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The effect of molecular weight on the rheological and tensile properties of poly(ϵ-caprolactone)

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Abstract

Molecular weight fractions of poly(ϵ-caprolactone) (PCL) were obtained by catalytic degradation and characterised by rheological measurements. Pseudoplastic behaviour was found in the higher molecular weight fractions, the degree of which lessened as the thermal motion of the polymer chains increased. The exponential factor of the viscosity/molecular weight relationship indicated that the fractions were above the critical molecular weight for viscous flow determined as 15–16 000. Activation energies for viscous flow showed an inverse relationship with molecular weight, the significance of which has been discussed. Melt quenching resulted in lower melt viscosities due to a reduction in melting point by formation of additional amorphous regions. Tensile measurements indicated that PCL was a brittle material with a molecular weight of $> 16\,900$ being required for free film formation. Elongation and tensile strength values increased with molecular weight although remaining low, indicating both the low molecular weight range investigated and the high degree of PCL crystallinity. PCL showed that it had rheological and tensile properties that with modification would make it a potential candidate in the novel technique of powder coating of pharmaceutical compacts.

Keywords: Poly(ϵ-caprolactone); Polymer molecular weight; Rheology; Melt viscosity; Film formation; Tensile properties

1. Introduction

Poly(ϵ-caprolactone) is a biodegradable polyester which has been used as a mould release agent, adhesive, pigment dispersant, synthetic wound dressing (Schwope et al., 1974; Gregory, 1981), as a replacement for plaster of Paris in splints and as a material for orthopaedic casts. It has also been investigated for subdermal delivery of levonorgestrel (Pitt and Schindler, 1984) and naltrexone (Pitt et al., 1980) and oral delivery of theophylline (Prapaitrakul et al., 1989). It is of interest in the new technique of powder coating of pharmaceutical tablets (Grosvenor, 1991 and Grosvenor and Staniforth, 1992) since it has a number of ideal polymeric properties. In powder coating the rheological properties of the polymer are critical to the formation of a film and are

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themselves determined by its molecular weight. Once the polymer has been melted by IR radiation flow occurs over the compact surface in order to produce a film. The tensile properties of the film are in turn dependent on molecular weight as well as film composition, structure and thickness. It was the purpose of this study to characterise the influence of molecular weight on the rheological and tensile properties of poly(ϵ-caprolactone).

2. Materials and methods

Different molecular weight fractions were produced by catalytic degradation of poly(ϵ-caprolactone) (PCL) having $M_W = 49\,500$ (Aldrich Chemical Co. Ltd.). Briefly a solution of PCL in methanol/chloroform was refluxed with p-toluene sulphonic acid with the reaction being quenched at different times. The degraded polymer was precipitated, purified and dried. Gel permeation chromatography was used for molecular weight determination with the Mark-Houwink constants determined by Schindler et al. (1982) being used. The rheological properties of PCL melts were determined using a cone and plate viscometer (Ferranti-Shirley, Ferranti Ltd., Manchester). The instrument settings were adjusted so as to reduce errors associated with cone inertia and torque spring compliance. Melt quenched samples were produced by rapid cooling through immersion of molten polymers in liquid nitrogen. The samples were kept below their glass transition temperature until used.

The melting temperatures and heats of fusion were determined using DSC (Type 910/9900 DuPont Thermal Analyser) using a sample weight of 3–5 mg and a heating rate of 10°C min^{-1}. A heat of fusion of 139.5 J g^{-1} for 100% crystalline PCL has been used to calculate crystallinity (Crescenzi et al., 1972).

Films were made by melt pressing at 85–100°C in a hydraulic press having heated platens (G. E. Moores and Son Ltd., Birmingham). Specimens were cut using a type 2 dumbbell template (BS 903: Part A2: 1971) and were visually inspected for flaws before being stored at 20°C/22%RH for at least 14 days. The thickness of each specimen was measured in three places along the gauge length using a linear variable displacement transducer (Metem 552, Advanced Metrology Systems Ltd., Leicester) and were required to be in the range 50 ± 10 μm. Static tests at 0.001 m min^{-1} strain rate were carried out using a tensile testing machine (Type 1122, Instron).

3. Results and discussion

As a result of the preparative method, fractions of PCL were obtained having molecular weights (M_W) in the range 16 900 to 35 500 with polydispersities between 1.7 and 1.9. PCL melts showed a non-linear shear stress/shear rate relationship typical of pseuodoplastic materials. However, deviation from Newtonian behaviour was slight due, mainly, to the low molecular weight of the PCL samples. The behaviour of PCL was found to be time-independent over a wide range of shear rates and relaxation times.

The observed reduction in apparent viscosity with increasing shear rate is an alternative way to depict pseudoplastic behaviour (Fig. 1) which occured as a result of changes in polymer chain configurations. In the rest state the chains were extensively entangled whereas under shear they become directionally oriented. The orientation may be opposed by the disorienting effects of brownian motion but at very high shear rates it would be complete and pseudo-Newtonian behaviour observed. For PCL $M_W = 16\,900$ these

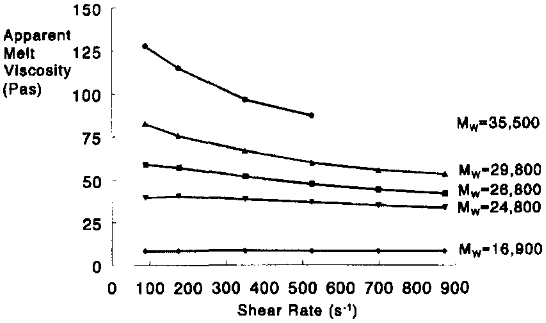

Fig. 1. The viscosity/shear rate relationship for different molecular weights of PCL at 100°C (95% C.I. < 3.5% of plotted mean value, $n = 5$).

alignment changes were incomplete at 70°C, although at 85 and 100°C gross conformational changes were complete as shown by the apparent viscosity at a shear rate of 872.5 s^{-1} being statistically insignificant ($P < 0.05$) from that at 174.5 s^{-1}. For higher molecular weight fractions chain alignment was incomplete at all temperatures with the deviation from Newtonian behaviour increasing as the molecular weight was raised. Some researchers (Shelland, 1967) have attempted to describe the degree of pseudoplastic behaviour using relationships such as the Ostwald-de-Waele equation. However, the exponential factor within this equation is of questionable theoretical value in describing the degree of non-Newtonian behaviour and such a description was not attempted in this study.

The basic equation relating viscocity at zero shear rate, η_0, to molecular weight for linear amorphous polymers was developed by Fox and Loshaek (1955) and is given by

$$\eta_0 = KM_W^a \quad (1)$$

The constant K depends on the polymer type, its M_n (Smith and Koleske, 1973) and temperature whilst the exponential factor a defines the slope of the log viscosity/log molecular weight plot. Factor a was predicted theoretically to have a universal value of 3.4 above the critical molecular weight, M_c (Fox and Loshaek, 1955). Values for η_0 were obtained by extrapolation of the apparent viscosity/shear rate relationship using a curve fitting program. Small errors in η_0 will be present due to the influence of the equation type used in the fitting procedure. The equations for PCL, obtained by linear regression are given below:

$$70°\mathrm{C} \log \eta_0 = -13.6 + 3.6 \log M_W$$

$$r^2 = 0.9884 \quad (2)$$

$$85°\mathrm{C} \log \eta_0 = -14.5 + 3.7 \log M_W$$

$$r^2 = 0.9923 \quad (3)$$

$$100°\mathrm{C} \log \eta_0 = -15.2 + 3.8 \log M_W$$

$$r^2 = 0.9923 \quad (4)$$

The values of a were close to the value of 3.4 with the observed differences probably being due to experimental errors and the low molecular weight range of the PCL samples studied. Whilst examples exist where the value of a is considerably greater than 3.4 (Porter and Johnson, 1960) we considered that the behaviour of PCL was satisfactorily described by this general equation. Since a has a value of 1 below M_c the results indicated that M_c was $< 16\,900$. Its precise value was obtained by determining the molecular weight at which melt viscosity was independent of shear rate as proposed by Bagley and West (1958). This treatment in which the apparent viscosity/shear rate curves coincided yielded a value for M_c, in the range 15–16 000 (Fig. 2). These values compare with 29 000 for polydimethylsiloxanes (Bagley and West, 1958), 38 000 for polystyrene (Rudd, 1960), 9000 for linear polyethylenes (Mills et al., 1960) and 10 000 for polyethylene glycols (Porter and Johnson, 1962). Such a value for PCL compared with polyethylene indicated the increased chain rigidity introduced by the ester linkage.

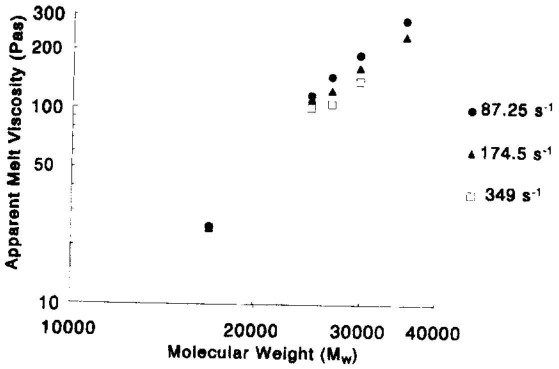

Fig. 2. The relationship between melt viscosity at 70°C and molecular weight at three shear rates (95% C.I. < 4% of plotted mean value, $n = 5$).

It is well established that for Newtonian liquids, viscosity is related to temperature by an Arrhenius-type equation of the form

$$\eta = Ae^{\frac{E}{RT}} \quad (5)$$

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where A is a constant and E is the activation energy for viscous flow. Whilst the behaviour of PCL and other polymer melts was pseudoplastic,

Table 1
Arrhenius parameters for poly(ϵ-caprolactone) at zero shear rate (mean with 95% C.I.)

M_W	E (kJmol^{-1})	A ($\times 10^{-5}$)	r^2
16 900	38.9 (2.7)	0.30	0.9994
24 800	38.3 (2.1)	1.84	0.9972
25 400	33.2 (1.7)	10.08	0.9976
26 800	31.8 (3.0)	20.29	0.9910
29 800	32.1 (2.7)	27.39	0.9950
35 500	31.5 (1.9)	49.92	0.9964

their flow properties can be considered Newtonian at zero shear rates since thermal forces continually regenerate a randomly entangled polymer network. The values for the activation energies are given in Table 1 together with the correlation coefficients of the least squares linear regression plots.

If η_0 is the viscosity of a polymer melt at temperature, T_0, the logarithmic form of Eq. 5 is given by Eq. 6. Therefore at a higher temperature, T_1, where its viscosity has been reduced by a factor, e, Eq. 7 applies.

$$\log_e \eta_0 = \log_e A + \frac{E}{RT_0} \quad (6)$$

$$\log_e \frac{\eta_0}{e} = \log_e A + \frac{E}{RT_1} \quad (7)$$

Subtraction of Eq. 7 from 6 yields Eq. 8

$$\frac{1}{T_0} - \frac{1}{T_1} = \frac{R}{E} \quad (8)$$

Thus by implication the higher the activation energy the lower the temperature change that is required for this degree of viscosity reduction. The activation energies showed an increase as the molecular weight was decreased which supported the intuitive idea that less thermal energy was required to disentangle short polymer chains compared with longer ones. Generally the degree of entanglement is a function of polymer chain length and as it increases so too does viscosity (Graessley, 1967). As the molecular weight increased the free volume decreased thus reducing the freedom the chains have to disentangle, hence the segmental jump frequency decreases. However, increase in chain length was compensated by increase in segment length and an increase in the coordination of segment motion. Our results appeared to show that on increasing the molecular weight the influence of the jump frequency predominated causing E to decrease. However, although Dienes (1953) developed a relationship between activation energy and short range order (regularity of molecular position) its significance is not well understood in terms of molecular conformational changes. Tung (1960) for polyethylenes and Drexler (1970) for isobutylene/isoprene copolymer found similar trends in activation energy to that observed with PCL whilst Porter and Johnson (1960) showed the opposite trend for polyethylenes. Rudd (1960), however, showed that E was independent of molecular weight.

The viscosity of the melt quenched samples was consistently lower than those allowed to crystallise slowly before subsequent remelting (Table 2). This was due to the melt quenched samples having lower onset and peak melting temperatures, as determined by DSC (Table 3), which resulted from the increase in amorphous content. Amorphous regions of semi-crystalline polymers increase in percentage after melt quenching due to the polymer chains having insufficient time to orient into a crystalline configuration. They would

Table 2
The effect of temperature on the melt viscosity of PCL M_W = 16 900 and 24 800 (Pas) at 174.5 s^{-1} shear rate (mean with 95% C.I.)

Thermal treatment	70°C		85°C		100°C	
	16 900	24 800	16 900	24 800	16 900	24 800
Slow crystallisation	24.6 (0.7)	113.1 (4.2)	15.1 (0.2)	69.3 (3.5)	8.3 (0.1)	40.5 (0.7)
Melt quenched	21.2 (0.1)	71.3 (1.0)	14.6 (0.4)	48.5 (1.8)	9.3 (0.6)	29.2 (1.8)

Table 3
Thermal properties of PCL (mean with 95% C.I.)

M_W	Thermal treatment	Melting temperature (°C)		% Crystallinity
		Onset	Peak	
16 900	Slow crystallisation	58.1 (1.2)	62.4 (0.7)	67
	Melt quenched	51.0 (5.1)	55.7 (2.1)	46
24 800	Slow crystallisation	56.9 (1.4)	62.4 (1.6)	53
	Melt quenched	52.6 (2.5)	56.3 (2.0)	50

be expected to melt at lower temperatures since crystalline regions have a higher degree of order and density and thus exert a greater resistance to shear through the crystallites functioning as additional crosslinks. Energy put into a crystalline material will first be used to disrupt the crystalline order before chain slippage and bulk flow is observed. The viscosity reduction after quenching would be a useful processing treatment to allow a higher molecular weight PCL for coating thus improving the mechanical properties of the formed film. Increased amorphous content would also be expected to increase the low permeability of PCL (Pitt et al., 1979).

Studies by Koleske and Lundberg (1969) on PCL/PVC blends found that for contents less than 20% PCL crystallinity reached equilibrium levels within a day whilst at 50% 8 days was required. The films in this study were, therefore, allowed to age for 14 days before testing to allow sufficient time for the crystallinity of PCL to develop. It was not possible to produce coherent films from PCL $M_W = 16\,900$ since the material was too brittle and could not be handled without disruption. However, PCL having $M_W > 24\,800$ formed films that had sufficient strength for tensile testing to be carried out. This requirement for a minimum molecular weight prior to free film formation is characteristic of both amorphous (Gent and Thomas, 1972) and crystalline polymers (Nielsen, 1974). It is due to the need for a minimum number of chain entanglements prior to the mechanical strength being sufficient for a load to be carried without disruption. For crystalline polymers the influence of tie-molecules (Peterlin, 1971) which hold crystalline domains together is superimposed on chain entanglements. This critical molecular weight was slightly greater than that obtained from rheological measurements probably due to the need for more extensive chain entanglements to form films of sufficient strength for testing.

The effect of molecular weight on film tensile properties, namely elongation, tensile strength and Youngs modulus are given in Table 4. The mechanical behaviour of PCL suggested that prior to failure the deformation induced in the film obeyed Hook's law, being directly proportional to the applied stress and was completely recoverable indicating elastic behaviour. Once the elastic limit was exceeded a crack formed in the films which led to rapid fracture as propagation occured across the film width. No yield point was found in any of the specimens probably due to the extreme brittleness of the films so the parameters shown in Table 4 were those corresponding to the fracture point. A general increase in elongation and tensile strength was found as the molecular weight was increased, in agreement with results for most polymers, although their values remained low. Youngs modulus showed an initial increase followed by a decrease after $M_W > 30\,000$. This indicated that the films decreased in stiffness sug-

Table 4
Tensile properties of 50 μm PCL films (mean with 95% C.I.)

M_W	% Elongation	Tensile strength (MPa)	Youngs modulus (MPa)
24 800	2.2 (0.4)	7.4 (1.1)	3.3 (0.2)
26 800	3.4 (0.7)	11.9 (2.4)	3.6 (0.3)
29 800	3.7 (0.8)	12.5 (2.1)	3.4 (0.4)
35 500	5.5 (0.9)	15.6 (2.2)	2.9 (0.2)

gesting that a greater degree of viscous flow may have occured beyond this point. This was possibly due to the shorter polymer chains acting as slippage areas between the longer polymer chains, the effect of which exceeded modulus increase through chain entanglement. A 50-μm film of PCL M_W = 49 500 could not be formed due to its melt viscosity being too high. However, Hubbell and Cooper (1977) obtained ultimate elongation and tensile strength values of 640% and 26.4 MPa for 70- to 100-μm films. Such a high elongation value suggests that PCL could be used for coating of swellable matrices or gastric flotation devices which need to accomodate large dimensional increases after interaction with bulk water.

These low values of tensile parameters clearly indicated the need for plasticisers to make the films sufficiently elastic for the stresses that tablets are subjected to to be accommodated without film rupture. Improved film characteristics have been obtained when polyethylene glycols and poloxamers were added, e.g. elongations of 4% in PCL M_W = 24 800 films containing 10% PEG 20 000, making the materials suitable for powder coating. In comparison with the PCL results HPMC M_W = 25 000 and 35 000 gave ultimate elongations of 5 and 7% (Methocel Technical Bulletin, Dow Chemical Company).

4. Conclusions

The melt viscosity of PCL M_W ~25 000 was considered to be too high for flow across the compact surface to occur after melting under the influence of the gravitational stress. Use of plasticisers has reduced this viscosity to levels at which flow occurs either directly or under the influence of an applied stress without compromising the functionality of the coat. Indeed the use of hydrophilic polymers has the additional benefit in that suitable selection enables pore forming characteristics to be incorporated into the film thus allowing wide control of coat permeability. The film forming properties of a polymer to be used as a compact coating material are not as demanding as one used for free films due to the mechanical support provided by the substrate.Whilst PCL was more brittle than HPMC it would not be unacceptable in compact powder coating applications provided suitable levels of plasticiser were present.

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