Thermal Properties of Wool-g-Poly(Methyl Methacrylate) Copolymers

V. J. ELANGOVAN* and S. SACCUBAI

Department of Polymer Science, University of Madras, Guindy Campus, Madras-600 025, India

SYNOPSIS

The thermal properties of wool fibers can be improved by graft copolymerization with vinyl monomers. Using TGA, DTG, and DSC techniques, the thermal behavior of methyl methacrylate grafted wool fibers was studied. Graft copolymerization was carried out using $KBrO_3$ and substrates such as Fe(II), Co(II), cysteine, cystine, tyrosine, and urea. Of all the systems studied the grafted fibers which involve Fe(II), Co(II), and cystine gave improvement in the thermal stability.

INTRODUCTION

Several authors have reported the graft copolymerization of methyl methacrylate (MMA) onto wool, but studies on the thermal properties of the graft copolymers are very few.[1,2] In this paper, it is our aim to analyze by TGA, DTG, and DSC and report on the thermal properties of the graft copolymers obtained from wool grafted with MMA using $KBrO_3$ by itself as well as redox combinations of $KBrO_3$ with cysteine, cystine, tyrosine, urea, Fe(II), and Co(II), as initiator systems.

The thermograms of PMMA and wool show that PMMA is more stable up to 375°C and the wool is highly stable from 375 to 570°C. Therefore, if these two polymers were welded together, then the thermal behavior of the resultant product may be expected to be better in the whole of the temperature range (0–600°C). For instance, the bisulfite-reduced and MMA-grafted wool had given better thermal properties to the grafted wool.[3]

It is generally known that when the keratin fibers are heated or drawn, they undergo physical or structural changes. These changes are accompanied by endothermic or exothermic changes as borne out in differential scanning calorimetry (DSC).

To study the structural changes, if any, due to grafting, DSC thermograms were taken for natural and grafted wool as only a limited amount of work has been done for wool using this technique.[4]

EXPERIMENTAL

Methods of grafting MMA onto wool have been reported earlier.[5] TGA, DTG, and DSC curves were recorded on a Mettler TA3000 system analyzer in the presence of air.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

From the results of the present investigation it was found that the general shape of the thermograms did not differ much after graft copolymerization using various initiator systems (Figs. 1–4). There were three zones of weight loss observed in all the thermograms.[1]

The initial weight loss occurred up to approximately 150°C. This weight loss was due to the evaporation of moisture and did not change very much for all the systems. The second stage decomposition took place up to 400°C accompanied by approximately 50% weight loss. This is attributable to the

* To whom correspondence should be addressed at Anabond Pvt. Ltd., Type-II, 36 V. S. I. Campus, Thiruvanmiyur, Madras-600 041, India.

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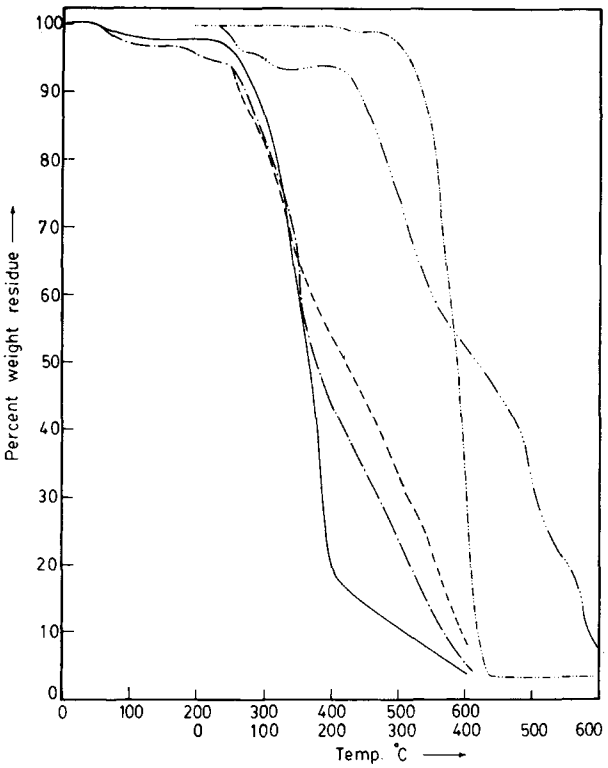

Figure 1 Thermograms of (- · · · -) ungrafted wool and (- · - -) PMMA. $KBrO_3$–Fe(II)–MMA–wool system: (- - -) 28.26% grafting; (- · -) 49.3% grafting; (—) 90.58% grafting.

degradation taking place at the side chain level. The weight loss generally decreased with increase in percentage graft-on for the grafted wool sample. The third stage decomposition happened almost up to 600°C and was covered by 30–40% weight loss. This was probably the destruction of the backbone by heat energy.

Of all the systems studied, the grafted fibers which came from the systems involving Fe(II), Co(II), and cystine registered an improvement in the thermal stability as revealed by the data obtained (Table I; Figs. 1, 3, and 4). It was found from the literature that ferrous sulfate gave bonds with wool fiber which were stable to refluxing action of boiling N/10 HCl, and the treatment of H_2S–H_2O solution for a longer period.[6]

Even though the same oxidant was used, as the reductants used were different, different effects on the thermal properties of wool were observed. Potassium bromate alone and $KBrO_3$–tyrosine redox systems produced grafted wool samples, where the percent graft-on was more and the stability was also higher (Fig. 2). Here, any damage done to the wool fiber during grafting reaction might have been compensated for by higher percentage of grafting.

All the other systems gave better results with lower graft-on percent (Table I; Figs. 1, 3, and 4). This is understandable, for any new protective linkages formed during minimum amount of grafting may be spoiled or masked by further deposition of graft chains.

Derivative Thermogravimetric Analysis (DTG)

Derivative thermogravimetric analysis gave a clear and distinct picture of the above three stages of thermal decomposition (Figs. 5–8) for the wool samples. The DTG of ungrafted wool gave three peaks at 70, 290, and 510°C, respectively and the DTG of PMMA showed only one peak at 410°C [Fig.

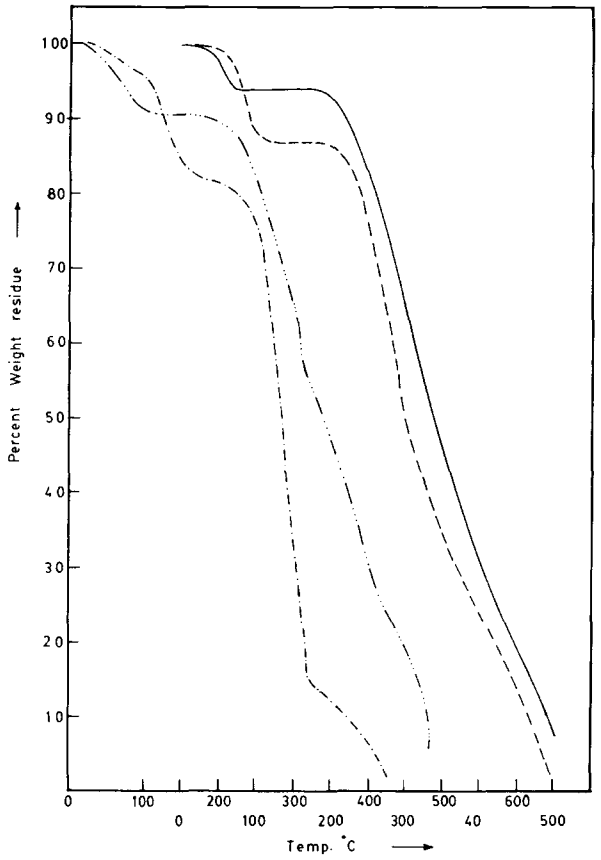

Figure 2 Thermograms of $KBrO_3$–MMA–wool system. [(- - -) 14.96% grafting; (—) 41.1% grafting] and $KBrO_3$–tyrosine–MMA–wool system [(- · -) 13.32% grafting; (- · · · -) 35.56% grafting].

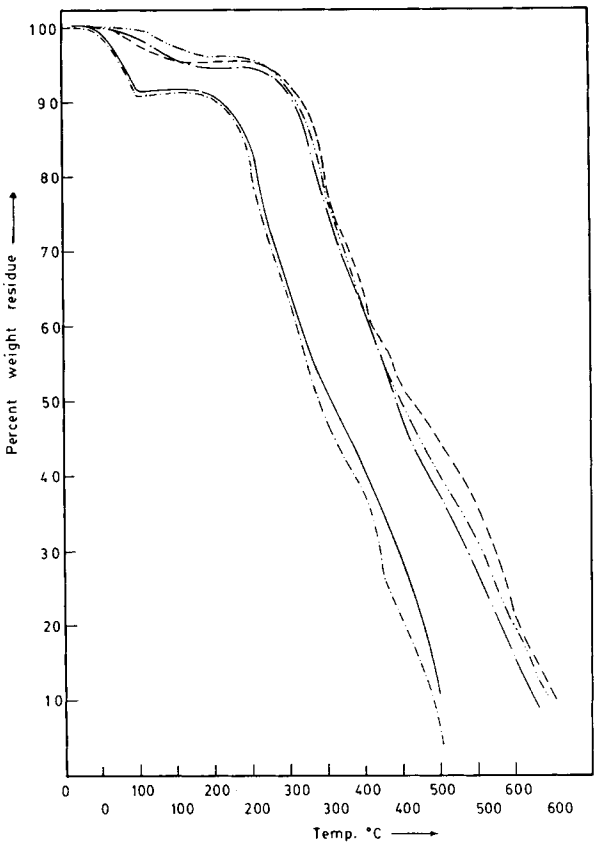

Figure 3 Thermograms of $KBrO_3$–Co(II)–MMA–wool system [(---) 20.22% grafting; (- · · -) 30.22% grafting; (- · -) 44.16% grafting] and $KBrO_3$–cysteine–MMA–wool system [(—) 8.14% grafting; (- · -) 30.08% grafting].

5(B)]. The first peak around 70°C corresponded to the removal of moisture. Moisture regain studies showed that as the graft-on percent increased, the moisture content of the wool sample decreased. The moisture-absorbing power was also reduced as is evidenced from the absence of the first peak in the case of wool–PMMA obtained from $KBrO_3$–Fe(II) initiator system for high graft-on [Fig. 6(C)]; and it was also absent in the case of PMMA graft chain obtained from the grafted wool by acid hydrolysis [Fig. 5(B)]. From the DTGs of the various grafted wool samples it is obvious that this peak height decreased with increasing percent graft-on.

The second peak may be due to the decomposition of amino acid residues present in the keratin fiber. This second peak at 290°C and the decomposition peak of PMMA at 410°C both overlapped with each other to produce a new peak pattern covering these two temperature regions for the PMMA-grafted wool samples, also giving evidence for graft copolymerization.

The third peak corresponding to the decomposition of wool was at about 510°C. As the graft-on percent increased, this peak was shifted to lower temperatures. Literature survey also showed that generally the PMMA-grafted wool showed better thermal properties in the lower temperature range up to 375°C, but in the higher temperature zone the stability of the grafted wool became less than that of wool.[1,2] Further, this peak attained smaller values and finally disappeared completely in the case of high graft-on wool from $KBrO_3$–Fe(II) system. For this sample only one peak was present at 370°C [Fig. 6(C)], which was closer to that of PMMA [Fig. 5(B)].

Differential Scanning Calorimetry (DSC)

In all the samples studied, endotherm peaks were observed (around 100–120°C) for grafted (Figs. 10 and 11) as well as for ungrafted natural fiber (Fig.

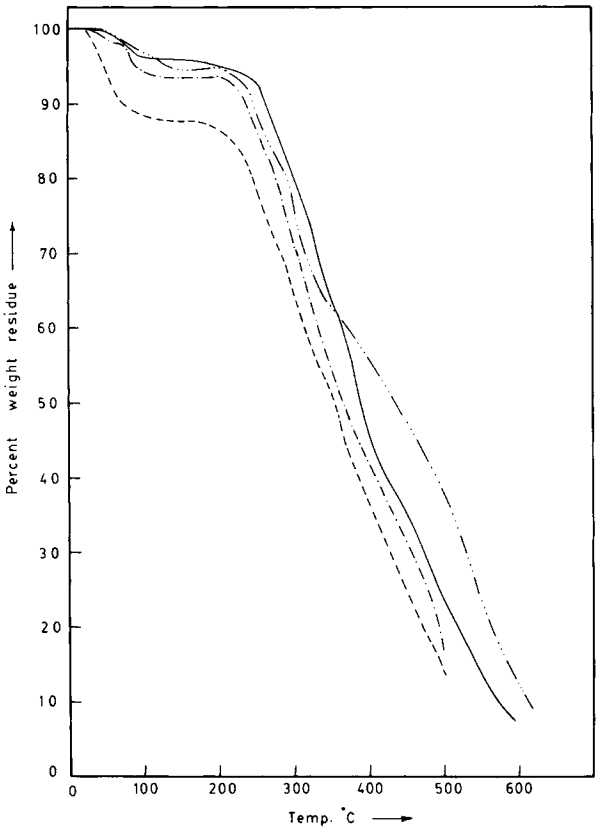

Figure 4 Thermograms of $KBrO_3$–cystine–MMA–wool system [(- · · · -) 6.02% grafting; (——) 43.7% grafting] and $KBrO_3$–urea–MMA–wool system [(- · -) 19.32% grafting; (---) 34.56% grafting].

Table I Decomposition Temperature of Natural Wool and Grafted Wool Samples

No.	Sample	% Grafting	Initiator System	DT (°C) for Every 10% Weight Loss								
				10	20	30	40	50	60	70	80	90
1.	Wool	—	—	245	285	320	350	420	480	510	560	585
2.	PMMA	—	$KBrO_3$–Fe(II)	340	355	370	380	390	400	405	415	420
3.	Wool-*g*-PMMA	14.98	$KBrO_3$	95	240	265	285	305	335	375	425	465
		41.10	$KBrO_3$	220	260	290	315	340	370	405	450	495
4.	Wool-*g*-PMMA	28.26	$KBrO_3$–Fe(II)	260	300	340	370	420	470	520	555	590
		49.30	$KBrO_3$–Fe(II)	270	305	335	355	380	415	470	520	570
		90.58	$KBrO_3$–Fe(II)	285	315	335	350	365	380	390	400	510
5.	Wool-*g*-PMMA	20.22	$KBrO_3$–Co(II)	270	305	320	365	415	475	520	550	600
		30.22	$KBrO_3$–Co(II)	265	300	330	360	400	450	505	545	—
		44.16	$KBrO_3$–Co(II)	270	305	335	365	395	440	485	535	575
6.	Wool-*g*-PMMA	8.14	$KBrO_3$–cysteine	210	260	285	320	350	400	445	480	—
		30.08	$KBrO_3$–cysteine	210	250	280	310	340	380	420	460	—
7.	Wool-*g*-PMMA	6.02	$KBrO_3$–cystine	265	290	325	375	440	490	530	565	—
		43.70	$KBrO_3$–cystine	270	300	330	360	390	420	475	520	—
8.	Wool-*g*-PMMA	13.32	$KBrO_3$–tyrosine	125	230	265	275	285	295	305	315	375
		35.56	$KBrO_3$–tyrosine	190	250	285	310	340	375	405	450	475
9.	Wool-*g*-PMMA	19.34	$KBrO_3$–urea	240	280	300	330	365	410	450	480	—
		34.56	$KBrO_3$–urea	75	245	280	315	355	385	430	470	—

9). These peaks may be attributed to the absorbed moisture present in the samples. In the case of grafted wool (it is reported that PMMA has a T_g of 105°C),[7] the endothermic peak around 100–120°C may be due to the overlapping of the T_g of PMMA with that of moisture.

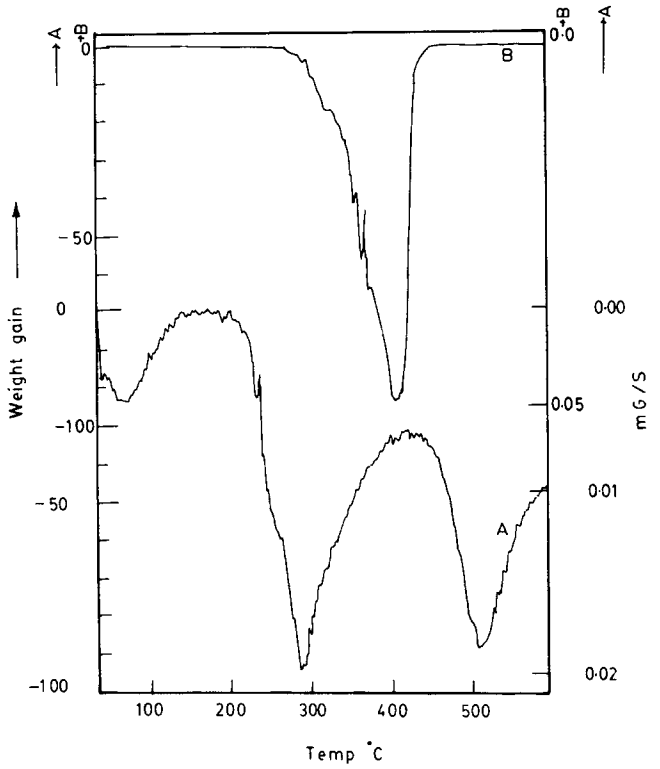

Figure 5 Derivative thermograms of (A) ungrafted wool and (B) PMMA.

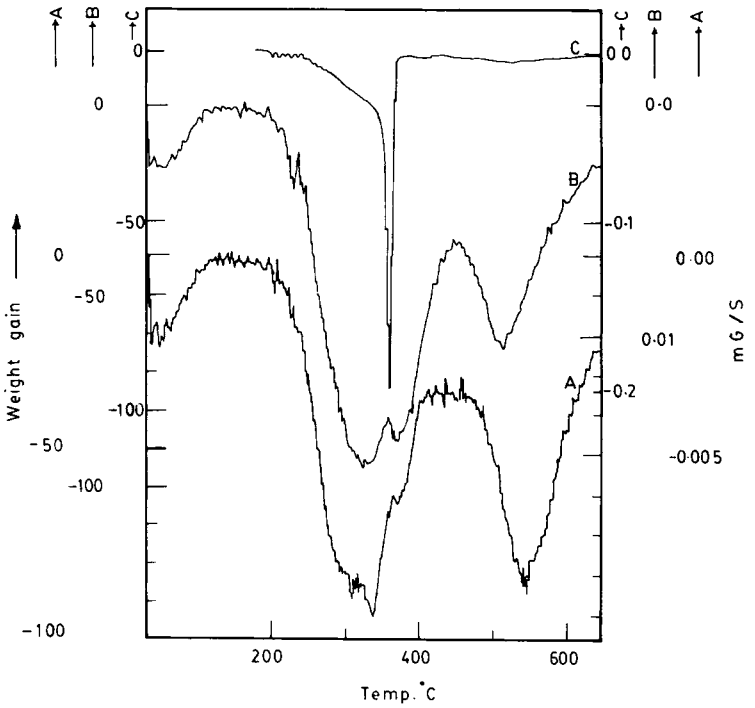

Figure 6 Derivative thermogram of $KBrO_3$–Fe(II)–MMA–wool system: (A) 28.26% grafting; (B) 49.3% grafting; (C) 90.58% grafting.

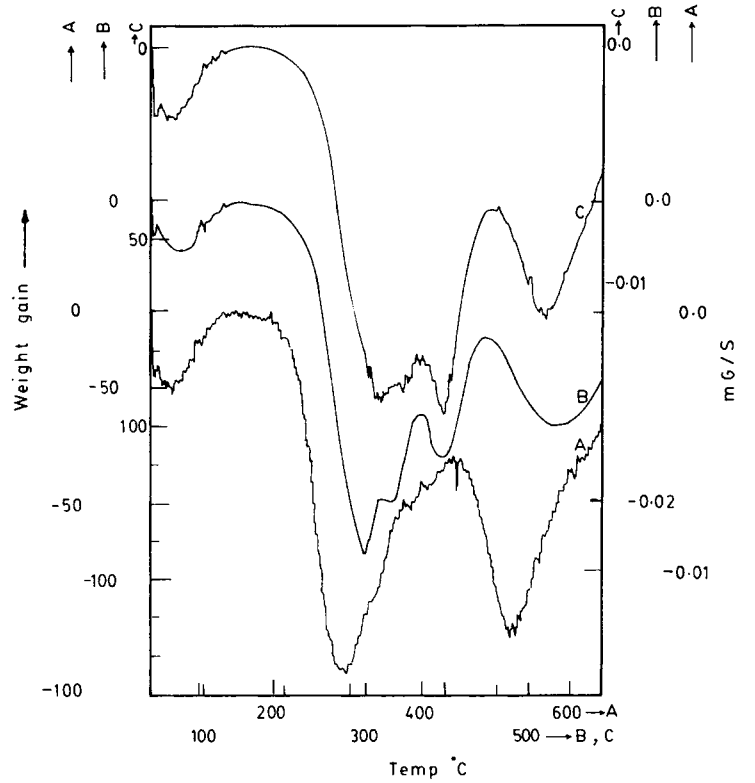

Figure 7 Derivative thermogram of $KBrO_3$–Co(II)–MMA–wool system: (A) 20.22% grafting; (B) 30.22% grafting; (C) 44.16% grafting.

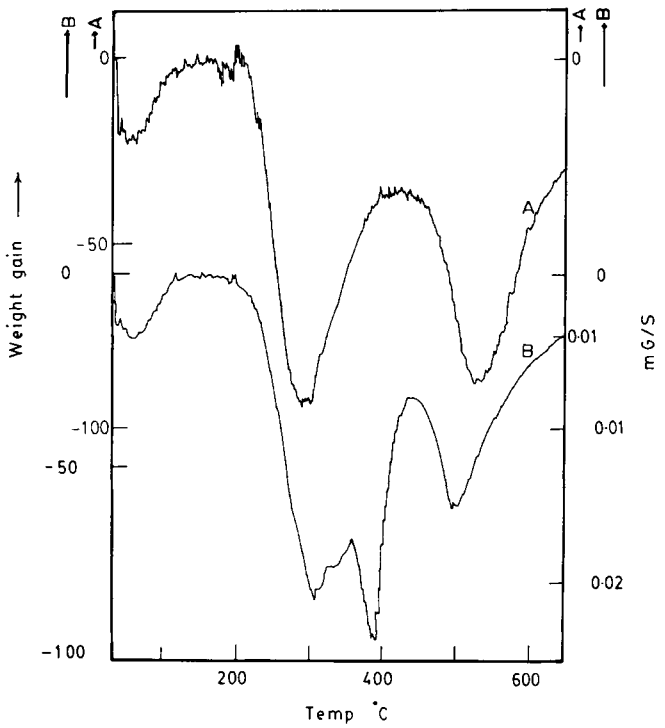

Figure 8 Derivative thermogram of $KBrO_3$–cystine–MMA–wool system: (A) 6.2% grafting; (B) 43.7% grafting.

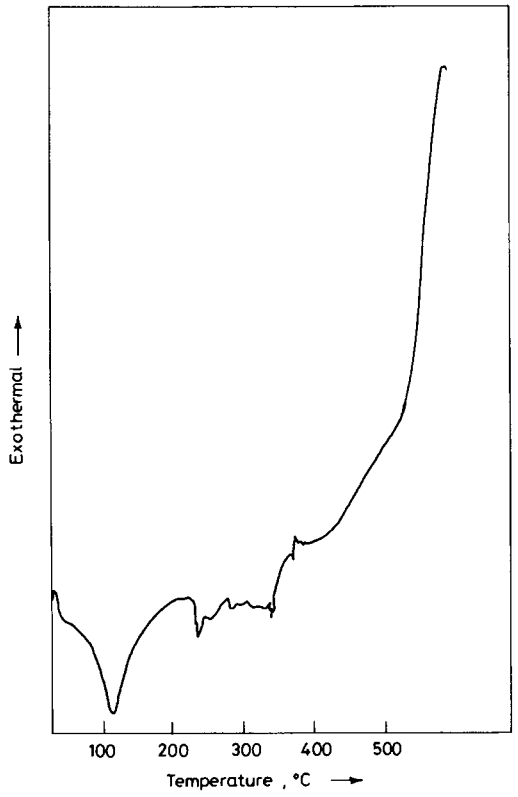

Figure 9 DSC thermogram of ungrafted wool.

An endothermic peak around 230°C was seen in all the cases (natural and grafted). This is due to the melting of α-helix, which is characteristic of all keratin fibers. In the system $KBrO_3$–cysteine, the endothermic peaks observed for the 8.14, 30.08, and 44.74% grafted wool were around 233, 231, and 230°C, respectively (Fig. 10). From these endotherms it is clearly seen that when the graft-on of PMMA increases, the intensity of the peak around 230°C, which is characteristic of keratins, decreases. This also serves as evidence for the grafting of PMMA onto wool. As the endotherm around 230°C did not show any perceptible shift with the extent of grafting, it can be assumed that the backbone of the wool did not undergo any structural change due to graft copolymerization of PMMA.

The same trend was also observed in the case of $KBrO_3$–Co(II) system, where the 11.66, 20.22, and 39.52% graft-on wool samples gave endotherm peaks again around 235, 234, and 233, respectively (Fig. 11), thus confirming the above conclusions.

A look at the DSC traces of wool grafted with PMMA fails to show any characteristic pattern that is attributable to the PMMA branches. This may be attributed to the fact that the T_g of PMMA (approximately 105°C) may be masked by the endothermic peak given by the moisture in the sample,

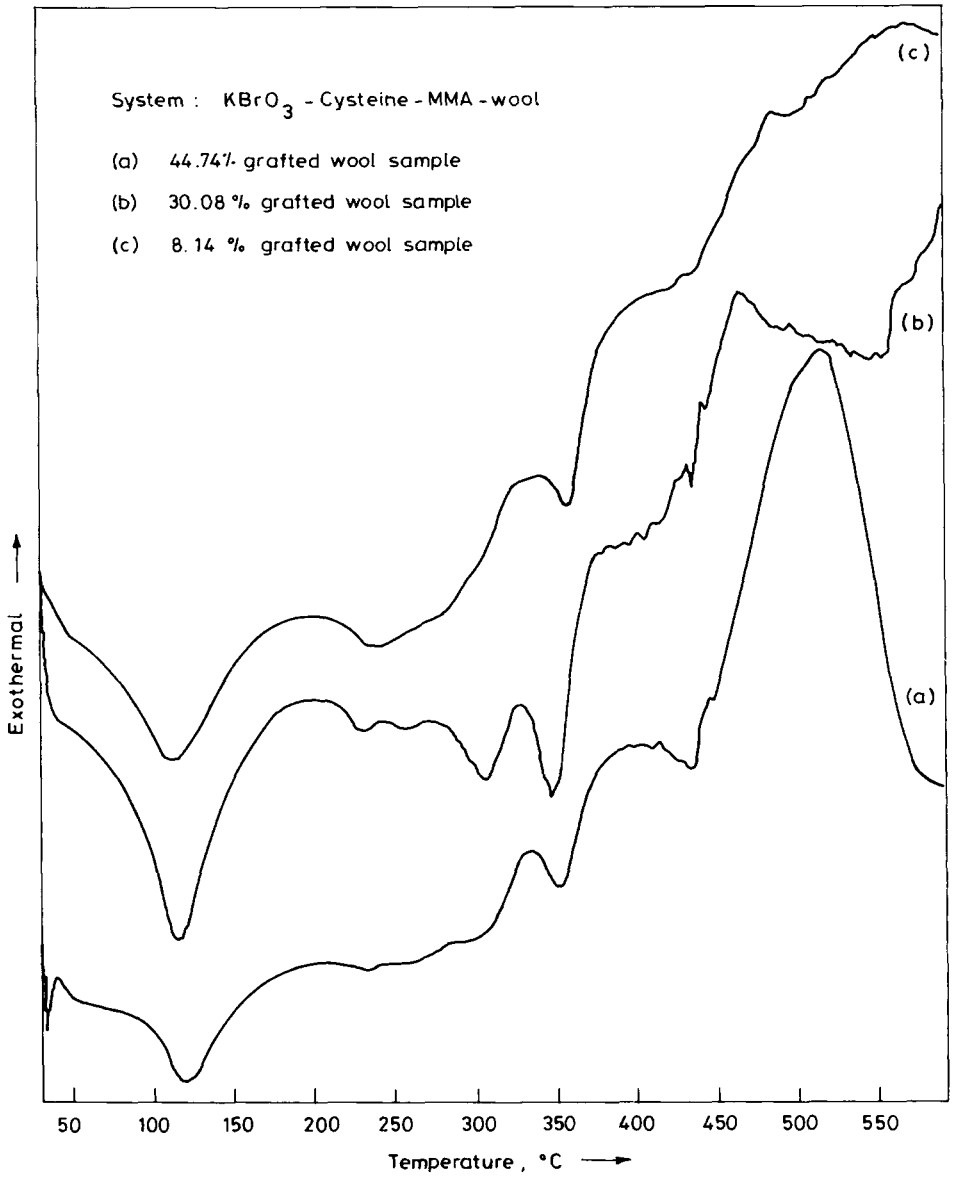

Figure 10 DSC thermograms of grafted wool.

and the endothermic peak due to the depolymerization of the grafted PMMA (approximately 220°C) may again overlap with the endothermic transition of the backbone fiber at approximately 230°C. Thus the presence of grafted PMMA on wool does not change the DSC trace of the backbone to any significant extent.

The system $KBrO_3$–Co(II) seems to affect the thermal behavior of the graft copolymer to the extent that there are many undefined exothermal and endothermal peaks of low intensity beyond 400°C. The less intense endotherm at approximately 360°C in grafted and ungrafted samples cannot be characterized without further studies.

CONCLUSION

Of all the systems studied, the grafted fibers resulting from redox systems involving Fe(II), Co(II), and cystine gave improvement in the thermal stability. From the DSC studies it was assumed that there was no structural change due to grafting reaction of MMA onto wool, which indicated that $KBrO_3$ could affect graft copolymerization without affecting much the wool backbone.

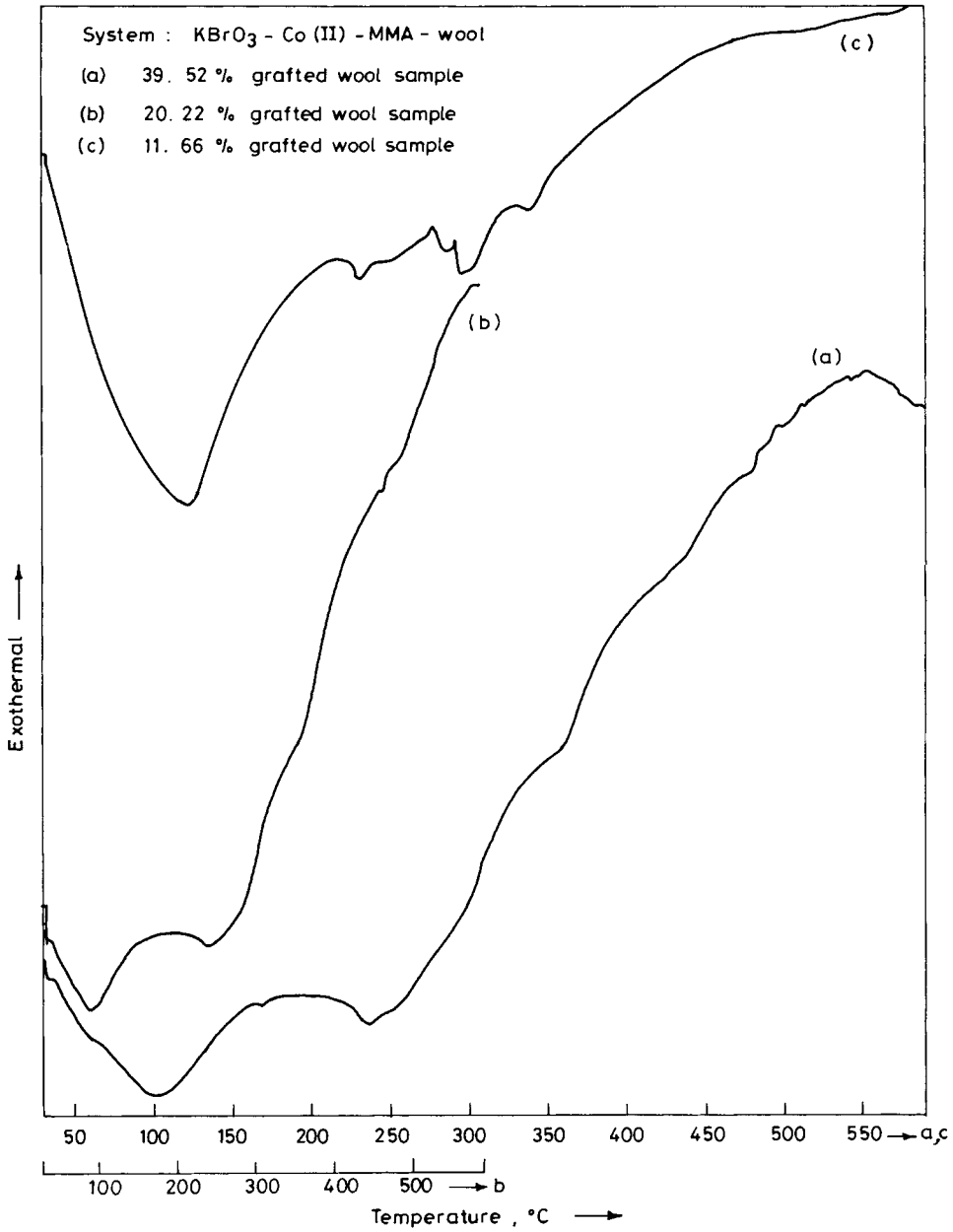

Figure 11 DSC thermograms of grafted wool.

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