Effect of Copolyether-Ester Additives on the Melt Rheology of Polyoxymethylene

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Synopsis

Small amounts of low-molecular-weight copolyether-ester additives were shown to augment shear thinning in polyoxymethylene melts. Non-Newtonian flow increased with the decreasing molecular weight of the additive. Mechanistic implications are discussed.

INTRODUCTION

Polyoxymethylene homopolymers and copolymers of commercial significance are most usually fabricated by extrusion and injection molding.[1] Additives which may alter the melt-flow characteristics of these polymers are of interest as processing aids. In this article, we report the effect of structural and molecular-weight variation in copolyether-esters as processing additives for polyoxymethylenes.[2] (A preliminary account and additional data is found in this reference.) The rheological behavior of two-phase polymer systems is of current theoretical interest.[3,4]

EXPERIMENTAL

Materials and Procedures

Commercial, acetate-capped polyoxymethylene homopolymers and commercial, uncapped polyoxymethylene copolymer (about 2.7 mol % oxyethylene linkages randomly dispersed; Celcon M25-01) were used as received. Copolyether-esters were either commercially available, synthesized from appropriate monomers, or obtained by thermal cracking of commercially available or newly synthesized resins. Polyoxymethylene–copolyether-ester blends were prepared using a Werner and Pfleiderer 28-mm twin-screw extruder (WP) or a 1-in. Killion single-screw extruder equipped with a "Kenics" static mixer (KK) at 185–190°C. Inherent viscosities of the copolyether-esters were measured at 30°C at 0.1 g/dl in *m*-cresol. All rheology measurements were made on a capillary rheometer[5] at 200°C with an *L/D* of 16.

The apparent viscosity ratio (AVR) reported here is the ratio of melt viscosities (Z_1/Z_2) at shear stresses of 2×10^5 to 2×10^6 dyn/cm^2 (2×10^4 to 2×10^5 Pa). Viscosities are reported in poise (Pa·S $\times 10^{-1}$).

Scanning electron micrographs (SEM) were determined on freeze-fracture specimen after argon etching for 5 min.

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RESULTS

Molecular Weight of Additive

A comparison of rheology curves is given (Fig. 1) for a 25,000–30,000 mol. wt. acetate-capped polyoxymethylene homopolymer (POM-A, Z_1/Z_2 = 5200/2600) and this resin is modified with 5 wt % of each of the two copolyether-esters. The copolyether-esters of the same structure, but high and low MW, were derived from 1000 MW poly(tetramethylene ether) glycol (PTMEG), butanediol (BD), and a 3.5 ratio of ter- to isophthalic acids (49% short-chain ester units), and coded 40D-1.2 (η_{inh} = 1.2; $Z_1/Z_2 \approx$ 15,000/8000), and 40D-0.33 (η_{inh} = 0.33). Figure 1 illustrates an additional shear-thinning effect obtained with the lower-molecular-weight additive. The extent of shear thinning as a function of additive molecular weight is indicated (Fig. 2) by plotting the AVR as a function of additive solution viscosity. Clearly, this phenomenon is independent of a mixing method or additive source (direct synthesis versus thermal cracking).

Additive Structure

A number of copolyether-esters with broad structural variation (Table I) were examined as shear-thinning additives. In Figure 3, these results are superimposed over the line for the 40D copolyether-ester series of Figure 2. Additives with higher polyester contents tend to fall below the line, but otherwise, shear thinning is independent of additive structure.
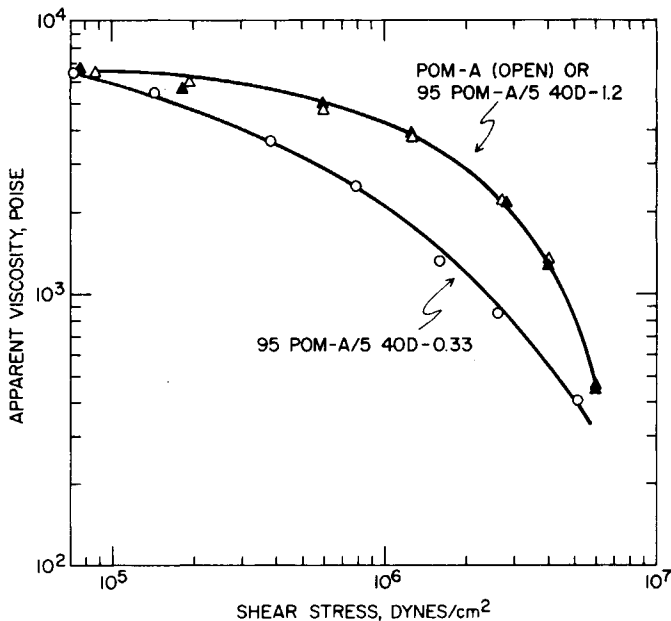

Fig. 1. Rheology of polyoxymethylene and polyoxymethylene modified with copolyether-ester additives. ▲, POM-A; △, 95 POM-A/5 40D-1.2. O, 95 POM-A/5 40D-0.33.
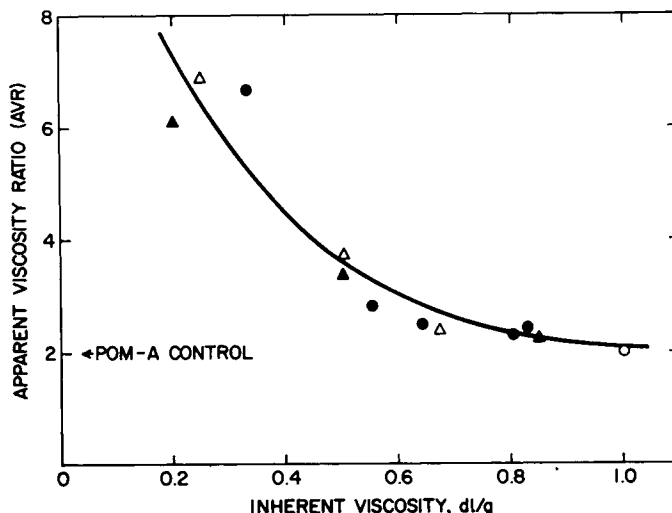
Fig. 2. Variation of AVR with inherent viscosity of additive (using POM-A). Solid points indicate WP-28 blending, open points indicate Killion–Kenics blending; circles indicate additive by direct synthesis, triangles indicate additive by cracking.

Polyoxymethylene Variations

Augmented shear thinning was also observed (Fig. 4) with higher molecular-weight acetate-capped polyoxymethylene (MW = 60,000; POM-B; Z_1/Z_2 = 37,000/18,000) and with a polyoxymethylene containing a few percent oxyethylene linkages (POM-C; Z_1/Z_2 = 26,000/12,000) (Table II).

TABLE I
Copolyether-Ester Additives (Structure Key to Figure 3)

Code	Source[a]	Poly(alkylene oxide) glycol[b]	MW polymer glycol	Low MW glycol[c]	wt %, short-chain ester units	T/I[d]
H	DS	PTMEG	1000	BD	60	all T
L	C	PTMEG	1000	BD	60	all T
O	DS	PPG	2100	EG	40	3.5
P	DS	PEG	1540	EG	50	3.5
Q	DS	PTMEG	2100	BD	27–30	2.4–9.0
R	C	PPG	2100	EG	40	3.5
S	C	PEG	1540	EG	50	3.5
T	C	PPG	1000	BD	48	3.5
U	DS	PPG	2100	EG	50	3.5
V	DS	PPG	2100	EG	75	3.5
W	DS	PPG	2100	EG	75	3.5
X	DS	PPG	2100	EG	50	3.5
Y	DS	PPG	1000	BD	48	3.5
Z	DS	PTMEG	1000	BD	85	all T

[a] Sources: DS = direct synthesis; C = cracking.
[b] PTMEG = HO$+$CH$_2$CH$_2$CH$_2$CH$_2$O$+_x$H; PPG = polypropylene glycol; PEG = polyethylene glycol.
[c] BD = butanediol; EG = ethylene glycol.
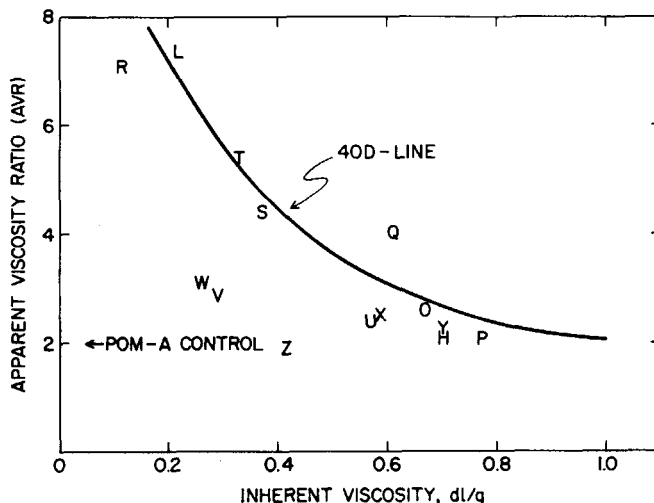[d] T/I = ratio of ter- to isophthalic acids.

Fig. 3. Variation of AVR with inherent viscosity of various copolyether-ester additives compared to variation in Fig. 2.   See Table I.

Scanning Electron Microscopy

Scanning electron micrographs of POM-A blended with copolyether-esters 40D of varying molecular weights were taken to establish the two-phase nature of the blends.   Particle size 40D is about 1 μm, independent of the molecular weight of the additive.   A typical SEM reproduction is given in Figure 5.
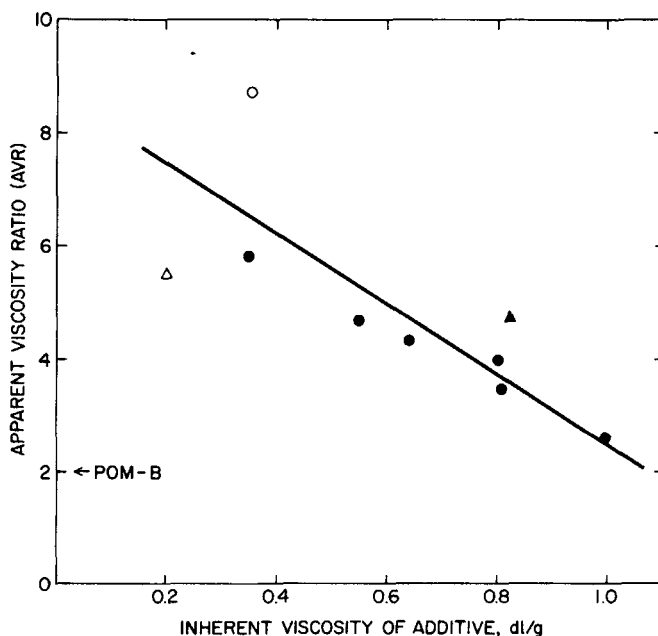

Fig. 4. Variation of AVR with inherent viscosity of additive (using POM-B). Solid points indicate WP-28 blending, open points indicate Killion-Kenics blending (some inhomogeneity); circles indicate additive by direct synthesis, triangles indicate additive by cracking.

TABLE II
Effect of 5% Copolyether-Ester Additives on Melt Flow of POM-C

Additive-η_{inh}	Source	AVR
None	(control)	2.2
40D-1.5	commercial	2.3
40D-0.55	direct syn.	4.8
40D-0.20	cracking	5.9

DISCUSSION

A reasonable model for the 5/95 copolyether-ester–polyoxymethylene system is that of the copolyether-esters which form deformable droplets dispersed in the viscoelastic polyoxymethylene fluid matrix. The higher-molecular-weight copolyether-ester additives would themselves exhibit viscoelastic (non-Newtonian) flow characteristics, but as molecular weight is reduced, the viscoelastic character should diminish and flow become more Newtonian. Han and Funatsu[6] have demonstrated that in contrast to viscoelastic droplets, shear-deformed Newtonian droplets do not recoil in the fully developed capillary region after flowing through a slit die. Thus, a gradual transition in flow characteristics of the copolyether-ester additives might explain the degree of shear thinning observed.

Newtonian Droplets in Viscoelastic Matrix

A blend with POM-A containing 5% stearyl alcohol was prepared for rheology studies. Apparent viscosities at both low and moderately high shears were substantially reduced ($Z_1 = 3500, Z_2 = 1300$ compared to $Z_1 = 5600, Z_2 = 2500$ for the unmodified control) but the extent of increased shear thinning was only modest (AVR increased from 2.2 to 2.9).
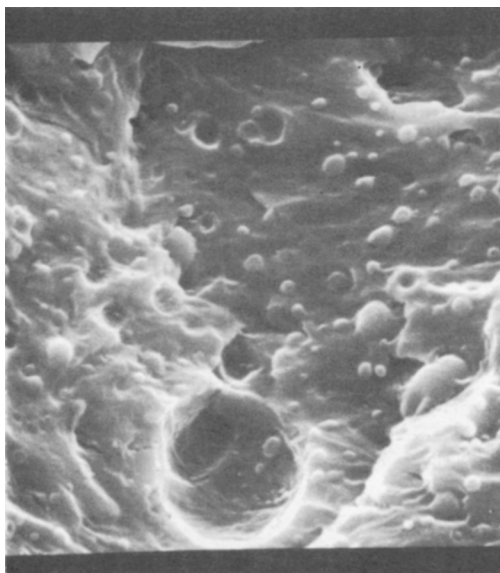

Fig. 5. SEM of 5% 40D copolyether-ester (inherent viscosity = 0.90 dl/g) in polyoxymethylene A.

Additive End-Group Analysis

As copolyether-ester molecular weight is varied, end-group concentration changes, and, to a certain extent, so does the polarity of dispersed droplets. To assess the importance of end-group polarity on the ability of these additives to augment shear thinning, we employed methods of additive synthesis that would change the nature of the ends. Direct synthesis led to mainly hydroxyl end groups, with an acidity of the lower-molecular-weight additives (η_{inh} of 0.2–0.3) of 12–13 meq./kg, whereas thermal cracking gave acidities of 300–400 meq./kg in a similar molecular-weight range (η_{inh} of 0.3–0.4). Since little or no effect on rheology could be attributed to this difference (Figs. 2 and 4), the nature or number of end groups is not likely to be of theoretical significance.

Structure of Additive

Copolyether-esters offer an unusual opportunity for structural variation. Certain high-molecular-weight resins in this class are well known, of course, as commercial thermoplastic elastomers. These are available in various degrees of "hardness." Also, various combinations of polyether glycols (variation in structure and molecular weight), short-chained glycols (variation in type and degree of incorporation), and dicarboxylic acids (variation in ratio of ter- to isophthalic acids) were used to prepare copolyether-esters. As already stated (Fig. 3), only when the additive hardness increased substantially (more ester content) did low-molecular-weight additives fail to induce substantial shear thinning. Most likely, these higher-melting additives do not disperse as well on mixing and may even contain substantially unmelted domains when suspended in the fluid matrix.

Variation in Polyoxymethylene Matrix

As already noted, changes in matrix molecular weight or incorporation of a few percent oxyethylene linkages did not affect the shear-thinning phenomenon. These changes, while substantially altering the absolute melt viscosity of the matrix, evidently do not sufficiently alter matrix–additive interactions to change the general rheological effect. Success in varying the intrinsic matrix structure and viscosity tends to argue against mechanisms that depend on slippage at the capillary wall because of variation in additive–matrix incompatibility.[7]

TABLE III
Molecular Weight Distribution of Additives in the 40D Series Determined by GPC

Sample origin	η_{inh}	$\overline{M_v}$	$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$
Commercial	1.5	118,000	131,000	63,000	2.08
Commercial	1.2	103,000	115,000	55,000	2.08
Cracking	0.82	60,000	67,000	29,000	2.29
Direct synthesis	0.35	11,000	12,000	7,300	1.66
Cracking	0.20	8,000	8,800	5,100	1.73

Molecular Weight Distribution of the Additive

Molecular weight distribution (MWD) in several of the additives in the 40D series were determined by GPC. To a certain extent, narrower MWD, if considered as a variable independent of molecular weight, should give rise to augmented shear thinning in the additive droplet itself, but differences are small compared to rheological changes expected from MW change, and not likely to alone explain the observed effects imparted to the polyoxymethylene matrix (Table III). Molecular weight values reported were measured versus polystyrene standards and are probably two- to threefold high.

CONCLUSION

Shear thinning in polyoxymethylene matrixes can be augmented by a variety of low-molecular-weight copolyether-ester additives. There is no clear theoretical explanation, although the absence of substantial viscoelastic character in the additive droplets may be a necessary but not sufficient condition.

References

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