Observations on the determination of polyamide 6 viscosity number

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The viscometric behaviour of high molecular mass polyamide 6, prepared by activated anionic polymerization of ε-caprolactam in a twin-screw extruder, has been studied in 90% formic acid. Results obtained show that viscosity number increases with polymer concentrations to ~0.001 or 0.0015 g ml^{-1}, but unexpectedly declines thereafter. Whereas anomalous results are obtained at a concentration level of 0.005 g ml^{-1}, as specified in ISO 307:1984, at very low solution concentration, viscometry data correlate well with findings from g.p.c.

(Keywords: polyamide 6; reactive extrusion; viscometry)

It is common practice to express the molecular mass of polyamides in terms of their viscosity number, determined by solution viscometry according to ISO 307:1984. This characterization procedure was applied to the analysis of polyamide 6 (PA6) made by the activated anionic polymerization of ε-caprolactam in a co-rotating twin-screw extruder, using polymer concentrations from 0.003 to 0.0002 g ml^{-1} in 90% formic acid solution, i.e. below the single point value of 0.005 g ml^{-1} specified in the ISO standard.

Using a suspended-level viscometer (size no. 2) clamped in a water bath at 25°C, efflux times for the PA6 solutions and formic acid were determined and calculated values of viscosity number were plotted against solution concentration.

Results shown in *Figure 1*, for PA6 synthesized at different extruder screw speeds, are unexpected, since the viscosity number recorded is seen to increase with concentration only up to ~0.001 or 0.0015 g ml^{-1}, decreasing in value thereafter. However, with commercial PA6 produced by hydrolytic polymerization (Capron 8202C, Allied Chemical Corp., USA), the viscosity number is found to increase linearly with solution concentration up to 0.003 g ml^{-1}. Indeed, with hydrolytic PA6 linearity up to 0.01 g ml^{-1} has been reported[1].

Limiting viscosity numbers, obtained for these polymers by extrapolating the data given in *Figure 1* to zero concentration, are listed in *Table 1*, together with corresponding values of viscosity-average molecular mass ($\bar{M}_v$), determined from:

$$[\eta] = K\bar{M}_v^{\alpha}$$

taking values of K and α of 3.77×10^{-2} and 0.80, respectively, for the polymer/solvent system under consideration[2].

To check the validity of these PA6 results, molecular mass data were also analysed by g.p.c. using 1,2-cresol at 120°C. Good agreement is seen between results obtained by solution viscometry and g.p.c., as seen in *Table 1*. PA6 samples made by anionic polymerization yield much higher degrees of polymerization than polymer produced by a commercial hydrolytic preparation route.

It is important to note that ISO 307 does not advocate the use of this procedure for polyamides prepared by anionic polymerization of lactams, or for polyamides produced with crosslinking agents, on account of their frequent insolubility in the specified solvents. However,

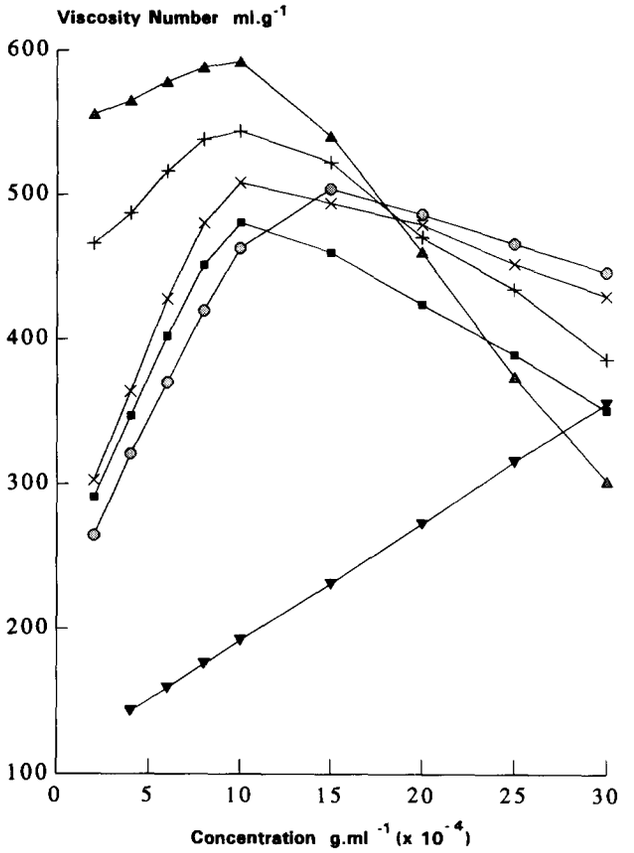

Figure 1 Relationship between viscosity number and solution concentration for PA6 variants. PA6 made by anionic polymerization of ε-caprolactam with screw speed (rev min^{-1}): (◎) 50; (+) 70; (▲) 90; (■) 120; (×) 150. (▼) Commercial PA6 material made by hydrolytic polymerization

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Table 1 Limiting viscosity number and viscosity-average molecular mass ($\bar{M}_v$) of PA6 variants, determined by solution viscometry and g.p.c.

	G.p.c.		Viscometry	
Screw speed[a] (rev min^{-1})	Limiting viscosity number (ml g^{-1})	$\bar{M}_v$ (kg mol^{-1})	Limiting viscosity number (ml g^{-1})	$\bar{M}_v$ (kg mol^{-1})
50	221	53.7	215	49.6
70	412	110.3	443	122.3
90	562	140.5	540	156.7
120	201	55.8	232	54.5
150	235	60.5	241	57.2
Capron 8202C[b]	100	25.1	110	21.4

[a] Conditions used during reactive extrusion process
[b] Commercial grade PA6 produced by hydrolytic polymerization

the present work has demonstrated that the limiting viscosity number of high molecular mass PA6 made by anionic polymerization can be successfully determined by solution viscometry in 90% formic acid solution. Meaningful results are, however, only obtained when solution concentrations are $<0.001\,g\,ml^{-1}$, well below the concentration level specified in ISO 307.

A likely explanation for the observed phenomena is a polyelectrolyte effect imparted on the formic acid solution, due to the extraordinary high molecular mass of the PA6 obtained by reactive extrusion. Indeed in an acid medium capable of dissociation, protonation of the amide linkage may occur, resulting in the formation of positively charged PA6 chains which have a tendency to repel each other and hence expand the polymer coils[3]. However, at very low PA6 concentrations, this effect is suppressed enabling the determination of viscosity number.

References

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