

A Study of the Thermal Behavior of Graft Copolymers of Wool and Methyl Methacrylate

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Synopsis

Thermal behavior of the natural and chemically modified wool fibers (treated with sodium hydroxide and formic acid and reduced with sodium bisulfite and thioglycolic acid) and of the graft copolymers of natural and modified wool with methyl methacrylate (MMA) monomer was studied using dynamic thermogravimetry in air at a heating rate of 6°C/min to 600°C. The thermograms showed three distinct regions of weight loss for all the cases. A comparison of the temperatures of various percentage decompositions reveals that the thermal stability increased slightly with chemical modification of wool as compared to natural wool. Caustic soda and sodium bisulfite probably forms more stable lanthionine linkages, whereas formic acid improves the thermal stability perhaps by modifying the noncrystalline region of the fiber. In the case of natural wool after graft copolymerization with MMA, thermal stability improves up to 325°C probably owing to the formation of new crosslinks, but after 325°C the thermal stability decreases owing to early decomposition of the polymer as compared to wool fiber. Similar effects are observed in all the chemically modified fibers except in wool reduced with sodium bisulfite, where thermal stability is found to increase after grafting even at higher temperature. The thermal stability was also computed from the primary thermograms by calculating the integral procedural decomposition temperature; the results show that thermal stability increases slightly with chemical modification of wool as compared to natural wool. In the case of natural wool with graft copolymerization with MMA, the overall thermal stability decreases, because the decrease of thermal stability after 325°C seems to be more prominent than the increase in thermal stability before 325°C. The same effects are observed in all the chemically modified fibers, except for fibers reduced with sodium bisulfite, where the overall thermal stability increases slightly with increase in graft-on.

INTRODUCTION

The thermal behavior of polymeric materials over a range of temperatures is an important aspect which influences their potential utility. Thermogravimetric analysis (TGA) is an effective technique for studying the thermal stability of polymers. Differential thermal analysis (DTA) and TGA have been carried out by Schwenker et al.¹ to investigate the thermal stability of textile fibers, both natural and synthetic.

The physical properties of wool fibers can be improved by graft copolymerizations with vinyl monomers,^{2,3} and there has been good progress recently in this direction.^{4,5} However, no work has so far been reported

about the thermal behavior of these graft copolymers. The present paper deals with the thermogravimetric analysis of graft copolymers of natural and chemically modified wool fibers with methyl methacrylate (MMA) monomer.

The thermal decomposition of wool is probably accompanied by denaturation, breakage of peptide linkages, and elimination of simple molecules like H_2O , CO_2 , H_2S , CH_3SH , and NH_3 , etc.⁶ The elimination of such simple molecules should be diminished by the grafting of MMA on the reactive sites, and this should increase the decomposition temperature of grafted wool compared to the natural sample. Chemical modification of wool which involves the breakage of hydrogen bonding (formic acid treatment), formation of lanthionine, or reduction should also affect the decomposition temperatures. The present investigations were undertaken to determine the effect of chemical modification and grafting on the thermal stability of the wool.

EXPERIMENTAL

Preparation of Samples

Chemical Modifications of Wool. The natural wool samples and four chemical modifications of wool were grafted with methyl methacrylate (MMA) monomer. The chemical modifications of wool were, (i) swelling by dilute caustic soda solution, (ii) swelling by 98% formic acid, (iii) reduction by sodium bisulfite, and (iv) reduction by thioglycolic acid. The chemical modifications were done with a view to increasing the percentage grafting at a particular time of reaction with optimum change in the mechanical properties. The details of the methods have been reported elsewhere.⁷

Preparation of Graft Copolymers. The wool fibers were extracted for 24 hr in ether to remove the greasy matter, washed thoroughly and dried before use. The graft copolymerization of natural as well as chemically modified wool with MMA was done by free-radical mechanisms using ferrous ammonium sulfate-hydrogen peroxide initiator at 45°C. After polymerization, the homopolymers were removed by Soxhlet extraction with benzene for 12 hr. The graft-on was calculated as the percentage increase in weight over the original weight of the sample. The details of the method of graft copolymerization are given in the earlier publication.⁷

Dynamic Thermogravimetric Analysis

The thermogravimetric analysis was done using a Stanton Model HT-D thermobalance in air. The fiber samples were cut into approximately $1/16$ -in. lengths, and 52 ± 3 -mg samples were taken for each experiment. The thermograms were run from room temperature to a temperature of 600°C at a heating rate of 6°C/min. Primary thermograms were obtained by plotting percentage residual weight against temperature.

RESULTS AND DISCUSSION

Figures 1 to 5 show the thermograms of natural and chemically treated wool fibers both without grafting and with different percentages of graft-on. The general shape of the thermograms do not differ much after various chemical treatments of the fibers as compared to natural wool. It is obvious from the thermograms in all the cases that there are three distinct zones of weight loss.

The initial weight loss occurs up to approximately 160°C. The weight loss found in this region is due to loss of moisture. The weight loss due to moisture does not change very much with the caustic soda treatment and reduction with sodium bisulfite, as compared to that of natural wool; it is approximately 9% in all these cases. However, the loss due to moisture is considerably low in the case of formic acid- and thioglycolic acid-treated wool, the actual value being 3-5%. The temperature up to which the weight loss due to moisture occurs is obtained from the starting point of the initial horizontal straight-line portion of the curves. This temperature decreases slightly with all the chemical treatments. For example, it is 160°C for natural wool, whereas for modified wool it is around 130°C.

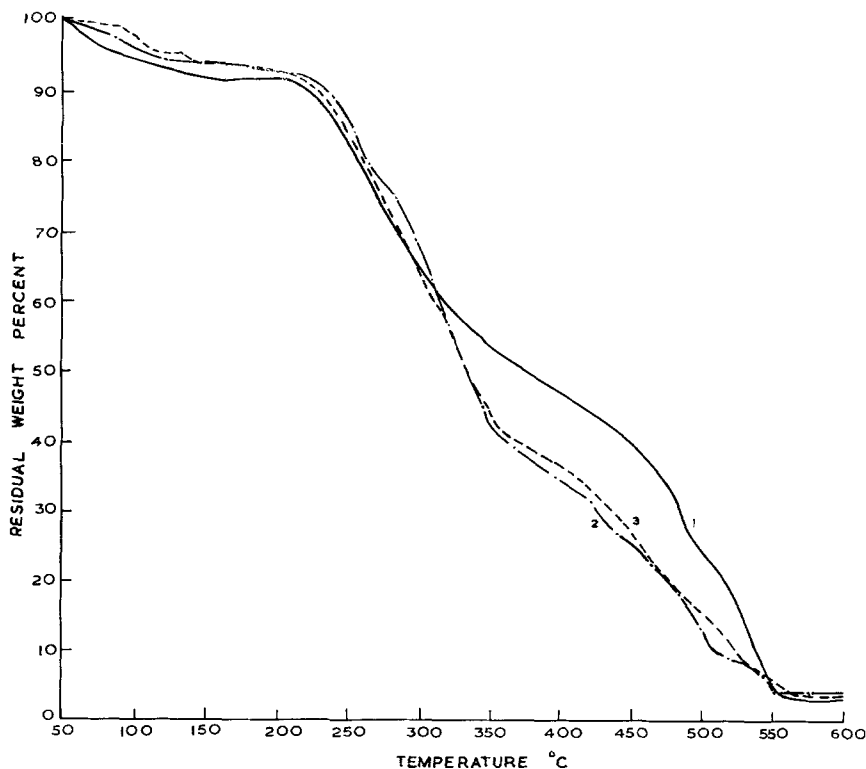


Fig. 1. TGA curves of natural and copolymerized wool fibers in air: (1) natural; (2) 31% graft copolymerized; (3) 49% graft copolymerized.

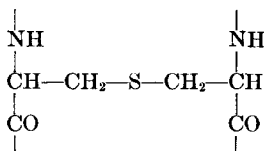
The second decomposition occurs up to $\approx 450^\circ\text{C}$ and is accompanied by a weight loss of approximately 50% in this region. The third zone of decomposition starts after this and continues up to 550°C , where decomposition is practically complete. Total weight loss in this region is 30–40%. Table I shows the values of decomposition temperature (T_D) at different percentage weight loss values. Comparing the behavior of various chemical treatments in the second and third zone of decomposition, it is seen that no significant change in behavior occurs up to 450°C , as compared to natural wool; this is evident from the T_D values in this range (Table I). After 450°C , the T_D values at different weight losses seem to increase a little with the various chemical treatments of the fiber. For example, at 80% weight loss, T_D for natural wool is 515°C , whereas all the chemically treated fibers give higher T_D values. The T_D value is maximum in the case of caustic soda-treated wool (550°C), followed by reduced wool (535°C) and formic acid-treated wool (530°C). Therefore, at higher temperatures, thermal stability is somewhat improved by the aforesaid chemical modifications of wool.

TABLE I
Decomposition Temperatures (T_D) at Different Weight Losses

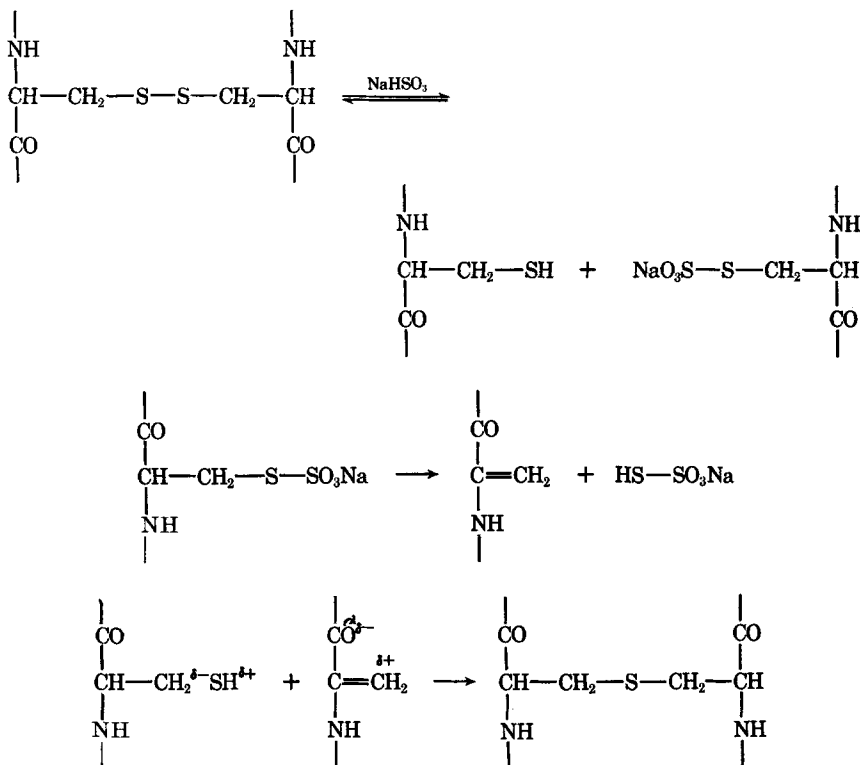
Sample	Graft-on, %	T_D , $^\circ\text{C}$, at weight loss of:					
		10%	20%	40%	60%	80%	90%
Natural wool	0	220	255	320	450	515	540
	31	235	260	315	365	475	510
	49	230	260	310	370	480	525
Caustic soda-treated wool	0	210	240	315	435	550	Above 600
	25	225	270	305	370	485	550
	64	230	270	310	340	410	485
Formic acid-treated wool	0	225	255	325	440	530	570
	24	245	265	320	400	495	540
	53	245	280	320	365	480	515
Sodium bisulfite-treated wool	0	205	255	315	435	535	Above 600
	22	235	265	325	455	540	Above 600
	59	235	280	330	440	525	Above 600
Thioglycollic acid-treated wool	0	225	255	330	455	535	565
	30	230	265	330	420	515	Above 600
	63	230	265	310	360	475	515

The thermograms and the T_D values reveal some similarity between wool treated with NaOH and wool treated with NaHSO_3 . In both the cases, the wool becomes more stable thermally. Cystine linkages in

wool are believed to be converted partly into lanthionine when wool is treated with NaOH:



These structures are more stable than the disulfide linkages. However, when wool is treated with NaHSO₃, the reduction of disulfide should give only thiol groups and sulfonates. There is some evidence⁸ that these sulfonates may eliminate —SO₃H groups to give aminoacrylic acid which can then react with thiols to give lanthionine:



Whether such structures are formed in wool by NaHSO₃ is yet to be confirmed by other work, but the TGA results do indicate some thermal stability that can be attributed to lanthionine structures which may be present in very low concentrations.

Formic acid breaks down the hydrogen bonding of wool molecule, and breakdown of some of the salt linkages may also occur. Although it was expected that the behavior of the formic acid-treated wool and natural wool would be identical, because after washing out the acid the wool is

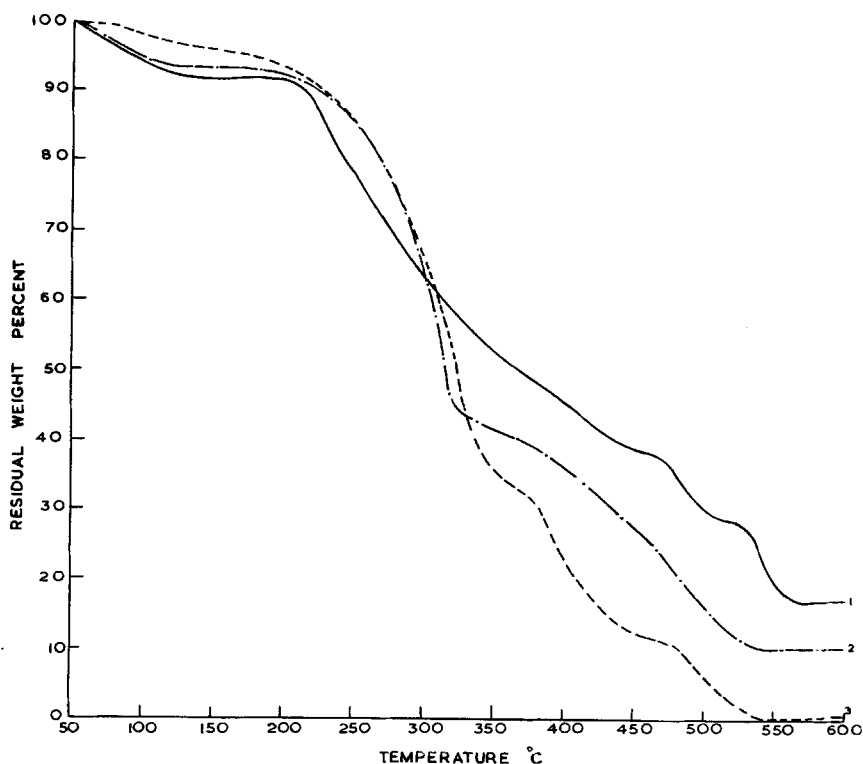


Fig. 2. TGA curves of caustic soda-treated and copolymerized wool fibers in air: (1) caustic soda treated; (2) 25% graft copolymerized; (3) 64% graft copolymerized.

considered to have regained its original state,⁹ the results indicate that formic acid has attacked the noncrystalline region. This perhaps is responsible for reduction of moisture content and greater thermal stability at higher temperatures (after 450°C).

Reduction by both sodium bisulfite and thioglycolic acid converts the cystine linkages into sulfhydryl ($-SH$) groups. The reduced samples were dry stored before copolymerization. This perhaps set in the process of rebuilding of disulfide bonds by atmospheric oxidation.¹⁰ Therefore, the thermal behavior of reduced and natural wool should have been identical. However, the results indicate that at high temperatures the thermal stability of reduced wool (both by bisulfite and thioglycolic acid) is better than that of natural wool.

The thermograms of natural and modified wool after graft copolymerization reveal that there are two distinct regions of different thermal behavior. There is a region around 325°C up to which the decomposition temperature at different weight loss values increases with increase in percentage graft-on, as is evident from Table I. For example, in natural wool, T_D at 10% weight loss is 220°C, but in samples with 31% and 49% graft-on, T_D is 235°C and 230°C, respectively. Similar observations are found in the

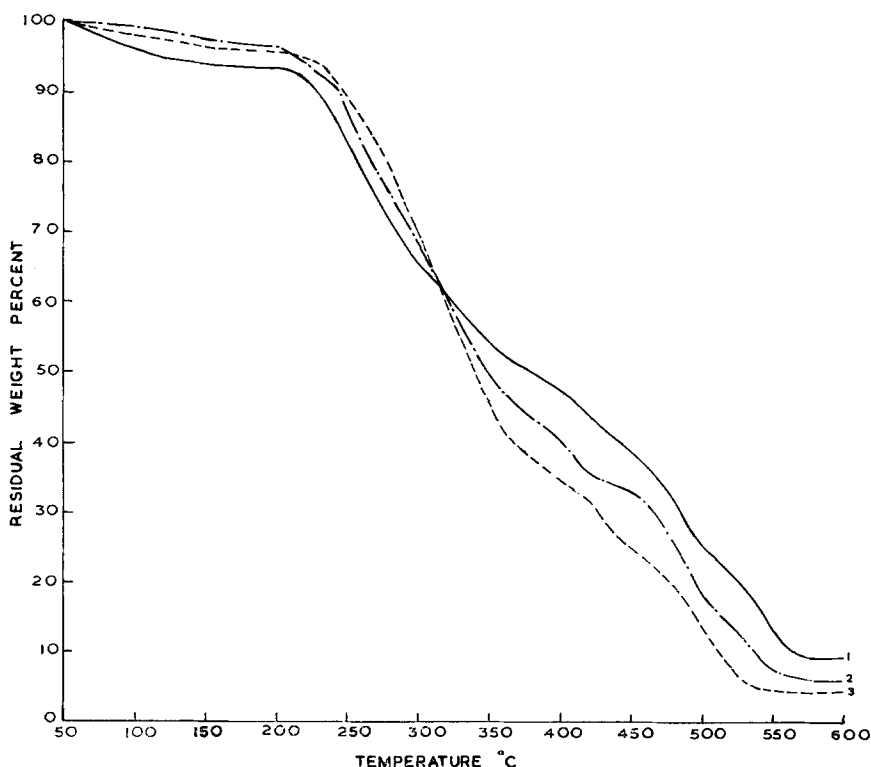


Fig. 3. TGA curves of formic acid-treated and copolymerized wool fibers in air: (1) formic acid treated; (2) 24% graft copolymerized; (3) 53% graft copolymerized.

case of chemically treated wool. This definitely indicates an improvement in thermal stability with graft copolymerization up to about 325°C.

After 325°C, the T_D decreases with increase in graft-on in all cases. For instance, T_D for natural wool at 90% weight loss is 540°C, but after 31% and 49% graft-on, T_D at the same point decreases to 510°C and 525°C, respectively. Similar effects are observed in all chemically treated fibers after graft copolymerization. An exception is found in the case of sodium bisulfite-treated fibers, where T_D is somewhat higher in the grafted samples even at temperatures higher than 325°C. Comparing the nature of the thermograms of all the chemically treated and copolymerized samples, it is seen that the behavior of formic acid-treated and thioglycollic acid-treated wool after grafting is similar. Again, there is a similarity between caustic soda-treated and bisulfite-treated wool after grafting. For most of the practical end uses of wool, we seldom treat them above 325°C. Hence, the improvement in thermal stability of both natural and modified wool by graft copolymerization up to this temperature seems to be significant for all practical purposes.

Graft copolymerization seems to form a sort of crosslinking in the wool molecule. In natural wool, it enhances the thermal stability. In modified

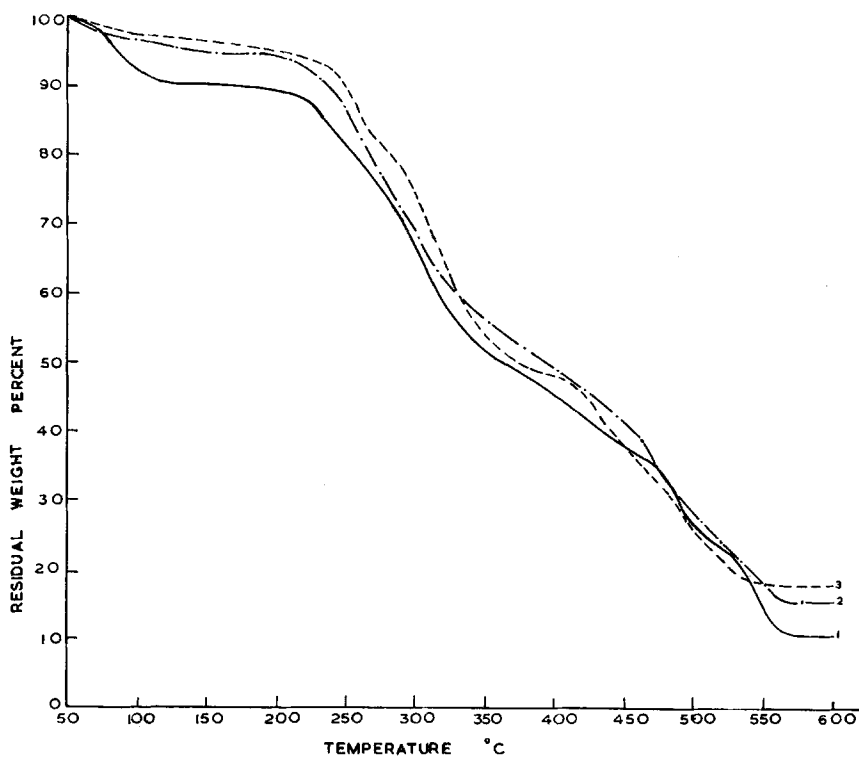


Fig. 4. TGA curves of sodium bisulfite-reduced and copolymerized wool fibers: (1) sodium bisulfite reduced; (2) 22% graft copolymerized; (3) 59% graft copolymerized.

wool, the breakage of various linkages by the chemicals is compensated by this new type of crosslink formed by the polymer. So, in the latter cases also thermal stability increases with graft-on due to better chemical stability of the molecules.

It has been reported¹¹ that PMMA decomposes completely at 300°–375°C. But complete decomposition of natural and chemically modified wool occurs at approximately 570°C. Hence, the fibers with different percentage graft-on values are found to decompose between these two values. The decomposition temperature decreases with increase in graft-on because of early decomposition of PMMA as compared to that of the polypeptide chain. Thus, the decrease in the thermal stability of grafted wool above 325°C can be explained on this basis.

Doyle¹² has proposed a comprehensive index of thermal stability, the "integral procedural decomposition temperature" (IPDT), which places all materials on a common basis and provides for the most valid comparison of different polymeric materials. This involves integrating the TGA curve on the basis of the total experimentally accessible temperature range and calculating an integrated end of volatilization temperature. The same method is applied in calculating the IPDT for each of the treated

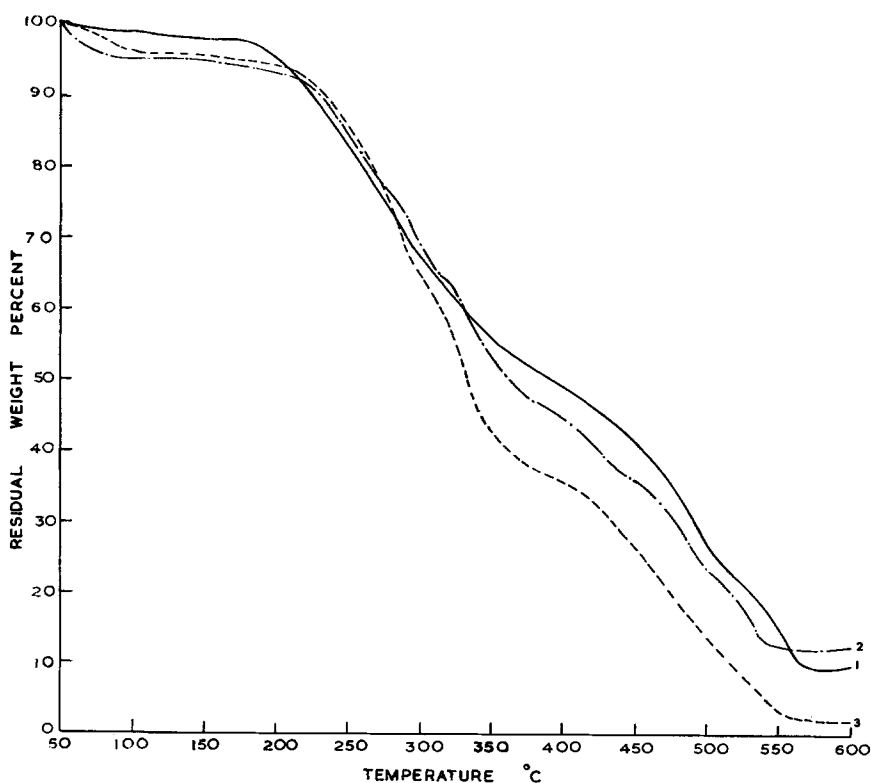


Fig. 5. TGA curves of thioglycolic acid-reduced and copolymerized wool fibers: (1) thioglycolic acid reduced; (2) 30% graft copolymerized; (3) 63% graft copolymerized.

and grafted wool fibers over the temperature range of 50°C to 600°C. It was observed that all the samples decomposed completely before 600°C, as found from actual experiments. The results obtained for different samples are shown in Table II along with initial decomposition temperatures (IDT).

It can be observed that IPDT does not change significantly. A slightly higher value of IPDT was found in all the chemically modified wool fibers as compared to natural wool, which indicates slight improvement in thermal stability with the chemical modifications. Comparing the individual cases of modified fibers, it is found that in formic acid-treated fibers the IPDT value is highest, whereas it is lowest in fibers reduced with sodium bisulfite where it is almost equal to that of natural wool.

With increase in percentage graft-on, there is a decrease in IPDT in all the cases, although the decrease is not strictly proportional to the percentage graft-on. The decrease in IPDT values in chemically treated wool with different graft-on per cent is most pronounced in fibers treated with caustic soda and formic acid. In the fibers reduced with sodium

TABLE II
Thermal Stability of Graft Copolymers of Natural and Modified Wool from TGA Curves

Sample	Graft-on, %	IDT, °C	IPDT, °C
Natural wool	0	205	373
	31	210	356
	49	210	358
Caustic soda-treated wool	0	200	381
	25	190	357
	64	200	337
Formic acid-treated wool	0	210	400
	24	205	380
	53	200	362
Sodium bisulfite-treated wool	0	210	378
	22	200	392
	59	200	394
Thioglycollic acid-treated	0	190	389
	30	200	395
	63	170	351

bisulfite, an opposite trend is found and the IPDT value increases slightly with the graft-on. The IPDT results indicate that at high temperatures the overall thermal stability decreases with increase in the amount of polymer formation inside the fibers for natural and chemically modified wool.

CONCLUSIONS

The thermal behavior of various chemically modified wool fibers, viz., swollen with caustic soda and formic acid and reduced with sodium bisulfite and thioglycollic acid, does not vary significantly from that of natural wool fibers up to around 450°C. At temperatures higher than this, the thermal stability is somewhat improved by the above chemical modifications. The thermograms show three distinct weight loss regions, and the decomposition is completed at about 570°C. In case of natural wool with different amounts of graft copolymerization by MMA monomer, the thermograms indicate two distinct regions of different thermal behavior. Up to 325°C, the thermal stability is improved with per cent graft-on; after that, the thermal stability decreases with graft-on. Similar observations are obtained in the case of chemically modified fibers. An exception is found in fibers reduced with sodium bisulfite, where the thermal stability appears to increase with the amount of polymer present inside the fiber, even at higher temperatures.

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