Thermal Behavior of the Graft Copolymers of Crosslinked Gelatin[†]

D. SATYANARAYANA and P. R. CHATTERJI*

*Division of Organic Coatings & Polymers, Indian Institute of Chemical Technology,
Hyderabad 500 007, India*

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ABSTRACT: The thermal behavior of crosslinked gelatin and some of its graft copolymers was assessed by TGA and DSC. The graft copolymers show marked improvement in thermal stability and could be easily compression moulded, probably due to the plasticizing effects of the grafts on the peptide backbone.

KEY WORDS Crosslinked Gelatin / Glass Transition / Graft Copolymers / Plasticization /

Grafting natural polymers with suitable synthetic polymers is a very promising route for the development of biodegradable plastics with improved thermal properties.^{1–4} Natural polymers have in general, very poor thermal tolerance. When heated they tend to char and decompose without passing through a melt zone. Grafting with a suitable synthetic polymer can vastly improve this situation. Synthetic polymers which have sufficient amorphous content possess well defined T_g , the glass transition temperature. Though there are various theoretical interpretation of T_g ranging from segmental mobility to the free volume concept, there is total consensus on its practical importance. Manufacturing operations take advantage of the thermomechanical properties of a polymer in the vicinity of T_g to fabricate items of desired shape and size, because below T_g a polymer is a hard glass and above T_g it is soft and pliable.

Here we discuss attempts to improve the

thermal processability of glutaraldehyde cross-linked gelatin (Gelx) by grafting it with poly(acrylic acid) (PAA) and poly(methyl methacrylate) (PMMA) either individually or in combination. The thermal properties of natural polymers grafted with various synthetic polymers have been reported.^{1–8} The primary objective of the grafting a natural polymer with synthetic polymer is to enhance its low temperature ($< 200^\circ\text{C}$) workability rather than improve high temperature stability. Thermoplastic materials, for which biodegradable alternatives are being sought, are themselves not stable at high temperature; a property most required. They have T_g in the range of $100\text{--}150^\circ\text{C}$ and hence their processing temperatures too are low.

EXPERIMENTAL

The synthesis and characterization of the graft copolymers, Gelx-*g*-(PMMA), Gelx-*g*-

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* Author to whom correspondence should be sent.

Abbreviations: Gelx, crosslinked gelatin; Gelx-*g*-(PAA), crosslinked gelatin with poly(acrylic acid) grafts; Gelx-*g*-(PMMA), crosslinked gelatin with poly(methyl methacrylate) grafts; Gelx-*g*-(PMMA, PAA), crosslinked gelatin with both PMMA and PAA grafts; DSC, differential scanning calorimetry; Gel, gelatin; PAA, poly(acrylic acid); PMMA, poly(methyl methacrylate); SEM, scanning electron microscopy; TGA, thermo gravimetric analysis.

(PAA), and Gelx-*g*-(PMMA, PAA) have been reported in detail elsewhere.⁹⁻¹¹ However to recount in brief, gelatin was first crosslinked using aqueous glutaraldehyde. The crisp granules were washed thoroughly with water and then acetone. The granules were then dried at 40°C under vacuum. Gelx was graft copolymerized with MMA or AA in aqueous medium using 0.1% potassium persulfate as initiator at 70°C. At this temperature, persulfate decomposes to yield radicals some of which generate free radical centers on the gelatin network. These centers initiate the chain polymerization of the monomer in the medium. The product is then subjected to soxhlet extraction with a suitable solvent to remove the homopolymer. The graft copolymer left behind is dried under vacuum and weighed. To get the amphiphilic system, Gelx-*g*-PMMA samples were subjected to a second graft copolymerization with acrylic acid as the monomer under the same experimental conditions.

Here we discuss Gelx-*g*-PMMA samples with 65, 115, and 212% grafting Gelx-*g*-(PAA) samples with 65, 94, and 180% grafting and amphiphilic matrices with *L/H* values 0.76,

1.05, 1.60, and 2.26. *L/H* indicate the ratio (wt%) of PMMA content (*L*) to PAA content (*H*) in a graft copolymers. The composition of the samples are given in Table I. TGA and DSC measurements were carried out in an oxidising atmosphere with Du Pont 951 and Du Pont 9900 model thermal analyzers. To avoid variation due to particle size, the powdered samples were sieved through analytical sieves (No. BSS 40 and 30) to yield particles of 360–500 μm . 5–10 mg of the material were used in all experiments. Details of the DSC curves in this paper differed slightly from those reported earlier,¹¹ because in the earlier study particle size was not considered. The heating rate was 20°C min⁻¹. Moisture content of the samples was determined by the isothermal method. Scanning electron micrographs were taken in a 5520 Hitachi Model Unit. The samples were gold coated in the usual manner prior to examination to prevent charging in the electron beam.

RESULTS AND DISCUSSION

Thermal softening is not a characteristic of protein. Most proteins, when heated undergo

Table I. Compositions details and moisture content of Gelx and graft copolymers^a

S. No.	Sample	% grafting		<i>L/H</i>	Moisture content/%
		PMMA	PAA		
1	Gelx	—			13.16
2	Gelx- <i>g</i> -(PMMA)	212			2.88
	Gelx- <i>g</i> -(PMMA)	115			5.42
	Gelx- <i>g</i> -(PMMA)	65			5.19
3	Gelx- <i>g</i> -(PAA)		180		7.67
	Gelx- <i>g</i> -(PAA)		94		7.24
	Gelx- <i>g</i> -(PAA)		65		6.95
4	Gelx- <i>g</i> -(PMMA, PAA)	212	94	2.26	3.06
	Gelx- <i>g</i> -(PMMA, PAA)	115	72	1.60	4.33
	Gelx- <i>g</i> -(PMMA, PAA)	212	202	1.05	4.05
	Gelx- <i>g</i> -(PMMA, PAA)	65	86	0.76	4.18

^a PMMA, poly(methyl methacrylate). ^b PAA, poly(acrylic acid).

charring and decomposition, without melting. Morita¹² studied several proteins by Differential Thermal Analysis (DTA) and observed that proteins in general exhibit a series of endotherms in the 120–300°C region and a major exotherm above 500°C. He attributed the low temperature endotherms to various of conformational transitions, moisture loss and small scale chain degradation. The exotherm above 500°C was assigned to total degradation.

Gelatin, in native and crosslinked states when heated, loses moisture and turns into a charred mass, without further weight loss, at $\approx 200^\circ\text{C}$. Our attempts to hot compress Gelx (120°C, 100 kg cm⁻²) into pellets, films or blocks were unsuccessful, all were brittle, and crumbled at the slightest pressure. Extensive degradation as indicated by steady large scale weight loss begins only at 300°C and by 500°C most of the material is lost (Figure 1).

With isothermal TGA methods, we estimated the moisture content of Gelx to be 13.6%. Comparing TGA and DSC curves in Figure 1, we conclude that the low temperature

Figure 1. Thermal behavior of crosslinked gelatin (Gelx). A, TGA; B, DSC.

endotherm spanning 50–120°C, with a peak at $\approx 74^\circ\text{C}$ is due to moisture loss, since this feature is conspicuously absent in preheated samples. The tendency of gelatin to char in the vicinity of 200°C might be due to extensive chain denaturation. DSC indeed records an endotherm beginning at 200°C, with a peak at $\approx 240^\circ\text{C}$. This endotherm smoothly changes into an exotherm at about 300°C. The point to be noted here is that this endotherm represents a purely conformational transition since there is no record of weight loss in the TGA curve in this region.

In marked contrast, no graft copolymer samples char on heating. All are translucent amber colored on compression moulding (temperature 120°C and pressure 100 kg cm⁻²) (Figure 2). Moisture content of the graft copolymers are low in comparison to Gelx (Table I). Extensive degradation sets in only after 300°C as indicated by the TGA curves shown in Figures 3 and 4.

The thermal behavior of Gelx-*g*-(PMMA)

Figure 2. Compression moulded strips and pellets of graft copolymer matrices. (a) Gelx-*g*-(PMMA, PAA) samples: I, $L/H=1.05$; II, $L/H=2.26$; IV, $L/H=1.60$. (b) 1, Gelx-*g*-(PMMA)-212; 2, Gelx-*g*-(PAA)-180; 3, Gelx-*g*-(PMMA, PAA) $L/H=1.05$.

Figure 3. Thermal behavior of Gelx-*g*-(PMMA) samples. A: TGA of $\square$ — $\square$, Gelx-*g*-(PMMA)-65; *—*, Gelx-*g*-(PMMA)-115; $\times$ — $\times$, Gelx-*g*-(PMMA)-212. B: DSC of Gelx-*g*-(PMMA)-115.

samples shown in Figure 3. T_g of PMMA is $\approx 120^\circ\text{C}$ and hence the broad endotherm spread over 50 – 150°C may indicate moisture loss and T_g of PMMA. DSC of Gelx-*g*-(PMMA) also registers an endotherm above 200°C with a peak at $\approx 240^\circ\text{C}$ resembling the one in Gelx (refer Figure 1 inset). Since PMMA does not have any known transition in this temperature range, it may be concluded that this endotherm belongs to the Gelx component.

Figure 4 shows the thermal behavior of Gelx-*g*-(PAA) samples. The salient features of the DSC of Gelx-*g*-(PAA) are the following:

- endotherm at $\approx 74^\circ\text{C}$: this is due to moisture loss since this does not appear in preheated samples.
- endotherm in the 100 – 150°C region: most probably this is due to the glass transition of the PAA chains, since TGA does not register weight loss in this region.
- endotherm in the 250 – 270°C : this endotherm may be a combination of

Figure 4. Thermal behavior of Gelx-*g*-(PAA). A: TGA of $\square$ — $\square$, Gelx-*g*-(PAA)-64; $\times$ — $\times$, Gelx-*g*-(PAA)-94, *—*, Gelx-*g*-(PAA)-180. B: DSC of Gelx-*g*-(PAA)-180.

transitions in Gelx, and anhydride formation in the PAA chain which begins above 250°C .

Thus we may reasonably infer that the transitions in Gelx above 200°C are responsible for charring. In the graft copolymer samples, pliant PAA and PMMA chains facilitate heat dissipation, mitigating the destructive transitions in the Gelx which would otherwise lead to charring.

Figure 5 gives the thermal behavior of Gelx-*g*-(PMMA, PAA). There are no unexpected endotherms or exotherms. T_g s of PAA and PMMA are so close that they overlap, expressing a single endotherm.

The ease with which the graft copolymers could be compression moulded into desired shapes at 120 – 150°C proves that the thermal response of the PAA and PMMA chains effectively influences the protein core. This may very well be a case of side chains plasticizing the main chain. The compression molded products are translucent with a homogeneous texture when examined under the microscope.

Even SEM pictures do not suggest any phase separation (Figure 6).

Logically, it is very difficult to envision phase

Figure 5. Thermal behavior of amphiphilic matrices. A: TGA of $\square$ — $\square$, $L/H=2.26$; $\times$ — $\times$, $L/H 1.60$; $*—*$, $L/H 1.05$; $\bullet$ — $\bullet$, $L/H 0.76$. B: DSC of $L/H 1.05$.

separation in the present case. The randomly and densely anchored PAA or PMMA (or both) chains may impose severe mobility constraints on the protein chains, which are crosslinked themselves. This rules out the possibility of phase segregation of the graft copolymer into gelatin rich and PAA/PMMA rich domains. Without mobility, the protein segments relax only when the segmental motion of the side chains is relayed to them. This would lead to relaxation of the protein in synchronization with the grafted chain at their T_g and the material as a whole would behave as a single phase.

The concept of cooperative relaxation in condensed macromolecular systems was originally introduced by Pakula^{13,14} to explain segmental mobility in severely constrained systems such as entangled, ring or branched polymers. Cooperative motion sets in at temperatures above T_g , where the same segments are free and energetic enough to induce motion in a neighboring segment.^{15–17} Such a mechanism may be operative here, to protect the protein core from heat denaturing effect.

Figure 6. Scanning electron micrographs of gelatin, Gelx, and graft copolymers. 1, gelatin; 2, Gelx; 3, Gelx-*g*-(PAA)-180; 4, Gelx-*g*-(PAA)-94; 5, Gelx-*g*-(PAA)-65; 6, Gelx-*g*-(PMMA)-212; 7, Gelx-*g*-(PMMA)-115; 8, Gelx-*g*-(PMMA)-65; 9–12, amphiphilic matrices L/H , 0.76, 2.26, 1.05, and 1.60, respectively.

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