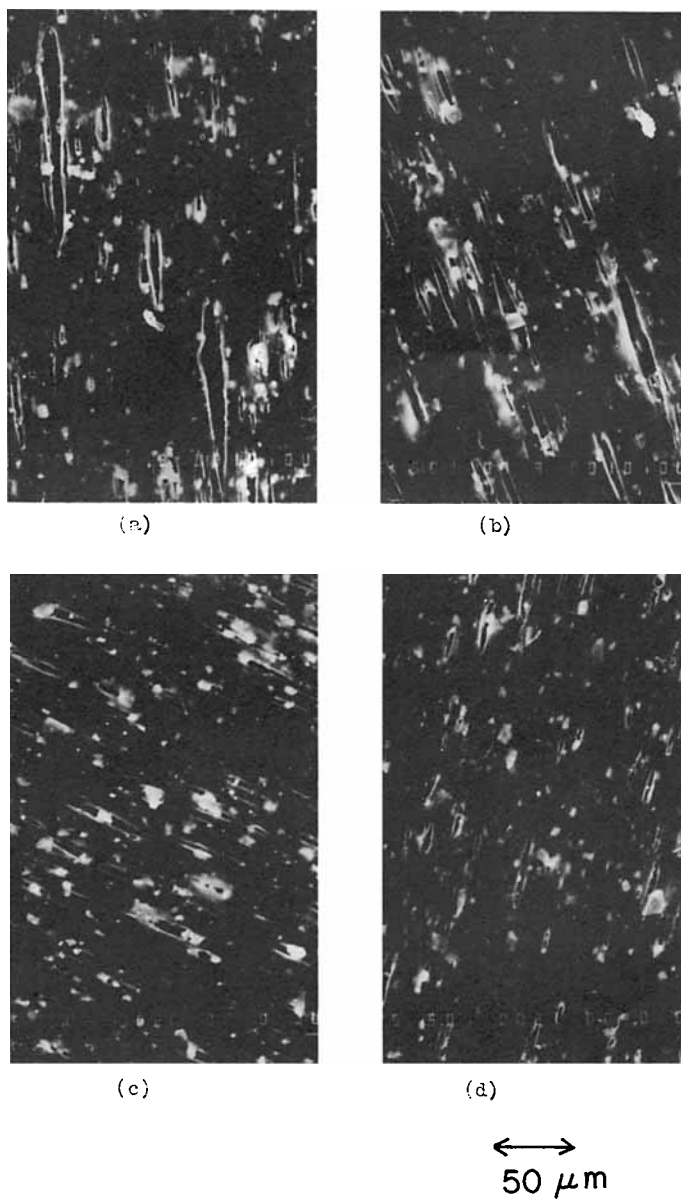


Fig. 8. SEM photographs of stretched sample ($\phi = 0.145$): (a) PEG400; (b) PEG600; (c) PEG1000; (d) PEG 4000; (e) PEG400; (f) PEG4000.

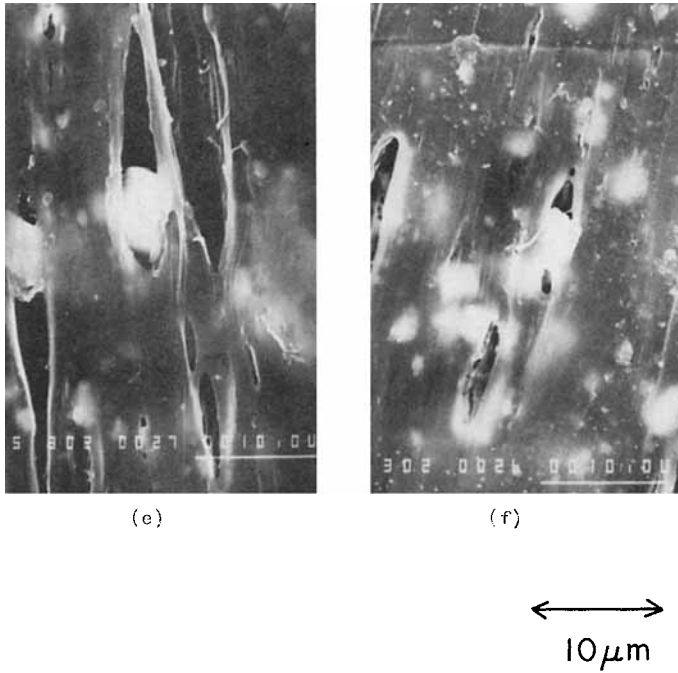


Fig. 8. (Continued from the previous page.)

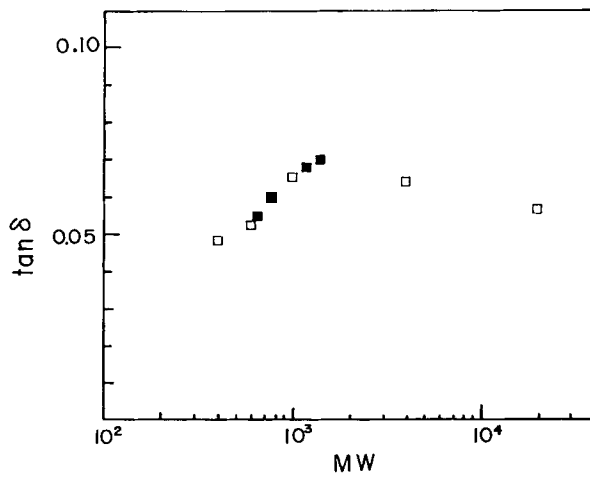


Fig. 9. Plots of loss tangent ($\tan \delta$) against molecular weight of PEGX or APEDN: (\square) PEGX; (\blacksquare) APEDN.

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