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SAMPLE ENCAPSULATION ON GLASS TRANSITION OF METHYLMETACRYLATE COPOLYMERS

TMDSC and DSC studies

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Abstract

The use of modulated temperature differential scanning calorimetry (TMDSC) and differential scanning calorimetry (DSC) in the measurement of the glass transition temperature (T_g) in polymer-water systems presents several important problems. These include the presence of water evaporation endotherms, partial water evaporation during scanning, changes in pan integrity due to vapour pressure developing in the pan headspace during analysis, and possible interaction between water and polymer at high temperatures. As a result, in most of the cases, only apparent T_g values can be obtained. In this study, TMDSC and DSC were used to determinate the thermal behaviour of methylmethacrylate copolymer-water systems. The samples were previously equilibrated at different relative humidities (RH) from 0 to 97% RH. Three different pan arrangements were used. In addition, thermogravimetric analysis (TG) was carried out to determine the initial amount of water in the sample. None of the pan arrangements was entirely suitable for the study of these systems. When sealed pans were used, the plastification effect of water was observed. Some evidence of degradation was also observed in which water and methylmethacrylate appeared to play roles.

Keywords: DSC, glass transition, methylmethacrylate copolymers, TMDSC

Introduction

The glass transition of a polymer generally occurs at a specific temperature, the glass transition temperature (T_g). A polymer at a temperature above its T_g is in the rubbery state, and is limp and flexible. A polymer below its T_g is in the glassy state, is brittle and is characterised by stiffness, hardness and often high-optical clarity or transparency [1–2]. A polymer may be considered as a number of sub-systems, all of differing

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segment lengths. The onset temperatures of segmental mobility for each sub-system are different. The overall glass transition is a consequence of all of the different segmental motions and is accompanied by an increase in heat capacity and often a small relaxation endotherm [1–3].

The glass transition temperature can be affected by polymer history and polymer nature (molecular mass, position of pendant side-chains, chain stiffness and polarity of the chain). Additionally branching, cross-linking, copolymerization and plasticizers alter its value [1]. The glass transition is exhibited by amorphous polymers or the amorphous regions of partially crystalline polymers. This amorphous state may appear in some proportion following each crystallisation or drying process, and is typically obtained during freeze-drying, spray drying, granulation, grinding or milling [4, 5].

The behaviour of water as a plastizier is unequivocal [4, 6, 7]. According to many authors, water associated with a polymer can display various types of interaction and at least three types of thermodynamic water are recognised. Type I water is freezing water or bulk free water, whose behaviour is as normal water in terms of melting and freezing. Type II water or freezing bound water is loosely bound to the polymer and displays a considerable supercooling. It therefore freezes at temperature lower than Type I water. Type III water, or non-freezing water, is tightly bound to the polymer and is incapable of freezing [8].

The thermal behaviour of grafted copolymers has been reported. Athawale and Lele [9] examined the influence of grafting vinyl monomers onto starch, giving an improvement to its thermal stability and a plasticization effect of the monomers, especially in the case of hydrophobic monomers. The thermal behaviour of the copolymers used in the present work (methylmethacrylate copolymers) has been previously determined using samples stored at room conditions of temperature and relative humidity [10].

Modulated temperature differential scanning calorimetry (TMDSC) involves the superposition of a modulation on the conventional linear temperature programme. One of the major advantages of TMDSC is that the technique allows direct measurement of the glass transition in the first heating scan when an associated enthalpic relaxation is also present, and it allows resolution without loss of sensitivity [11–17]. TMDSC has, however, some important disadvantages [3, 12]. To satisfy the requirements for at least six modulations throughout the duration of each thermal event, low underlying heating rates are required. In addition, TMDSC is complex and involves the use of a number of experimental parameters (heating rate, pan type, sample mass, period and temperature amplitude of the oscillation, etc.) whose correct choice plays an important role in the quality of the final results [13–17]. TMDSC is allegedly suitable in the examination of the effect of sorbed water on the glass transition [15].

Many problems have been reported in the measurement of T_g in water-polymer systems. One such problem is the presence of an endotherm corresponding to water evaporation in the same range of temperature as the T_g when non-sealed pans are used. This problem can be eliminated using TMDSC. Evaporation is a non-reversible event so both processes are separated. However, another problem appears when part of the water is evaporated: the T_g value has to be considerated as an 'apparent T_g' of that polymer-water system because it is not possible to know what proportion of water remains in the sample during its partial evaporation. Alternatively, if sealed pans (which have been reported to be the most suitable pans to study water-polymer systems) are used, some shape changes in the pans may be observed when the sample has a high moisture level because of the developing vapour pressure in the pan headspace [5, 8, 15]. Additionally, the presence of water coupled with high temperature may produce some degradation [9, 18].

The aim of this study was to examine the influence of sample pans on the detection of a glass transition in some methylmethacrylate copolymers using TMDSC following storage at different relative humidities. Additionally the freezing and recrystallisation of different types of water during TMDSC and DSC at subambient conditions were studied.

Materials and methods

Materials

Hydroxypropylstarch (HPS) and carboxymethylstarch (CMS) were obtained from Avebe. Hydroxypropylcellulose (HPC) was supplied from Aldrich. The copolymers were synthesised as previously described [19, 20] by graft copolymerization of the main carbohydrates with methyl methacrylate (MMA). The products obtained were dried using two different techniques: oven-drying to constant mass under vacuum at 50°C and freeze-drying using a lyophilization apparatus (Cryodos-45, Telstar). For two of the three resultant products from the former technique, milling was necessary (Blade-mill, Retsh. Haan, Germany) because of the glassy nature of the copolymers. The 25–500 μm size fractions for all the copolymers were selected. Three pairs of products were produced: hydroxypropylstarch-methylmethacrylate oven-dried (HPS-MM OD) and freeze-dried: (HPS-MM FD); hydroxypropylcellulose-methylmethacrylate oven-dried (HPC-MM OD) and freeze-dried (HPC-MM FD), carboxymethylstarch-methylmethacrylate oven-dried (CMS-MM OD) and freeze-dried (CMS-MMA FD).

The unreacted homologous polymeric carbohydrates and their corresponding copolymers were kept in vacuum dessicators using silica-gel as desiccant to obtain products dried to constant mass, and were subsequently equilibrated at five different relative humidities (18.8, 37.1, 58.3, 80.5 and 97.5% RH) using hermetically sealed dessicators containing sulphuric acid solutions of different concentration to obtain the desired RH [21]. The samples were regularly weighed on a balance (LJ16 Moisture Analyzer, Mettler Toledo) until constant mass was obtained. A constant temperature (25°C) was maintained during equilibration.

Thermal analysis

A Perkin Elmer DSC 7 and Intracooler I (Beaconsfield, UK) were used, controlled by a Perkin Elmer TAC 7/DX. The instrument was calibrated for temperature at each heating rate using indium and zinc. Samples, carefully weighed between 4–6 mg (Model WA 205, Oertling, England), were used in the DSC and TMDSC experiments.

Differential scanning calorimetry (DSC)

Standard aluminium pans and covers (Perkin Elmer) were used with the following scanning conditions: (a) heating from 40 to 140°C at 10°C min^{-1}, (b) cooling from 20 to –40°C at 5°C min^{-1}, followed by an isothermal step at –40°C for 5 min and final heating to 20°C at 5°C min^{-1} or (c) cooling from 25 to –60°C at 2°C min^{-1} followed by an isothermal step at –60°C for 5 min and final heating to 25°C at 2°C min^{-1}.

Modulated temperature differential scanning calorimetry (TMDSC)

Glass transition temperatures were determined by the half-C_p method, where the specific heat (C_p) change is half of that of the complete transition. Three types of pan arrangements were used:

a) Standard aluminium pans and covers (Perkin Elmer) were used in the following two scanning conditions (i) heating from 40 to 200°C at a heating rate of 6°C min^{-1} and a cooling rate at 3°C min^{-1}, each for 40 s, repeating 80 times, and (ii) heating from –40 to +40°C using a heating rate of 6°C min^{-1} and a cooling rate of 3°C min^{-1}, each for 40 s, repeating 50 times.

b) 40 μL aluminium pans and their corresponding covers (Perkin Elmer) were used, scanning from 40 to 140°C using a heating rate of 6°C min^{-1} and a cooling rate of 3°C min^{-1}, each for 40 s, repeating 50 times.

c) Two 40 μL aluminium pans (Perkin Elmer) were used as pan and cover, scanning from 40 to 150°C using a heating rate of 6°C min^{-1} and a cooling rate of 3°C min^{-1}, each for 40 s, repeating 55 times.

Thermogravimetric analysis (TG)

TG, using a Perkin Elmer TGA 7 (Beaconsfield, UK), was carried out on samples (7–11 mg) on open platinum pans (Perkin Elmer) at a heating rate of 10°C min^{-1} from 20 to 200 or 250°C when the initial amount of water in the samples was high. First derivative data were provided by the installed software.

Results and discussion

TG data

TG was used to determine the water content of samples equilibrated at different RHs. As examples, the results obtained for HPC-MM OD samples are shown in Table 1 and Fig. 1. Three possible mass loss steps were identified in the TG data. Step 1, generally with a maximum rate of loss at 25 to 30°C (Table 1) probably corresponded to the loss of very labile water. Step 2 also probably corresponded to the further loss of water. However the Stage 2 mass loss event could be more complicated because, at that range of temperature, more than one thermal event may occur. The temperature of maximum rate of mass loss in the derivative TG curves were in good correlation with the peak temperatures of the endotherms found later during DSC. Table 2 gives the gravimetrically determined mass gain of water. There gains during equilibration at different relative humidities were higher than the mass loss in Step 1 and so at least part of the loss of mass in Step 2 must be due to water evaporation. However, the possibility of degradation events over that temperature range can not be discounted, especially in the light of the TMDSC data reported later. Step 3 has already been observed [10] and was identified as a probable degradation event.

Table 1 Onset temperatures (T_{onset}) and temperature of maximum rate of mass loss (T_{max}), derived from first derivative data, and mass loss, determined by TG, of oven dried hydroxypropylcellulose-methylmethacrylate samples following storage at six relative humidities

RH%	Step 1		Step 2		Step 3	
0.0	T_{onset}/°C	–	T_{onset}/°C	50.0	T_{onset}/°C	125.0
	T_{max}/°C	–	T_{max}/°C	75.0	T_{max}/°C	160.0
	mass loss/%	–	mass loss/%	0.8	mass loss/%	1.8
18.8	T_{onset}/°C	–	T_{onset}/°C	45.0	T_{onset}/°C	130.0
	T_{max}/°C	–	T_{max}/°C	63.0	T_{max}/°C	170.0
	mass loss/%	–	mass loss/%	1.7	mass loss/%	1.83
37.1	T_{onset}/°C	20.0	T_{onset}/°C	48.1	T_{onset}/°C	130.0
	T_{max}/°C	28.2	T_{max}/°C	73.4	T_{max}/°C	168.4
	mass loss/%	1.0	mass loss/%	0.9	mass loss/%	1.6
58.3	T_{onset}/°C	20.0	T_{onset}/°C	40.2	T_{onset}/°C	128.0
	T_{max}/°C	25.0	T_{max}/°C	69.0	T_{max}/°C	168.0
	mass loss/%	0.9	mass loss/%	2.3	mass loss/%	2.8
80.5	T_{onset}/°C	20.0	T_{onset}/°C	39.9	T_{onset}/°C	117.4
	T_{max}/°C	25.0	T_{max}/°C	63.3	T_{max}/°C	154.1
	mass loss/%	1.5	mass loss/%	2.6	mass loss/%	2.4
97.5	T_{onset}/°C	20.0	T_{onset}/°C	40.2	T_{onset}/°C	130.0
	T_{max}/°C	29.0	T_{max}/°C	71.9	T_{max}/°C	170.0
	mass loss/%	2.4	mass loss/%	4.6	mass loss/%	1.7

TMDSC data using standard pans and covers

Two samples were run using standard aluminium pans and covers from 40 to 200°C. Separate data are shown in Tables 3 and 4. The three oven dried products gave similar data (Table 3). In the heat flow data (Figs 2 and 3), an endotherm frequently appeared at ~80–110°C. The endotherm became larger and shifted to lower temperatures as the amount of water increased and was probably due to water loss that typically takes place in the temperature range of 50–120°C for many starches [21]. In some scans

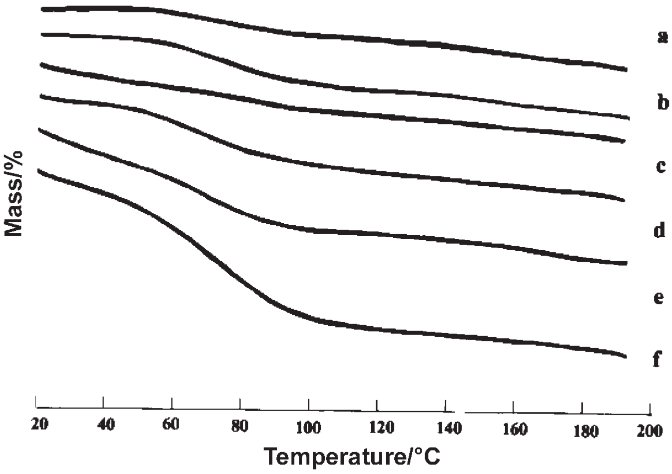

Fig. 1 TG curves of HPC-MM OD equilibrated at different relative humidities, a – 0.0%RH; b – 18.8%RH; c – 37.1%RH; d – 58.3%RH; e – 80.5%RH; f – 97.5%RH, obtained at β=10°C min^{-1}

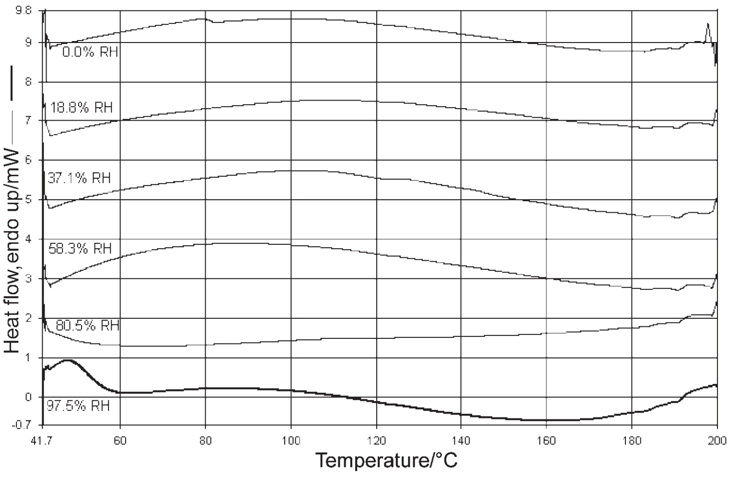

Fig. 2 Heat flow curves of HPS-MM OD samples equilibrated at different relative humidities, obtained by TMDSC using standard aluminium pans and covers

Table 2 Equilibrium moisture content (% dry polymer), determined gravimetrically, of oven dried (OD) or freeze dried (FD) samples of hydroxypropylstarch-methylmethacrylate (HPS-MM) , hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarch-methylmethacrylate (CMS-MM) and hydroxypropylstarch (HPS), hydroxypropylcellulose (HPC) or carboxymethylstarch-(CMS) following equilibration at six different relative humidities

RH/%	HPS-MM OD	HPC-MM OD	CMS-MM OD	HPS-MM FD	HPC-MM FD	CMS-MM FD	HPS	HPC	CMA
0	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18.8	0.82	0.860	2.01	1.07	1.48	2.20	3.76	2.79	7.16
37.1	2.14	1.608	2.90	1.80	1.82	2.49	5.65	4.29	9.57
58.3	5.37	3.142	5.58	4.66	3.83	4.70	10.10	8.08	14.96
80.5	9.15	5.961	11.39	7.85	6.64	9.57	14.91	16.38	30.01
97.5	14.94	8.630	19.58	13.65	9.25	17.23	23.62	23.80	50.76

Table 3 Glass transition temperatures (T_g), initial temperatures of the transition ($T^a_{initial}$), transition temperature ranges (T^a_{range}) and changes in specific capacity (ΔC_p) of oven dried (OD) samples of hydroxypropylstarch-methylmethacrylate (HPS-MM), hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarch-methylmethacrylate (CMS-MM) equilibrated at different relative humidities (%RH), derived from TMDSC scans using standard aluminium pans and covers

Polymer	RH/%	Sample				Duplicate			
		$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}	$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}
HPS-MM OD	0.0	100.2	129.3	40.6	0.100	100.5	128.9	39.4	0.134
	18.8	86.3	124.7	51.4	0.196	108.5	127.9	31.3	0.140
	37.1	85.4	122.7	53.8	0.228				
	58.3	84.8	127.7	55.3	0.185	85.4	123.3	50.6	0.211
	80.5	86.2	125.3	52.0	0.165				
	97.5	105.8	127.3	30	0.140				
HPC-MM OD	0.0	96.8	122.2	36.7	0.149	103.9	121.3	27.4	0.135
	18.8	89.9	121.7	41.6	0.173	93.1	121.4	39.2	0.182
	37.1	91.9	121.4	40.9	0.172				
CMS-MM OD	0.0	94.8	126.4	40.6	0.174	90.6	124.9	45.5	0.215
	18.8	86.2	124.8	49.4	0.214	92.3	124.8	42.6	0.195

Table 4 Glass transition temperatures (T_g), initial temperatures of the transition ($T^a_{initial}$), transition temperature ranges (T^a_{range}) and changes in specific capacity (ΔC_p) of freeze-dried (FD) samples of hydroxypropylstarch-methylmethacrylate (HPS-MM), hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarch-methylmethacrylate (CMS-MM) equilibrated at different relative humidities (%RH), derived from TMDSC scans using standard aluminium pans and covers

Polymer	RH/%	Sample				Duplicate			
		$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}	$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}
HPS-MM FD	0.0%	91.4	126.9	47.9	0.159	101.7	127.0	40.0	0.153
	18.8%	85.5	121.4	47.7	0.253	85.3	122.4	49.4	0.116
	37.1%	110.5	126.9	24.4	0.127				
HPC-MM FD	0.0%	100.2	123.3	32.5	0.136	99.8	122.1	30.8	0.137
	18.8%	93.4	123.4	39.8	0.175	90.1	124.3	42.8	0.155
	37.1%	101.3	123.3	30.0	0.158				
CMS-MM FD	0.0%	91.9	126.9	42.9	0.150	92.1	128.0	44.5	0.157
	18.8%	104.8	127.8	32.2	0.169	79.4	114.2	56.7	0.226
	37.1%	97.8	126.8	37.3	0.174				

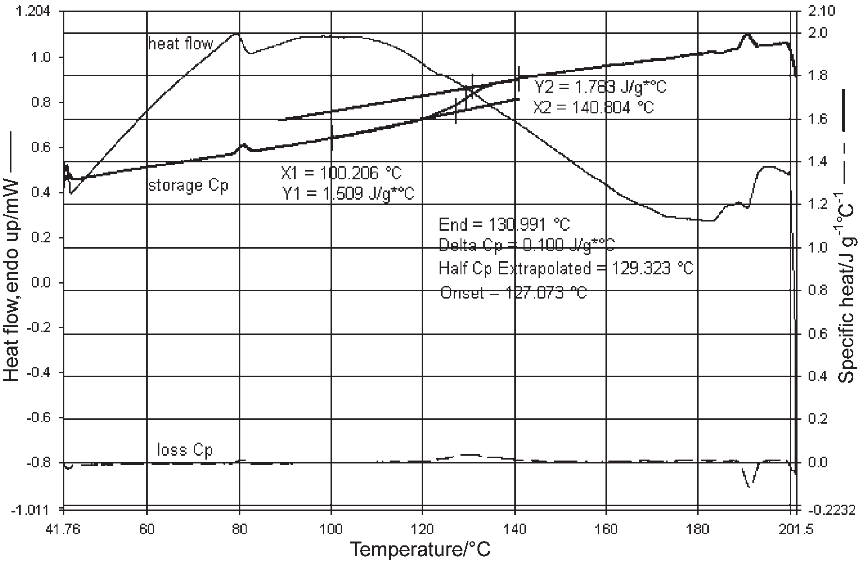

Fig. 3 Heat flow, storage C_p and loss C_p curves of HPS-MM OD dried at 0% RH, obtained by TMDSC using standard aluminium pans and covers

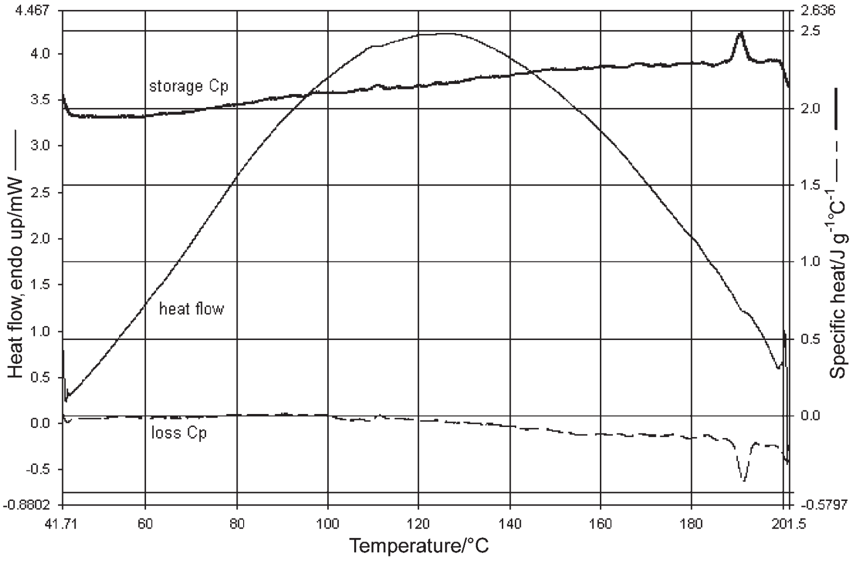

Fig. 4 Heat flow, storage C_p and loss C_p curves of HPC equilibrated at 58.3% RH, obtained by TMDSC using standard aluminium pans and covers

(e.g. following storage at 97.5% RH; Fig. 2), a broad exotherm appeared at ~160°C that may represent degradation. It is likely that part of the moisture initially present in the sample would not be lost and may contribute to degradation at higher temperatures.

Table 5 The peak temperatures of exotherms in the heat flow curves of oven dried (OD) or freeze dried (FD) samples of hydroxypropylstarch-methylmethacrylate (HPS-MM), hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarch-methylmethacrylate (CMS-MM) following equilibration at six different relative humidities (%RH) obtained by TMDSC using 40 μL aluminium pans and their corresponding covers

Polymer	RH/%	Exotherm peak temperatures/°C			
HPS-MM OD	0.0	95		128	
	18.85	95		130	
	37.1	85		135	
	58.3	95		125	
	80.5	85	95		105
	97.5	80	95		130
HPC-MM OD	0.0	95	110		128
	18.8	–	–		130
	37.1	95		130	
CMS-MM OD	0.0			95	
	18.8	70	95		130
	37.1	70	90		135
HPS-MM FD	0.0	95	105		135
	18.8	95	–		130
	37.1	80	105		132
HPC-MM FD	0.0	75	95		110
	18.8	95		120	
	37.1	95		130	
CMS-MM FD	0.0	95	105		135
	18.8	95		125	
	37.1	95		130	
	58.3	85	95	105	115

Glass transitions were apparent in the storage specific heat curves (Fig. 3) and are detailed in Table 3. Values of the T_g were almost constant despite the fact that the amount of water in the sample increased on storage at higher humidities (Table 2). This is probably a result of the loss of water during heating and it's therefore not remaining held in the sample to act as plasticizer, or due to degradation that occurred during heating. The glass transition, however, occurred over a broad range of temperature (Fig. 3; Table 3) probably because of the complex composition of the polymers.

The temperature range over which the transition took place broadened as the moisture in the samples increased (Table 3). A slight decrease in T_g values was observed in HPS-MM OD and CMS-MM OD samples as their initial moisture content increased. An endothermic relaxation generally occurred at the same range of temperature as the glass transition in the loss C_p curves and appeared clearly in most of the scans of the oven dried samples (Fig. 3).

The heat flow and loss specific heat curves of the three freeze-dried samples (HPS-MM FD; HPC-MM FD; CMS-MM FD) displayed similar behaviour to the heat flow curves of the oven-dried samples. Additionally the storage specific heat curves showed similar, but often slightly higher, T_g values to the freeze-dried products (compare the data Table 4 with those in Table 3). Both heat capacity changes and range of temperature over which the transition occurred were also in the same order of magnitude (Table 4). The T_g data of each polymer in this study were in good correlation with the previously obtained values [10], where TMDSC was carried out on similar co-polymers stored under room conditions.

The three carbohydrates, hydroxypropylstarch (HPS), hydroxypropylcellulose (HPC) and carboxymethylstarch (CMS) were equilibrated at three relative humidities (0.0, 58.3 and 97.5%) for comparison. However, following storage at 97.5% RH, only HPS was studied because CMS and HPC formed gels. A broad endotherm appeared in the heat flow signal of each of the samples in the same range of temperature range with a broad peak at ~110–120°C.

Occasionally, other transitions were found. For example, in the storage specific heat curve of HPC, equilibrated at 58.3% RH, a very broad transition occurred from 74 to 148°C (Fig. 4), although little evidence of transitions could be seen on the loss curve.

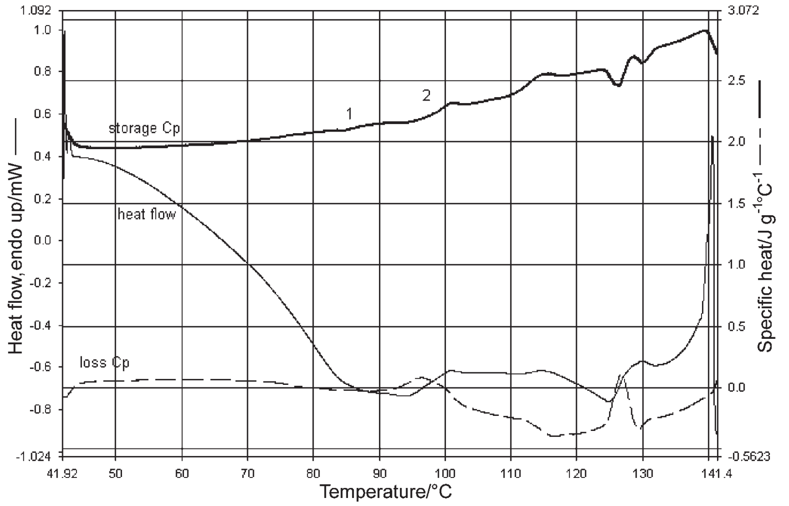

Fig. 5.1 Heat flow, loss C_p and storage C_p curves of HPS-MM OD equilibrated at 58.3% RH obtained by TMDSC using 40 μL aluminium pans and their corresponding covers. The two transitions marked as 1 and 2 are more detailed in Figs 5.2 and 5.3 respectively

In summary, when standard aluminium pans and covers were used, TMDSC scans showed T_g values that did not change as the RH at which the samples were stored, and therefore as the moisture content in the samples increased (Tables 1, 2). However, the temperature range over which the transition occurred took place tended to be larger as the RH was increased. This indicates that the pan seal allowed moisture to leave the vicinity of the sample and, as the pans were not hermetically sealed, from the inside and headspace of the pan. An endothermic event (probably water evaporation) occurred in all the heat flow curves and increased in size as the moisture in the sample increased. This loss of moisture would explain the lack of decrease in the T_g values that might have initially been expected in samples stored at higher humidities.

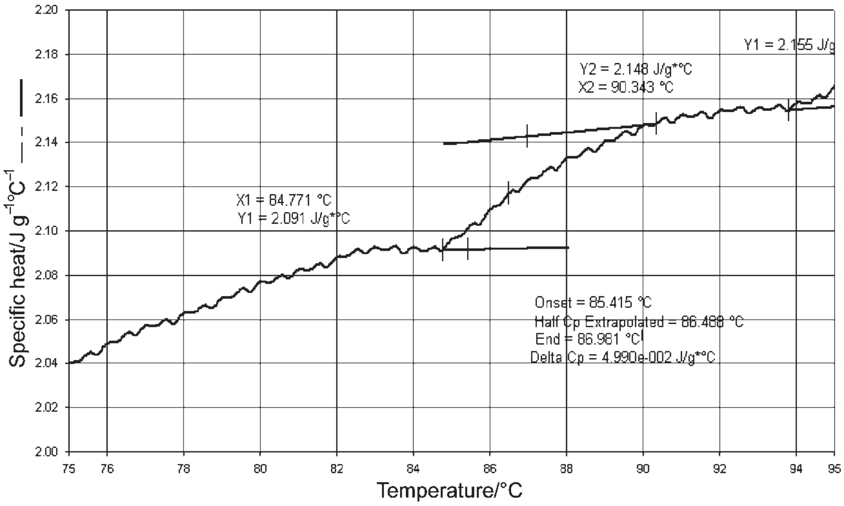

Fig. 5.2

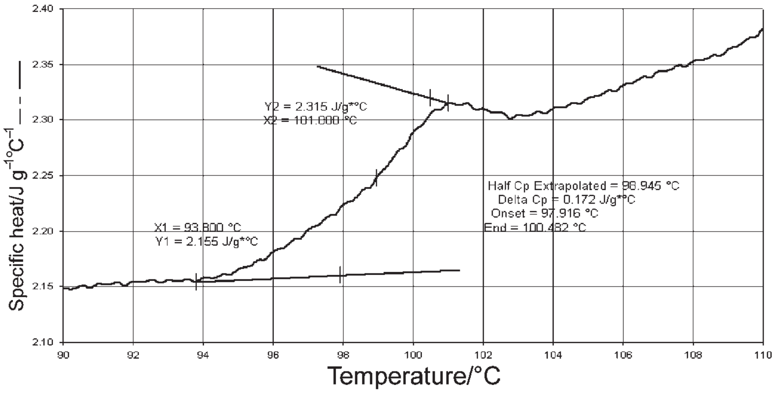

Fig. 5.3

Table 6 Glass transition temperatures (T_g), initial temperatures of the transition ($T^a_{initial}$), transition temperature ranges (T^a_{range}) and changes in specific capacity (ΔC_p) of oven dried (OD) samples of hydroxypropylstarch-methylmethacrylate (HPS-MM), hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarch-methylmethacrylate (CMS-MM) equilibrated at different relative humidities (%RH), derived from TMDSC scans using 40 μL aluminium pans and their corresponding covers

Polymer	RH/%	Sample				Duplicate			
		$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}	$T^a_{initial}$/°C	T_g/°C	T^a_{range}/°C	ΔC_p /J g^{-1} °C^{-1}
HPS-MM OD	0.0%	93.1	97.4	7.8	0.106	–	–	–	–
	18.8%	94.7	98.9	6.2	0.006	–	–	–	–
	37.1%	87.7	89.3	3.3	0.002	94.7	98.0	6.1	0.008
	58.3%	84.7	86.5	5.6	0.005	93.8	99.0	7.2	0.175
	80.5%	88.7	89.9	2.6	0.002	94.6	98.7	6.3	0.106
	97.5%	86.1	88.7	5.8	0.113	102.8	105.9	7.2	0.203
HPC-MM OD	0.0%	93.8	98.4	7.2	0.010	–	–	–	–
	18.8%	97.8	99.4	3.2	0.006	–	–	–	–
	37.1%	92.9	98.3	7.7	0.127	–	–	–	–
CMS-MM OD	0.0%	94.8	97.8	6.7	0.005	–	–	–	–
	18.8%	92.9	98.8	8.1	0.008	114.3	115.9	2.8	0.009
	37.1%	92.9	99.0	8.1	0.147	113.7	116.0	6.3	0.129
HPS-MM FD	0.0%	94.2	98.5	6.8	0.122	–	–	–	–
	18.8%	94.3	98.5	6.6	0.008	–	–	–	–
	37.1%	97.3	99.3	3.7	0.008	–	–	–	–
HPC-MM FD	0.0%	72.6	73.8	2.3	0.002	93.7	98.8	7.4	0.123
	18.8%	94.8	99.0	6.3	0.008	–	–	–	–
	37.1%	94.8	98.8	6.1	0.135	–	–	–	–
CMS-MM FD	0.0%	94.4	96.9	10.3	0.007	–	–	–	–
	18.8%	93.8	98.4	7.2	0.214	–	–	–	–
	37.1%	93.9	98.4	7.1	0.157	–	–	–	–

The later exotherms that appeared in the heat flow curves of the grafted samples may be considered as part of a degradation phenomenon indicated by mass loss in the TG data. The presence of MMA is indicted as a possible cause as these exotherms were not found in the untreated polymeric carbohydrates. There was no apparent evidence that the two methods of drying caused differences that were detectable in the TMDSC scans.

TMDSC data using 40 μL aluminium pans and their corresponding covers

Sealed 40 μL aluminium pans and their covers were used, scanning from 40 to 140°C in an attempt to minimize the effect of the loss of moisture during heating. The temperature range was reduced in an attempt to avoid the possible degradation that took place at high temperature in the previous TMDSC scans. However, in some samples irreproducible peaks were sometimes obtained that were attributed to changes in pan shape due to the build up of vapour pressure inside the pan headspace.

In many samples the evaporation endotherm appeared in the heat flow curves, despite the samples being constrained in these sealed pans. Several exothermic events (again probably degradation-induced) appeared, generally at ~95 or ~130°C for all samples (Table 5 and as an example Fig. 5.1). As the moisture content in the samples increased, the exotherm occurred at the lower temperatures (Fig. 5.1). Again the freeze-dried samples displayed similar to the oven-dried derivatives.

The scans using 40 μL pans showed lower values of T_g (Table 6) than in the standard pans (Tables 3 and 4), probably because of the greater efficiency of the encapsulation arrangement allowing more of the water to remain in the sample and therefore some degree of plasticization.

As the moisture content of the samples increased, two apparent glass transitions were often observed in the storage specific heat curves of the oven dried derivatives, again supporting the suggestion that the previously mentioned exotherms were due to degradation (Figs 5.2; 5.3; Table 6). The temperature range (Table 6) over which the transitions take place and the heat capacity changes were smaller than those found using standard aluminium pans (Tables 3 and 4). Again the loss specific heat curves displayed endothermic relaxations that generally occurred at a similar temperature range as the glass transition (Fig. 5.1).

In summary, when sealed 40 μL aluminium pans and covers were used in TMDSC scans, the T_g values were lower than when using the standard pans, probably due to their ability to retain moisture in the headspace. Perversely, in many cases changes in pan shape. i.e., warping, occurred because of the build up of vapour pressure in the pans. As the amount of water in the samples increased, several exothermic events appeared indicating that both entrapped moisture and methylmethacrylate contributed to degradation. Simultaneously, more than one transition was detected in the storage specific heat curves of the oven-dried starch derivatives that may also be due to degradation reactions.

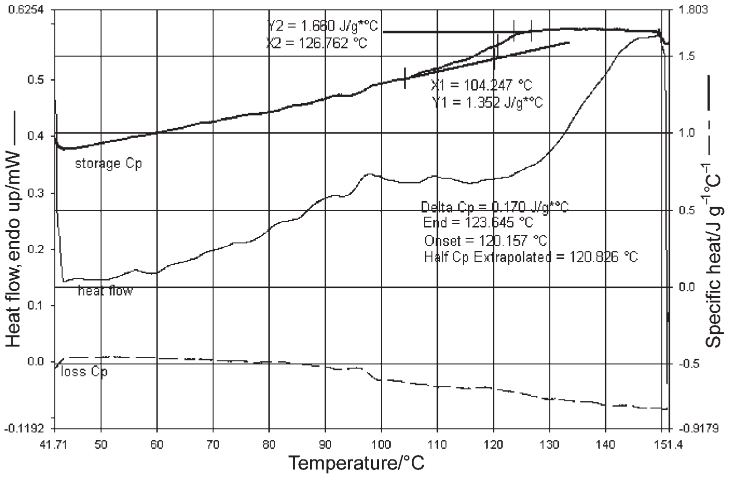

Fig. 6 Heat flow, loss C_p and storage C_p curves of CMS-MM OD dried (0% RH) sample obtained by MTDSC using two 40 µL aluminium pans as pan and cover

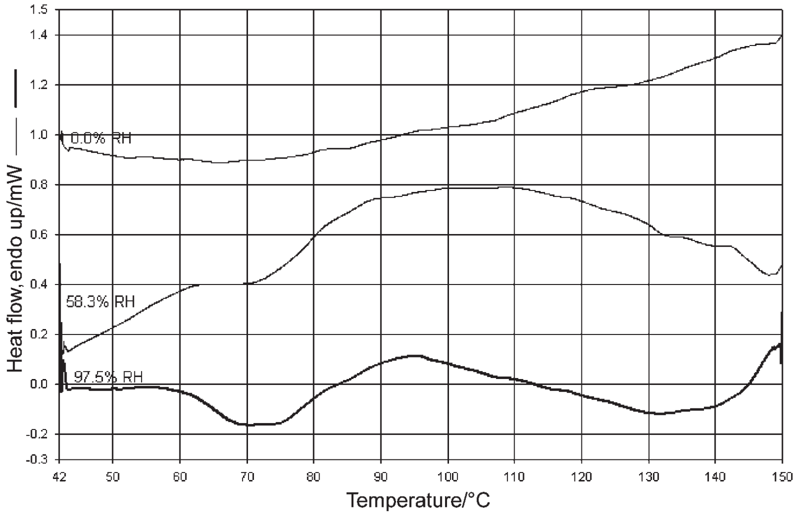

Fig. 7 Heat flow curve of HPS equilibrated at different RHs (0.0, 58.3 and 97.5%) obtained by TMDSC using two 40 µL aluminium pans as pan and cover

TMDSC data using two 40 µL aluminium pans as pan and cover

The use of two 40 µL pans as pan and cover was attempted to further reduce the headspace. It was hoped that this pan arrangement would also give a better contact and therefore heat transmission between the sample and the pan base. Only oven-dried samples and the carbohydrates stored at 0.0, 58.3 and 97.5% RH were used as examples of samples stored over the range of relative humidities.

A number of exothermic events were obtained, probably degradation, for HPS-MM OD, HPC-MM OD and CMS-MM OD samples in the heat flow curves. The exotherm peaks shifted to lower temperatures as the moisture content of the samples increased (Table 7). Endotherms in the HPC-MM OD and CMS-MM OD samples were probably a result of water loss from the sample. The complex endothermic/exothermic events found at higher moisture levels were again probably due to failures in pan integrity. Some variations in the storage specific heat curves were noticed, but a glass transition was only observed in CMS-MM OD samples equilibrated at 0.0% moisture. For this sample the T_g was ~120°C (Fig. 6). The loss specific heat curves were very irregular.

Table 7 Peak temperatures of endotherms (↑), exotherms (↓) or complex endotherms/exotherms (↓↑) found in the TMDSC heat flow curves of oven dried hydroxypropylstarch-methylmethacrylate (HPS-MM), hydroxypropylcellulose-methylmethacrylate (HPC-MM) or carboxymethylstarchmethylmethacrylate (CMS-MM) equilibrated at different relative humidities (%RH), using two 40 μL aluminium pans as pan and cover

Polymer	RH/%	Peak/°C	
HPS-MM FD	0.0	↓120–140	
	58.3	↓90	↓130
	97.5	↓75	↓↑130
HPC-MM FD	0.0	↓100	
	58.3	↑80	
	97.5	↑90	
CMS-MM FD	0.0	Relatively unchanged	
	58.3	↓75	↓123
	97.5	↓47–100	

No important events seemed to happen in the heat flow curves of HPS, HPC or CMS except for the presence of an exotherm (possibly degradation) at 70°C in HPS samples equilibrated at 58.3 and 97.5% RH (Fig. 7).

In conclusion, the integrity of the pan improved considerably, when two 40 μL aluminium pans were used as pan and cover. However, some failures in pan integrity were detected at higher temperatures. The exothermic events became bigger with increase in moisture content of the samples, again in concordance with the idea that the presence of water influenced degradation.

DSC data using standard aluminium pans and covers

In order to examine the loss of water from the samples, HPS-MM OD was chosen following storage at different RHs. Samples were scanned from 40 to 140°C using a heating rate of 10°C min^{-1}, and standard aluminium pans. The results are shown in Table 8. The evaporation endotherm appeared in all samples (Fig. 8), at similar temperatures. Their associated enthalpies (Table 8) increased as the amount of water in the samples becomes bigger and the data clearly supported the TMDSC data.

Table 8 Peak temperatures and enthalpies of moisture loss endotherms of oven dried hydroxypropylstarch-methylmethacrylate (HPS-MM OD) obtained by DSC of samples equilibrated at six different relative humidities (RH) and scanned from 40 to 140°C at 10°C min^{-1} in standard sample pans and lids

RH/%	Peak temperature/°C	Enthalpies ΔH/J g^{-1}
0.0	81.9	6.3
18.8	73.6	19.6
37.1	65.3	34.5
58.3	62.8	30.2
80.5	73.7	159.5
97.5	63.7	42.3

In an attempt to characterize the water polymer interactions, DSC was used with standard aluminium pans and covers. Cooling from 20 to –40°C at 5°C min^{-1} and holding at –40°C for 5 min was attempted to produce recrystallisation of any free (Type I) water in the samples which were subsequently reheated at to 20°C at 5°C min^{-1} to allow the subsequent melting of any recrystallised water. Samples of OD HPS-MM and FD HPS-MM were scanned under these conditions. Under these heating and cooling rates, no crystallisation or melting of water occurred indicating that no free water existed in the samples (Fig. 9).

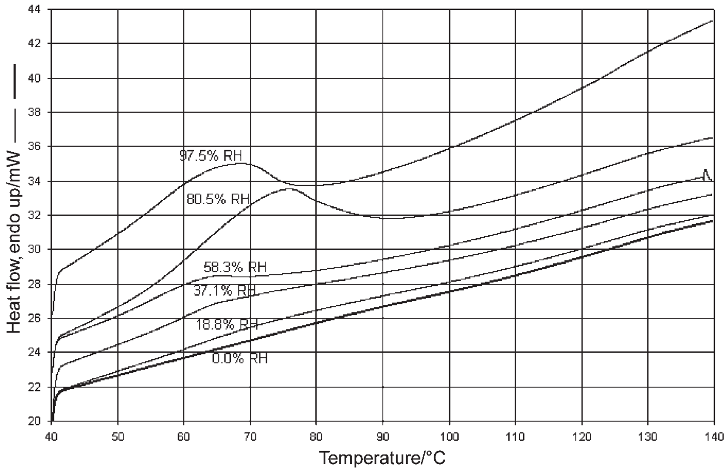

Fig. 8 Heat flow curves obtained by DSC of HPS-MM OD samples stored at different RHs and scanned, run between 40 and 140°C at 10°C min^{-1}

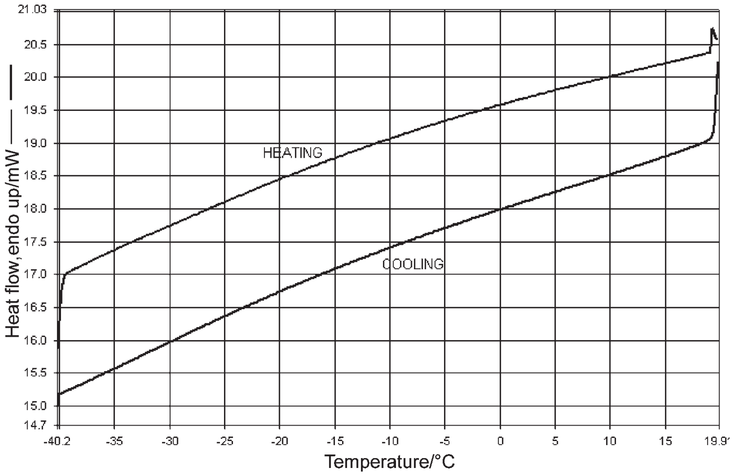

Fig. 9 DSC curves of a sample of HPS-MM OD sample equilibrated at 37.5% RH by cooling from +20 to –40°C at 5°C min^{-1}, holding at –40°C for 5 min and heating to +20°C at 5°C min^{-1}, using standard aluminium pans and covers

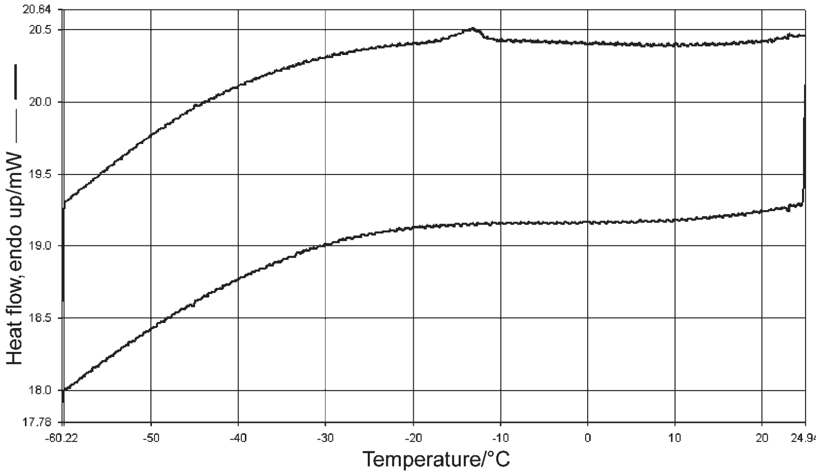

Fig. 10 DSC of a CMS sample equilibrated at 97.5% RH, by cooling from +25 to –60°C at 2°C min^{-1}, holding at –60°C for 2 min and heating to +25°C at 2°C min^{-1}, using standard aluminium pans and covers

The conditions were therefore further moderated. Again standard aluminium pans and covers were used but samples were cooled from 25°C to a lower temperature of –60°C at the slower rate of 2°C min^{-1}, held at –60°C for 5 min before reheating to 25°C at 2°C min^{-1}. The grafted co-polymers and the plain carbohydrates, following equilibration at 97.5% RH, were studied in an attempt to detect water loosely bound (Type II) to the polymer. Again no thermal events were apparent in the co-polymers indicating a lack of either Type I or Type II water. With regards the plain carbohy-

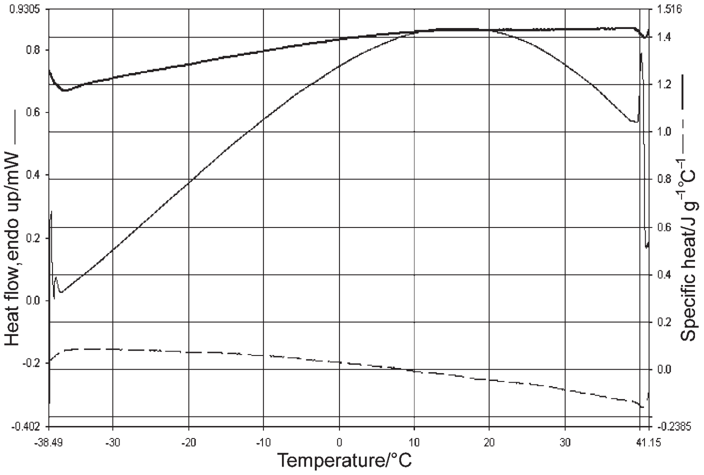

Fig. 11 Heat flow, storage C_p and loss C_p curves of HPS-MM OD equilibrated at 58.3% RH, obtained by TMDSC using standard aluminium pans and covers, scanned from –40 to +40°C

drates, whereas no transition was found in the samples of HPS or HPC, CMS indeed displayed a small endotherm on the heating step between –20 and –10°C, indicating the possibility of the existence of free water (Fig. 10).

TMDSC data using standard aluminium pans and covers from –40 to 40°C

TMDSC was used to examine the samples from –40 and 40°C to elucidate the DSC data. Samples from three storage conditions (0.0, 58.3 and 97.5% RH) of the three OD co-polymers and the plain carbohydrates were examined. The heat flow curves of each of the samples displayed an apparent endotherm throughout the temperature range. The peak temperature of these broad endotherms shifted to higher temperatures as the amount of moisture increased in the sample, from ~0°C to 10–20°C (Fig. 11). Presently no explanation can be given for this phenomena. No events were apparent in the storage or loss specific heat curves of the grafted polymers. However, the storage specific heat curve of HPC equilibrated at 0.0% RH displayed a very broad transition in the –10 to 10°C temperature range.

Conclusions

Only apparent values of the T_g were obtained in the TMDSC scans of the copolymer–water systems under study. When standard aluminium pans were used water evaporated on the heating released showing endotherm peaks. The plasticization effect of water can be observed in TMDSC scans of the copolymer-water systems under study when 40 μL aluminium pans and their corresponding covers (Perkin Elmer) were used.

Changes in shape problems appeared when sealed pans were used because of the high water vapour pressure into the pan headspace, that could make difficult the T_g determination. Generally the temperature range of the glass transition became broader as the RH of the storage conditions, and hence the amount of water contained in the copolymers, increased. However none of the pans used in this work were found to be completely suitable. The copolymers seemed to undergo exothermic degradation reactions in which the presence of water has an important role. Copolymerization with MMA worsened the degradation phenomenon since no degradation exotherms were evident in the TMDSC scans of the unreacted carbohydrates. Neither Type I or Type II water was detected in the copolymers.

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