

A study in thermal properties of graft copolymers of cellulose and methacrylates

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ABSTRACT

Benzoyl peroxide (BPO) initiated grafting of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) onto cellulose extracted from pine needles along their binary monomer mixtures with acrylamide (AAm), acrylic acid (AAc) and acrylonitrile (AN) have been reported earlier. Graft copolymers have been possess improved thermal stability as compared to cellulose as has been observed from initial decomposition temperature (IDT) of the graft copolymers. In case of Cell-g-poly(MMA) highest IDT is observed at 241.0 as compare to 232.0, the IDT of cellulose. In case of graft copolymers cell-g-poly(GMA-co-AN) highest IDT is recorded at 283.2°C and in DTA curve single exothermic peak is observed at 520.9°C. Thermal degradation behaviour of cellulose is very important and evaluation of flammability and char formation on impregnation of additives and grafting offers scope for developing new cellulose for various end uses.

Keywords: Methacrylates, Cellulose, Graft Copolymers, Thermal degradation

INTRODUCTION

Thermal behaviour of carbohydrates like cellulose involves a variety of physical and chemical transformation. The latter reactions often referred to as pyrolysis, are responsible for converting solid cellulosic materials to a variety of lower molecular weight and volatile compounds. Production of flammable volatile compounds by this process leads to combustion of cellulosic materials and propagation of fire that constitutes a major force in shaping the destiny of man and his environment[1]. The interest in pyrolytic reactions has also been stimulated by the academic discussion about the origin of coal and investigation of a variety of commercial processes such as drying, laundering destructive distillation of wood and manufacturing of activated carbon, tire yarn, electrical insulation paper and more recently carbonized fiber.

In an attempt to unravel the pyrolytic behaviour of a complex material including cellulose and graft copolymers are investigated by thermal analysis methods to show how the grafting affect the thermal properties of original cellulose. Dynamic thermal analysis methods including differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are used for detecting and measuring the sequence and extent of physical transition and chemical transformations.

An experimental study has been performed in which optimum grafting conditions for a single monomer were used to co-graft it with other co-monomers (CM) so as to improve the intrinsic properties of the cellulose backbone[2,3]. The graft copolymers obtained have been found to improve the thermal stability of cellulose. Thermograms (TG) of cellulose and grafted cellulose reveal that decomposition processes of both the samples are quite different. Nishioka et al. [4] reported thermal decomposition of cellulose blends with its poly(acrylonitrile) graft copolymers. Thermal degradation of cellulose and its derivatives involves the loss of moisture, dehydration (in the 180-280°C temperature range), glycosan formation and depolymerization (by breakage of 1,6 glycosidic linkage). It is followed by volatilization (very rapid in the temperature range 310-350°C) and char formation[5]. There is appreciable overlapping of endothermic and exothermic processes in different degradation stages[6]. The unzipping type of

depolymerization which fits zero-order kinetics is compatible with a chain reaction process [7,8]. The presence of acrylate chains is reported to increase polymer stability by decreasing the tendency of methacrylates to unzip [9]. Jute is one of the most important cellulose fibers, many workers have graft copolymerized it with vinyl monomers [10-14] to improve upon some of its intrinsic drawbacks. One of the most important attributes affected by the grafting of vinyl monomers is thermal stability. Kosik et al. [15] grafted acrylonitrile on to cotton and wood cellulose and observed that appreciable effect in the course of thermo-oxidation and dehydration was only at higher nitrogen content. Similarly, residue and temperature of maximum volatilization are proportional to nitrogen content [16]. Grafting of HEMA [17,18] and other acrylate monomers [19] onto cotton cellulose resulted in increased thermal stability with increase in graft-on per cent. Chauhan and coworkers [20,21] reported two stage degradation of Ceric ion initiated graft copolymer of Jute with MMA and also reported that grafting of MMA enhances thermal stability of cotton, rayon and *Cannabis indica* fibre. UV and ceric ammonium nitrate (CAN) initiated grafted cotton samples were reported to show less thermal stability with increase in add-on as compare to the original fibre [22]. Rajeev Jindal et al [23, 24] have reported the thermal studies of graft copolymers of Gum ghatti.

MATERIALS AND METHODS

Cellulose was extracted from Pine needles by ammonia digestion by earlier reported method. At the optimum reaction conditions evaluated for grafting of MMA[25], HEMA[26] and GMA[27] on cellulose, other vinyl monomers such as acrylamide (AAM), acrylic acid (AAc) and acrylonitrile (AN) have also been grafted by initiation with BPO. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of cellulose and graft copolymers are studied using Shimadzu simultaneous TG/DT analyzer in air at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

3.1 Thermal Analysis of Cellulose

Two-stage decomposition for ungrafted cellulose and single stage decomposition for their graft copolymers have been reported [28]. Cellulose degrades mainly by dehydration, depolymerization and glucosan formation. Dehydration leads to 1,4 and 1,6 anhydroglucopyranoside in the temperature range of 180° - 280°C (Fig. 1). Chain scission at 1,4 glycosidic bond results in depolymerization and it starts around 310°C. Pyrolysis to lower products is followed at higher temperatures.

3.2 Thermal Analysis of Cell-g-poly(MMA)

Primary thermograms of cell-g-poly(MMA) exhibits single stage decomposition. The region between 33.9°-222.0°C in cellulose is due to loss of the absorbed moisture and ammonia, which accounts for 11% weight loss. The first stage of decomposition of cellulose begins from 222.0°-472.0°C and the second stage from 472.0°-575.0°C (Figs. 2 and Table 1). Similar trends have been reported when thermogravimetric analysis of cellulose and their poly (methyl methacrylate) graft copolymer was studied [20]. In primary thermogram of cell-g-poly(MMA), there is one stage of decomposition from 241.0° - 473.7°C. It is observed that initial decomposition temperature (IDT) of 241.0°C is higher as compared to 222.0°C of cellulose, hence, increase in thermal stability has been observed. The rate of degradation is faster in the region 280° - 354.1°C resulting in 20.98% weight loss. It then slows down between 354.1° - 473.7°C resulting in 11.16% weight loss (Fig. 2 and Table 1). The final decomposition temperature (FDT) is recorded at 473.7°C leaving behind large (67.86%) residue. In case of cell-g-poly(MMA-co-AAm) IDT is observed at 243.7°C indicating tremendous thermal stability as evident from much higher IDT of the graft copolymer (Fig. 3). Degradation completes at 545.4°C leaving 24.13% residue. Decomposition curve shows high degradation rate between 280°-380°C region resulting 65.00% weight loss and 10.87% weight loss is observed between 425.8-545.4°C. In case of cell-g-poly(MMA-co-AAc) degradation starts at 216.5°C and curve between 320°-420.0°C is very sharp, slows down till final degradation temperature of 517.2°C is reached and leaves 17.03% residue (Fig. 4). In the thermal degradation of AAm and AAc grafted copolymers first stage of degradation shows higher weight loss, which accounts for dehydration amide and acid groups. Cell-g-poly(MMA-co-AN) undergoes 56.40% weight loss in a single stage of degradation in the temperature range of 236.4° - 406.0°C and 43.60% residue is left (Fig. 5). Maximum degradation is observed in temperature range from 280° - 360°C.

Differential thermal analysis (DTA) of cellulose shows many exothermic and endothermic peaks. The endothermic peaks for cellulose at 167° is may be ascribed to some transition changes. The exothermic peak at 365°C corresponds to the decomposition between 222°-472°C in the TG curve. Exothermic peaks at 446.2° and 543.9°C correspond to the second decomposition region in TG curve. An exothermic peak at 346.6°C has been observed in the DTA curve of cell-g-poly(MMA) (Fig. 2). The binary monomer graft copolymers show different degradation pattern and it has been observed that grafting of other monomer with MMA increases IDT, indicative of improved thermal stability of graft copolymers. In case of cell-g-poly(MMA-co-AAm) highest IDT is recorded at 243.7°C and two important exothermic peaks are observed at 404.1 and 457.1°C (Fig. 3). Three main exothermic peaks are

recorded at 391.0, 475.0 and 505.8°C in case of cell-g-poly(MMA-co-AAc) (Fig. 4). DTA curves of cell-g-poly(MMA-co-AN) shows only one sharp peak at 397.9 °C, the last part of degradation (Fig. 5). DTA studies of graft copolymers suggest that degradation pattern of all the polymers studied is uniform. In fact, MMA has been known to degrade by anhydride formation and exothermic peak is ascribed to the loss of ether from the grafted Poly(MMA) chains[29].

Table 1: Thermogravimetric Analysis of Cellulose and Its Graft copolymers

Cellulosic	Thermogravimetric Data					DTA Peaks (°C)	
	Degrad. Stages (°C)	Wt. Loss (°C)	Residue (%)	IDT (°C)	FDT (°C)	Exo	Endo
Cellulose	222.0-472.0 472.0-575.0	30.40 24.32	21.74	222.0	575.0	365.0 543.9	167.0 418.1
Cell-g-poly(MMA)	241.0-473.7	20.98 11.16	67.86	241.0	473.7	346.6	--
Cell-g-poly(MMA-co-AAm)	243.7-545.4	65.00 10.87	24.13	243.7	545.4	404.1 457.1	--
Cell-g-poly(MMA-co-AAc)	216.5-517.2	61.80 21.09	17.03	216.5	517.2	391.0 475.0 505.8	--
Cell-g-poly(MMA-co-AN)	236.4-406.0	56.40	43.60	236.4	406.0	397.9	--
Cell-g-poly(HEMA)	202.3-386.7 386.7-445.1 445.1-499.3	50.60 6.751 5.304	37.345	202.3	499.3	345.3 385.1 437.2 482.1	
Cell-g-poly(HEMA-co-AAm)	247.8-471.9 471.9-572.6	89.64 29.00	---	247.8	572.6	242.1 428.6 537.1	
Cell-g-poly(HEMA-co-AAc)	68.6-355.1 355.1-449.7 449.7-584.5	11.69 32.25 12.90	24.52	355.1	584.5	512.6	436.1
Cell-g-poly(HEMA-co-AN)	136.8-271.1 271.1-470.5 470.5-560.8	11.53 114.3 28.31	---	271.1	560.8	376.8 523.2	
Cell-g-poly(GMA)	68.3-235.4 235.4-514.7	1.833 78.87	14.665	235.4	514.7	273.8 353.0 381.4 436.8	
Cell-g-poly(GMA-co-AAm)	30.1-219.8 219.8-471.5 471.5-541.9	6.956 55.64 20.33	17.074	219.8	541.9	267.5 388.6 464.2 516.5	
Cell-g-poly(GMA-co-AAc)	231.7-487.4 487.4-526.6	78.12 16.87	5.01	231.7	526.6	391.6 497.6	
Cell-g-poly(GMA-co-AN)	75.1-283.2 283.2-421.0 421.0-558.9	7.50 45.62 25.00	21.88	283.2	558.9	520.9	

3.3 Thermal Analysis of Cell-g-poly(HEMA)

Decomposition of cell-g-poly(HEMA) is one stage of decomposition from 202.3° - 499.3°C resulting in 62.655% weight loss (Table 1) It is observed that initial decomposition temperature (IDT) of 202.3°C is lower as compared to 222.0°C of cellulose (Fig. 6). The final degradation temperature (FDT) is recorded at 499.3°C leaving behind 37.345% residue. In case of cell-g-poly(HEMA-co-AAm) decomposition takes place in two stages. IDT is observed at 247.8°C and degradation completes at 572.6°C. Decomposition curve shows that degradation completes between two stages from 247.8° - 471.9°C and second starts at 471.9° - 572.6°C (Fig. 7). In case of cell-g-poly(HEMA-co-AAc) degradation curve between 355.1° - 449.7°C is very sharp. Again in this case degradation is takes place in two stages. Where as, in second degradation stage (449.7° - 584.5°C) with total weight loss of 56.84 (Fig. 8). In the thermal degradation of AAm and AAc grafted copolymers first stage of degradation shows higher weight loss due to dehydration of amide and acid groups. Cell-g-poly(HEMA-co-AN) shows two stages of decomposition in the temperature range 271.1° - 470.5°C and second stage from degradation 470.50° - 560.8°C (Fig. 9).

Many important exothermic and endothermic peaks are observed in differential thermal analysis (DTA) of grafted cellulose. A number of exothermic peaks at 345.3°, 385.1°, 437.2.2° and 482.1°C have been observed in the DTA curve of cell-g-poly(HEMA) (Fig. 6). The binary monomer based graft copolymers show quantitatively different degradation pattern. Generally two-stage degradation process is observed but it has been observed that grafting of other monomer with HEMA leads to increase of initial decomposition temperature (IDT) indicative of improved thermal stability of graft copolymers. In case of cell-g-poly(HEMA-co-AAm) one important exothermic peak is

observed at 537.1°C (Fig. 7). Main exothermic peak is recorded at 512.6°C in case of cell-g-poly(HEMA-co-AAc) (Fig. 8). In case of DTA curve of cell-g-poly(GMA-co-AN) single exothermic peak is observed at 523.2°C (Fig. 9).

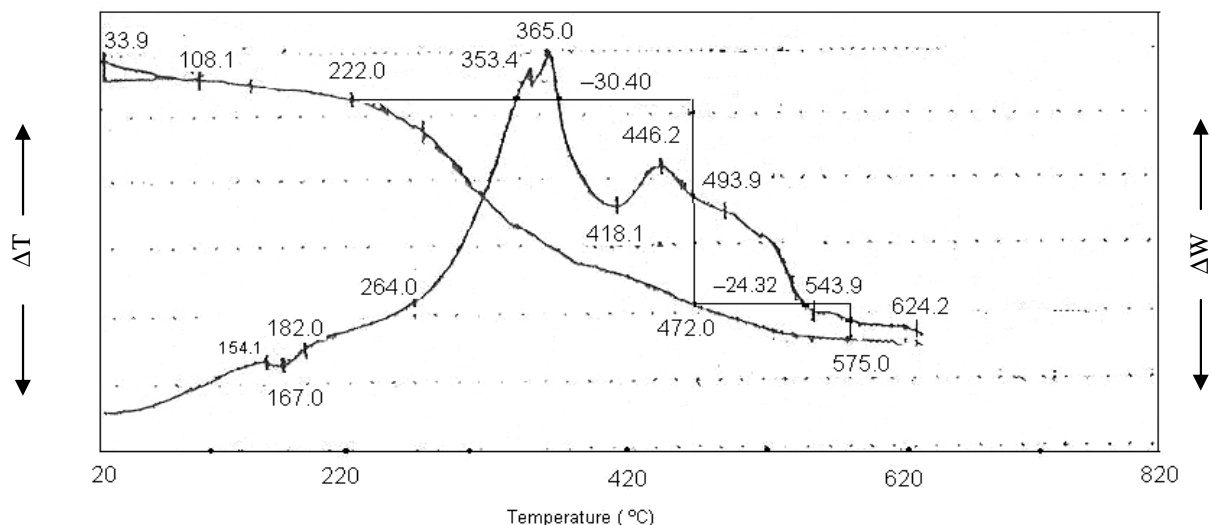


Fig. 1: TG and DT of Cellulose

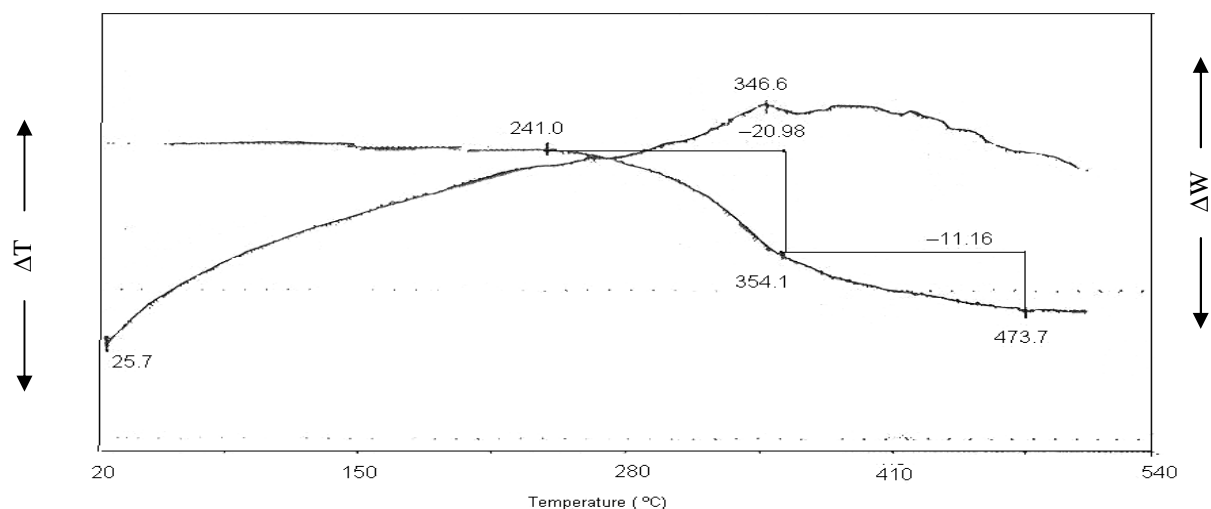


Fig. 2: TG and DT of Cell-g-Poly(MMA)

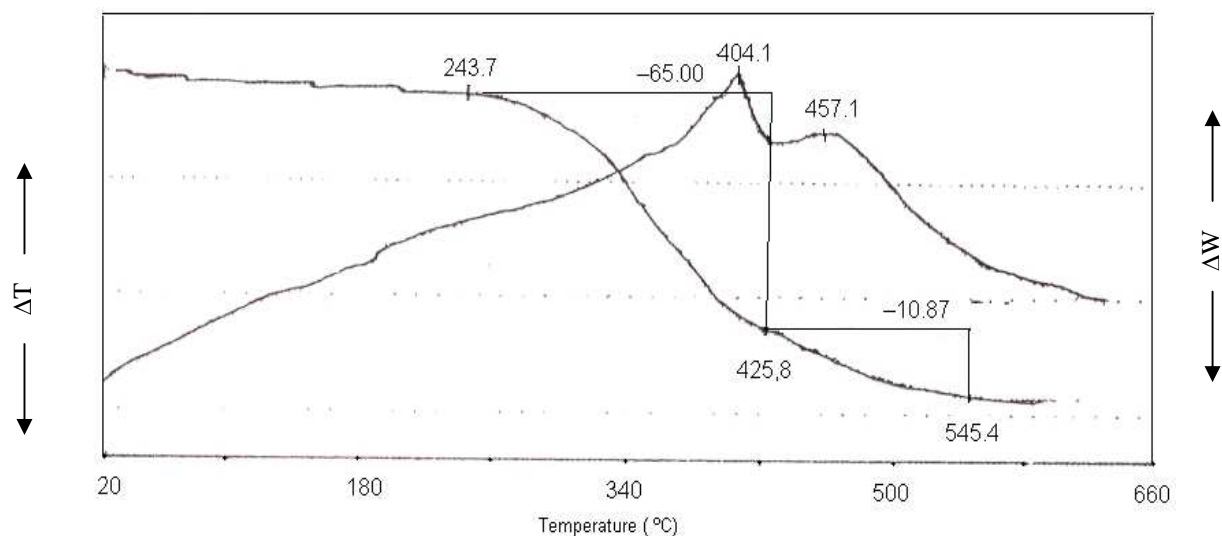


Fig. 3: TG and DT of Cell-g-Poly(MMA-co-AAm)

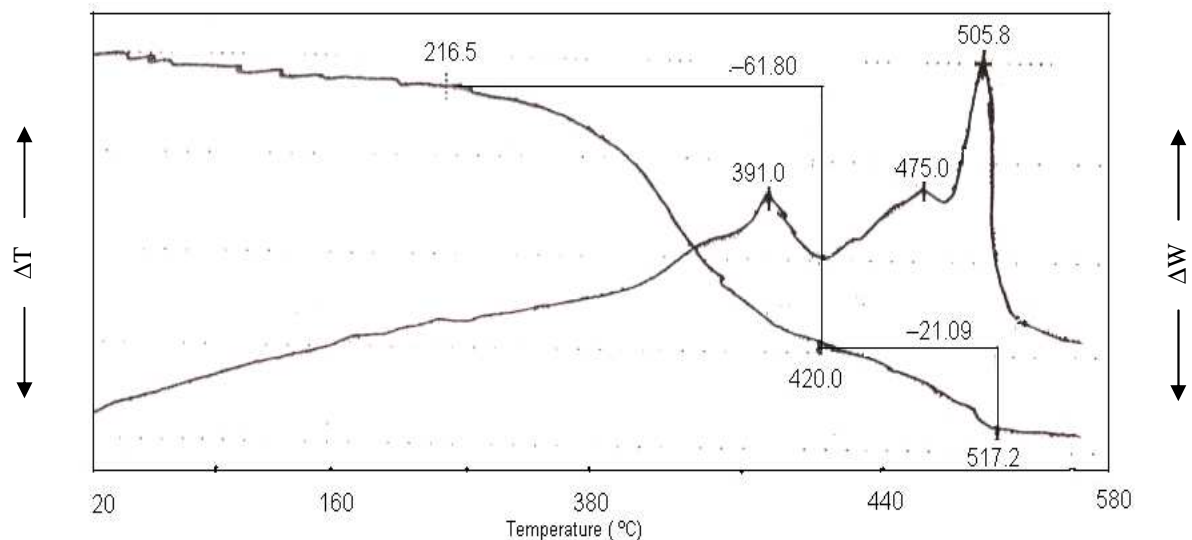


Fig. 4: TG and DT of Cell-g-Poly(MMA-co-AAc)

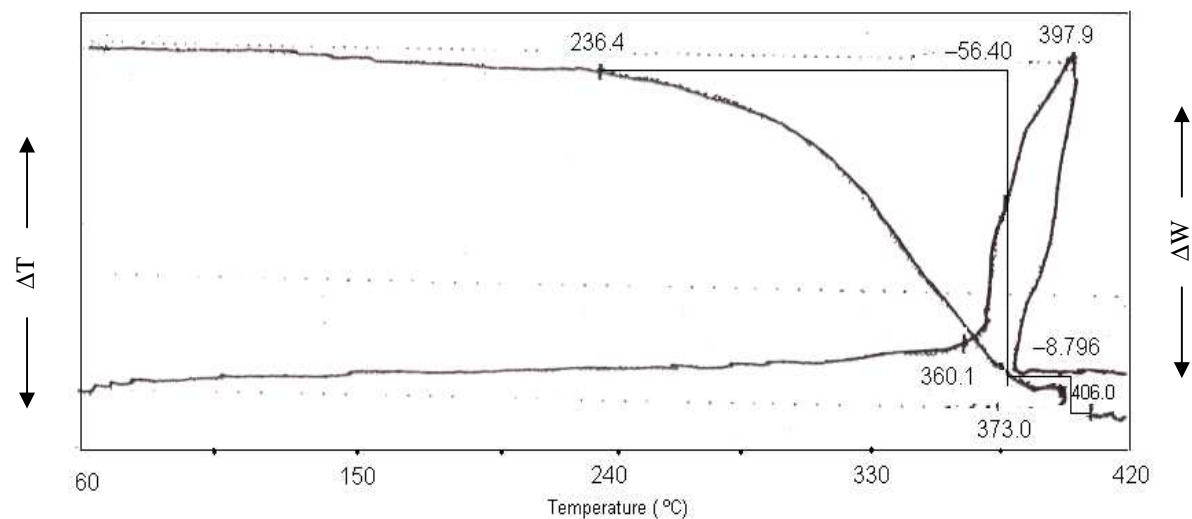


Fig. 5: TG and DT of Cell-g-Poly(MMA-co-AN)

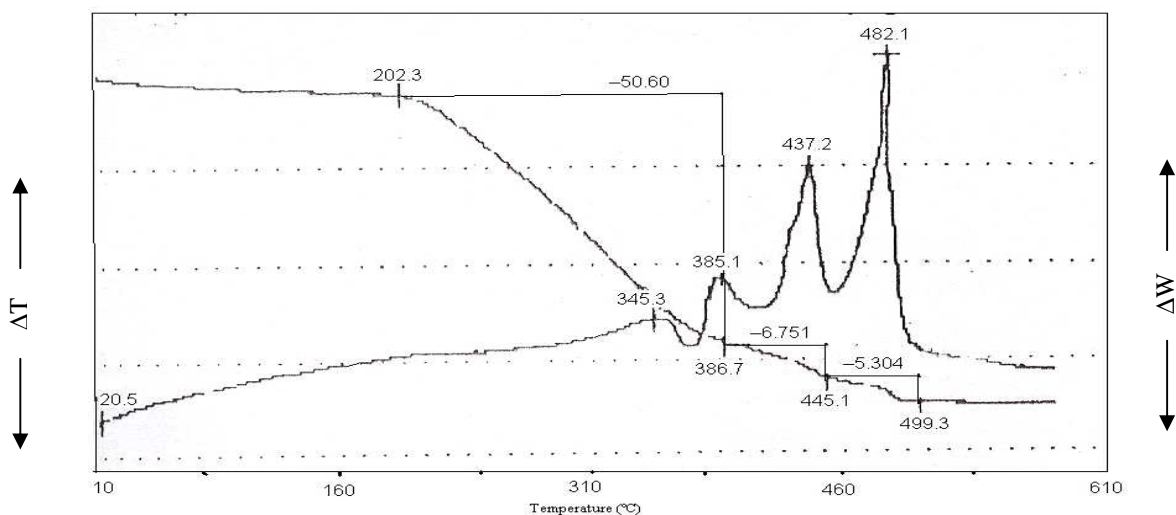


Fig. 6: TG and DT of Cell-g-Poly(HEMA)

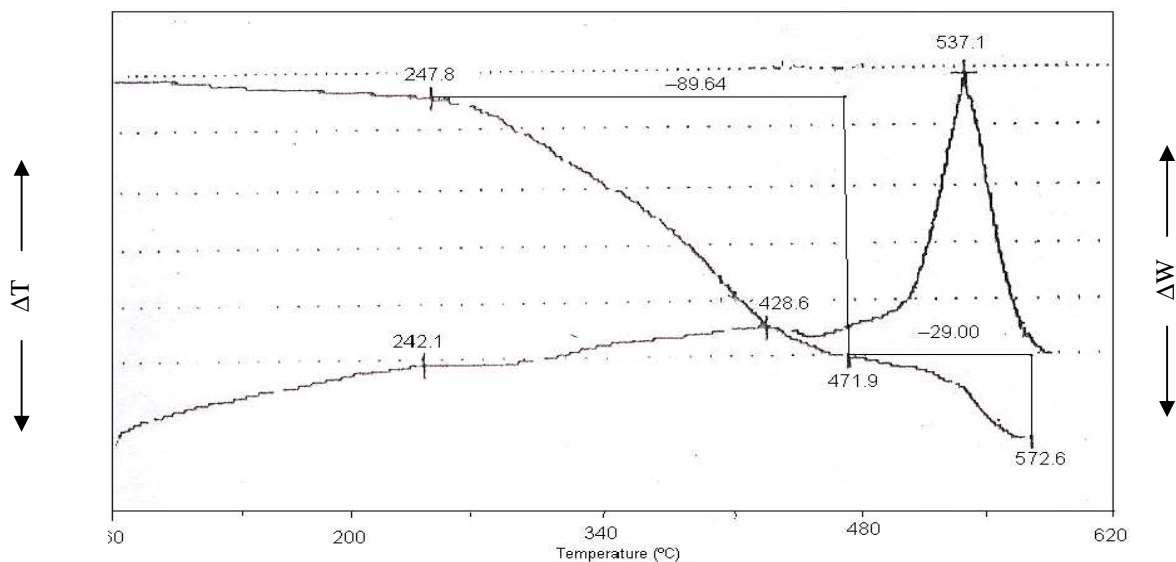


Fig. 7: TG and DT of Cell-g-Poly(HEMA-co-AAm)

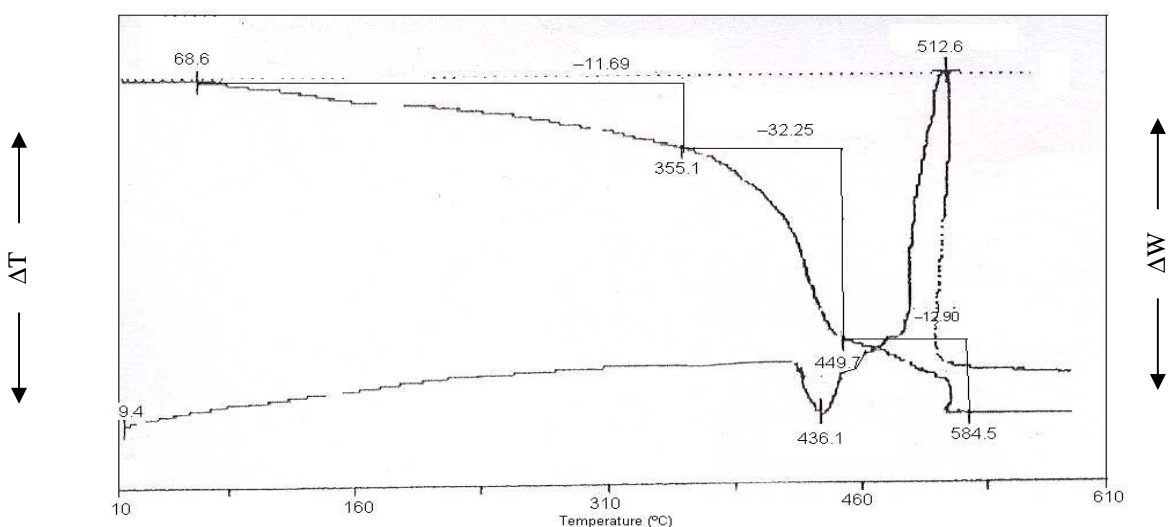


Fig. 8: TG and DT of Cell-g-Poly(HEMA-co-AAc)

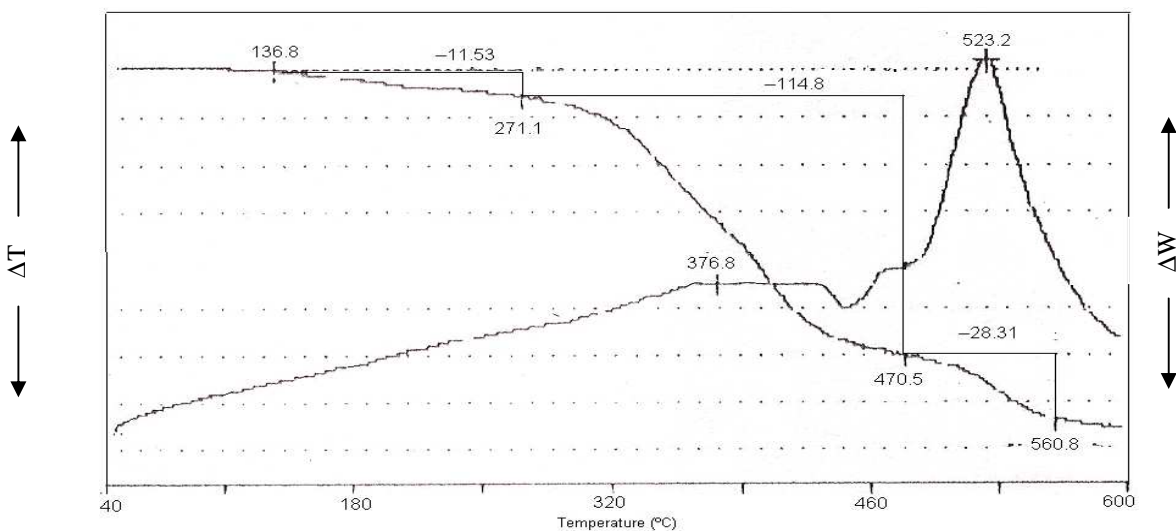


Fig. 9: TG and DT of Cell-g-Poly(HEMA-co-AN)

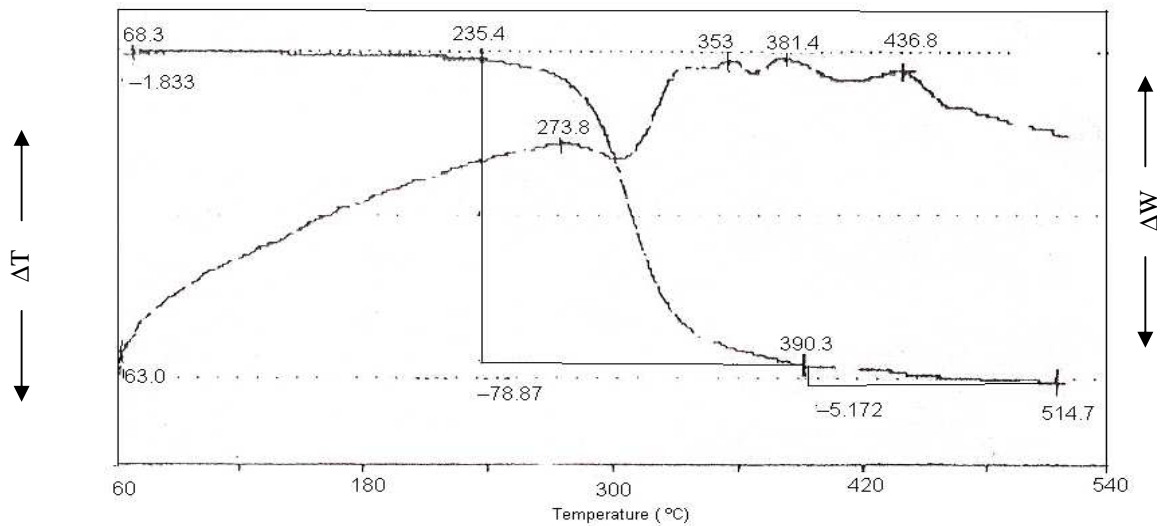


Fig. 10: TG and DT of Cell-g-Poly(GMA)

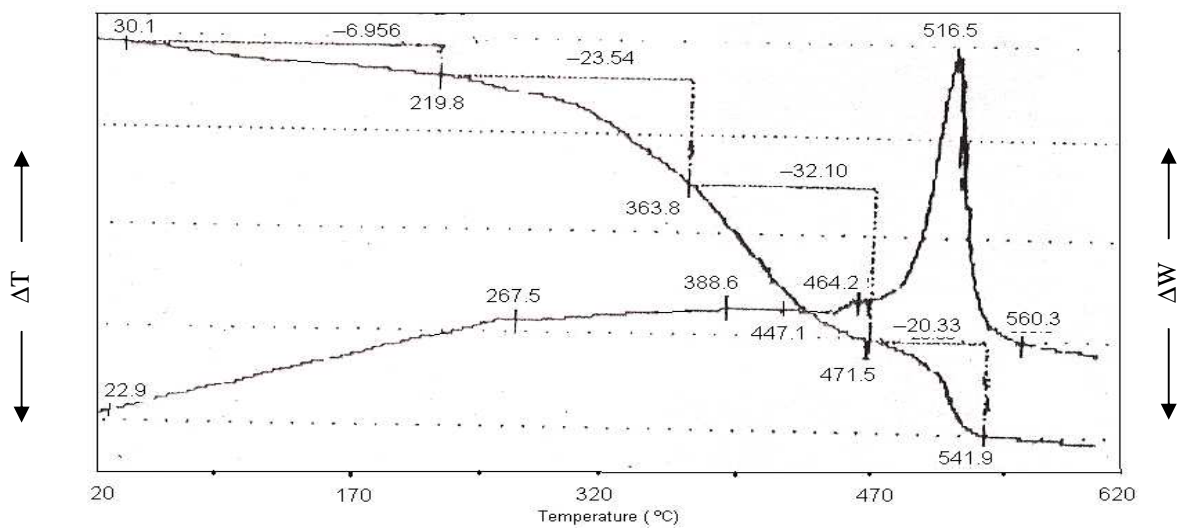


Fig. 11: TG and DT of Cell-g-Poly(GMA-co-AAm)

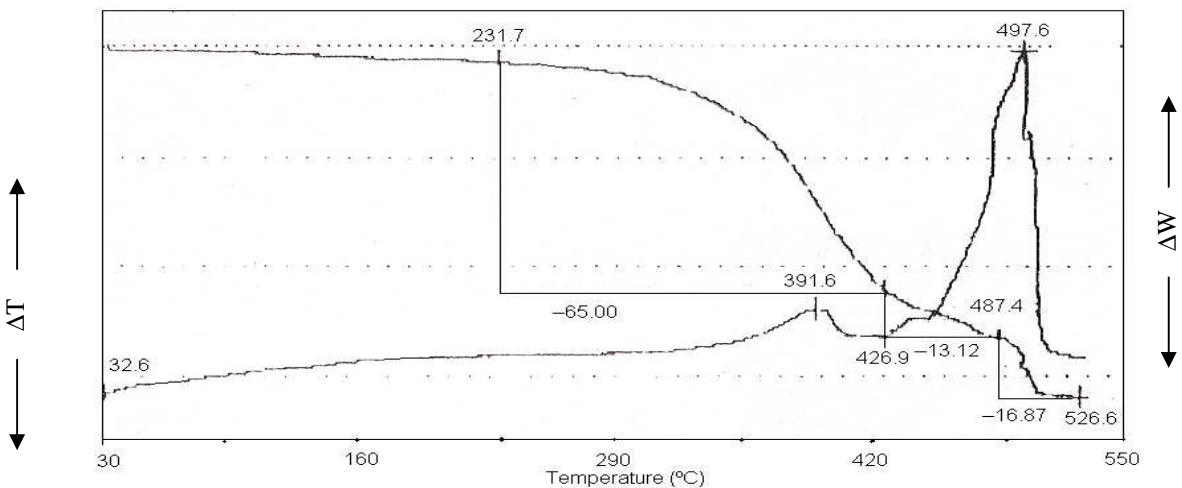


Fig. 12: TG and DT of Cell-g-Poly(GMA-co-AAc)

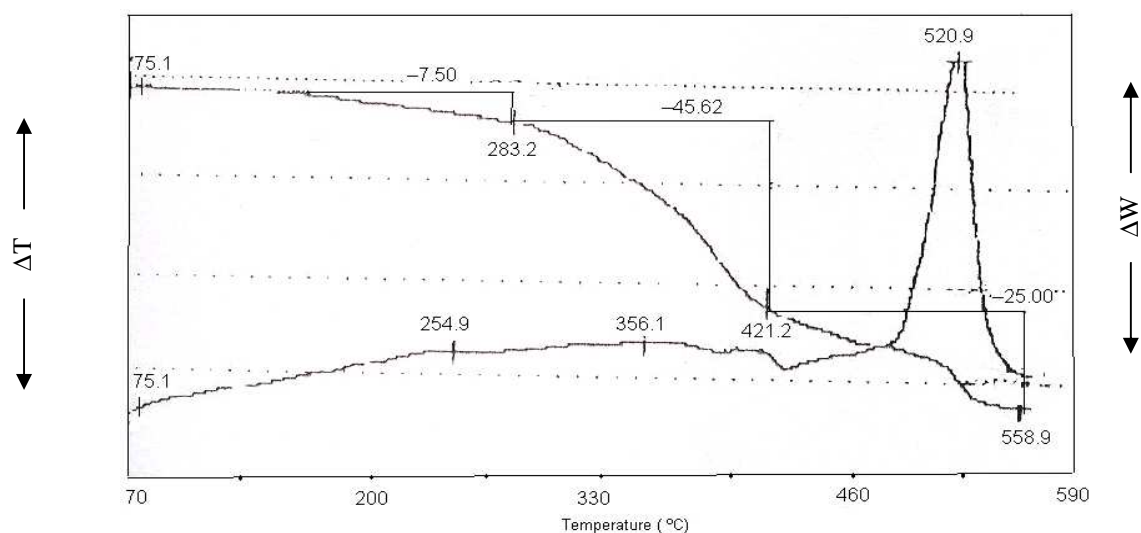


Fig. 13: TG and DT of Cell-g-Poly(GMA-co-AN)

3.4 Thermal Analysis of Cell-g-poly(GMA)

Thermogram of cell-g-poly(GMA) exhibits single stage decomposition starting from 235.4 to 514.7°C (Fig. 10 and Table 1). The region between 68.3° - 235.4°C in grafted cellulose is almost linear and accounts for meager 1.29% weight loss due to moisture. It is observed that initial decomposition temperature (IDT) of 235.4 is higher as compared to that of cellulose, increase in thermal stability has been observed. Rate of decomposition is very fast between the region 260° - 350°C resulting in 78.87% weight loss. It can be ascribed to dehydration, depolymerization and pyrolysis at higher temperature. It stabilizes and tremendously slows down in the temperature range 390°-514.7°C, accounting for only 5.172% weight loss. The final degradation temperature (FDT) is recorded at 514.7°C leaving behind 14.665% residue.

In case of cell-g-poly(GMA-co-AAm) decomposition between regions 30.1°-219.8°C in grafted cellulose is due to loss of the absorbed moisture which account for 6.956% weight loss. IDT is observed at 219.8°C and degradation completes at 541.9°C leaving 17.074% residue. Decomposition curve shows that degradation completes between two stages 219.8° - 471.5°C and 471.5° - 541.9°C regions, resulting 55.64% and 20.33% weight loss, respectively (Fig. 11 and Table 1). In case of cell-g-poly(GMA-co-AAc) degradation curve between 350° - 420.0°C is very sharp. Again in this case, degradation is completes in two stages (Fig. 12 and Table 1). In first stage (231.7° - 487.4°C) 78.12% weight loss is observed. Where as in second degradation stage (487.4° - 526.6°C) only 16.87% weight loss is observed. After 526.6°C only 5.01% residue is left. In the thermal degradation of AAm and AAc graft copolymers in the first stage of degradation most of the weight loss is due to dehydration of amide and acid groups. Cell-g-poly(GMA-co-AN) undergoes 7.500% weight loss in a temperature range of 75.1° - 283.2°C due to moisture present. Cell-g-poly(GMA-co-AN) shows two stages of decomposition. First degradation is very fast in the region 283.2° - 421.0°C resulting in 45.62% weight loss. Second degradation stages shows a loss of 25.00% weight and FDT is recorded at 558.9°C leaving 21.88% residue (Fig. 13 and Table 1). In case of comonomer grafting, second stage of degradation though not very significant, may be due to crosslinks developed in the grafting process. It is of interest that grafting of both the N containing monomers improves residue left by the polymers and in case of grafting of AN, IDT improves appreciably.

Many important exothermic and endothermic peaks are observed in differential thermal analysis (DTA) of grafted cellulose. A number of exothermic peaks at 273.8, 353.0, 381.4 and 436.8°C have been observed in the DTA curve of cell-g-poly(GMA). In case of cell-g-poly(GMA-co-AAm) only one important exothermic peak is observed at 516.5°C. Two main exothermic peaks are recorded at 391.6° and 497.6°C in case of cell-g-poly(GMA-co-AAc). In case of cell-g-poly(GMA-co-AN) highest IDT is recorded at 283.2°C and in DTA curve single exothermic peak is observed at 520.9°C.

CONCLUSION

Higher IDT of graft copolymers along with appreciable amount of residue left reflect on retardation in flammability and enhanced thermal stability of the graft copolymers. The binary monomer graft copolymers show different degradation pattern and it has been observed that grafting of other monomer with MMA increases IDT, indicative of improved thermal stability than other graft copolymers. The highest IDT is recorded at 283.2°C for cell-g-

poly(GMA-co-AN) and in DTA curve single exothermic peak is observed at 520.9°C. DTA curves of graft copolymers suggest that degradation pattern of all the polymers studied is uniform.

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