

Glass transitions of some methylmethacrylate copolymers

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Some methylmethacrylate-based copolymers were synthesized and their powder, viscosity, swelling ratio and compression characteristics assessed (Castellano et al 1997a,b). These copolymers were hydroxypropylstarch-methylmethacrylate (HS-MMA), carboxymethylstarch-MMA (CS-MMA) and hydroxypropylcellulose-MMA (HC-MMA). The aim of this study was to determine the glass transition temperatures (T_g) of these copolymers using dynamic differential scanning calorimetry (DDSC) and to assess if the T_g was modified by the drying methods.

Three graft copolymers were examined following synthesis and were oven-dried (OD) or freeze-dried (FD) (Castellano et al 1997a). Samples (9-13 mg) were weighed into 40 µL aluminum pans, and sealed with lids pin-holed to avoid sample expansion and warping. A Perkin-Elmer DSC 7 Differential Scanning Calorimeter was used. For DDSC a heat-cool programme was used, scanning from 40° to 200°C with a heating step of 4°C, a cooling step of 2°C over a period of 80s, repeating 80 times. Conventional DSC curves were also obtained at 10°C min⁻¹ from -40°C to 240°C. Liquid nitrogen as coolant and nitrogen as purge gas were used.

DSC of FD or OD HC-MMA showed a broad endotherm peaking at ~117°C, followed by a small exotherm at ~130°C. HS-MMA gave a broad endotherm from ~50° to ~200°C, peaking at ~120°C. FD HS-MMA also gave an exotherm at ~180°C. CS-MMA samples showed a broad endotherm from ~70°C and an exotherm at ~190°C. The endotherms and exotherms may be due to dehydration and decomposition. T_gs were not apparent.

Heat flow DDSC curves displayed similar trends to DSC curves but the events were shifted to lower temperatures. Loss specific heat curves, which represent the dynamic specific heat that is out of

Glass transition temperatures derived by DDSC

Polymer	T _g / °C	
HC-MMA (OD)	115.3	117.1
HC-MMA (FD)	107.6	112.6
HS-MMA (OD)	129.1	127.6
HS-MMA (FD)	126.6;	127.1
CS-MMA (OD)	126.1	126.1
CS-MMA (FD)	124.1	125.2

phase with the temperature change, showed small capacity changes at 100-140°C. However, the T_gs were seen in storage specific heat curves, which result from energy uptake via atomic and molecular mechanisms of energy storage, as changes that occurred from ~80°C to ~130°C. T_gs, determined by the half Cp method where the specific heat (Cp) change is half of the change of the complete transition, are given for duplicate samples in the table. The OD products appeared to have slightly lower T_gs that may partly explain differences between the physical performances of the OD and FD products (Castellano et al 1997a).

DDSC, rather than DSC, allowed differentiation of the T_gs of methylmethacrylate copolymers. Moisture loss, through the lid pin-holes, was not controlled and may have influenced the absolute values of the data. However in preliminary studies, the use of fully sealed pans, did not produce scans stable enough to determine the T_g values.

Castellano, I., Gurruchaga, M., Goñi, I (1997a) *Carbohyd. Polym.* 34: 83-89

Castellano, I., Goñi, I, Gurruchaga, M., Velasco, M.V., Muñoz, A., Jimenez-Castellanos, M.R., (1997b) *Int. J. Pharm.* 146: 71-79

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