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# Synthesis and characterization of graft copolymers of nylon 6 with maleic anhydride and methylmethacrylate

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## ABSTRACT

*In the present work, the polyamide nylon6 was grafted in formic acid with maleic anhydride (MAH) and methyl methacrylate (MMA) using ceric ammonium nitrate as an initiator in aqueous nitric acid medium. Variation of synthetic parameters such as grafting percentage, grafting efficiency, percentage monomer conversion and grafting yield with solvent, reaction time, temperature, monomer and initiator concentrations were investigated for the binary graft copolymer (N6-g-MAH-g-MMA). The observed results indicate that the grafting parameters were increased at first and then decreased with increase in the concentration of initiator, monomer, N6-g-MAH and temperature. Graft copolymers with both high grafting efficiency and high grafting percentage were obtained indicating that ceric ammonium nitrate was an efficient initiator for this graft copolymerization. The synthesized graft copolymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and X-ray diffraction(XRD) studies. The FT-IR measurements clearly suggest that monomers were effectively grafted onto polyamide Nylon6 and N6-g-MAH. The XRD studies elucidates the change in the crystallinity of the grafted polymeric samples.*

**keywords:** Nylon-6, methylmethacrylate, maleic anhydride, redox initiation, graft copolymerization, ceric ammonium nitrate.

## INTRODUCTION

Polymers have played an important role from the beginning of life. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify properties, viz. blending, grafting, and curing. Grafting is a useful method for modifying some of the properties of natural and synthetic polymers [1]. Two major types of grafting may be considered; 1. grafting with a single monomer and 2. grafting with a mixture of two (or more) monomers [2].

Graft copolymerization is an attractive method to impart a variety of functional groups to a polymer. Considerable work on the graft copolymerization of natural and synthetic polymers with the vinyl monomers has been reported [3]. Russell and his coworkers have studied grafting of acrylonitrile (AN), methyl methacrylate (MMA) and vinyl acetate (VAC) onto starch using ceric ion technique. Graft copolymers are essential components of many materials, including chemically and thermally resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers [4]. They are required widely in various application fields of polymer alloys (blends), compatibility improvements, surface modifications, and so on [5]. It has a wide range of applications deriving from the possibility to tailor their properties through the combination of monomers that form the backbone and the side chains. Graft copolymers are prepared by first generating free radicals on polymeric chains and then allowing these free radicals to serve as macro initiators for the vinyl or acrylic monomer polymerization [6]. In recent years, the graft copolymerization of various monomers was initiated by ceric ammonium nitrate [7-10], ammonium persulphate [11], potassium persulphate [12-14] ferric ion hydrogen peroxide [15] and gamma rays [16].

Among the chemical initiation methods, redox initiated grafting offers advantages since in the presence of redox system, grafting can be carried out under milder conditions and the side reactions are at a minimum. Of the redox systems initiated so far the tetravalent ceric ion has received considerable interest [17-19] because of its high grafting efficiency and very low homopolymer formation. Graft copolymerization by the free radical mechanism is an interesting method for the preparation of polymeric system with specific properties.

In this paper, graft copolymerization of maleic anhydride(MAH) and methylmethacrylate (MMA) onto nylon6 has been investigated in detail using ceric ammonium nitrate as a redox initiator in aqueous nitric acid medium. The object of the present work is to prepare the N6-g-MAH and N6-g-MAH-g-MMA graft copolymers. At the same time, some structure and properties of the graft copolymers were characterized by FT-IR and XRD. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

## MATERIALS AND METHODS

### Materials

The polyamide nylon6 was kind gift from Formulated Polymers Limited, Chennai, Tamil Nadu. The monomers methyl methacrylate and maleic anhydride was obtained from Central Drug House Private Ltd and Thomas Baker Chemicals Private Ltd, Mumbai. Solvents such as formic acid and ethanol were obtained from SD Fine Chemicals Private Ltd. Nitric acid and Ceric ammonium nitrate  $Ce(NH_4)_2(NO_3)_6$  used were of analytical grade reagents from Thomas Bakers Chemical and Company. The initiator solution was prepared by dissolving 0.5g CAN (Thomas Baker chemicals and Co) in 10ml of 1N nitric acid.

### Preparation of nylon 6-g-maleic anhydride

In a typical experiment, the graft copolymerization was carried out as follows: A required amount of polyamide nylon6 (5g) was dissolved in formic acid (30ml) with constant stirring to form a homogeneous solution. The maleic anhydride monomer (2.5 g) dissolved in 30ml of water was then added to that homogeneous solution. Then to initiate the polymerization process, the initiator ceric ammonium nitrate prepared in the above manner (10ml) was then added. After all the addition is over the above mixture was heated to 70°C. Simultaneously, the stirring of that mixture was performed using a magnetic stirrer. This solution is then poured into excess sodium hydroxide solution to precipitate the graft copolymer. After the desired time the products

were taken out and washed thoroughly with acetone to remove the homopolymer formed during the graft copolymerization completely. Finally the graft copolymer was then dried in an oven, cooled to a room temperature and weighed.

### **Preparation of binary graft copolymer of nylon-6**

To prepare the binary graft copolymer of nylon6, initially a certain amount of nylon6- g –MAH copolymer (0.5g) was dissolved in formic acid (30ml) with constant stirring to form a homogeneous solution. The methyl methacrylate (2.5 g) dissolved in 30ml of alcohol was then added to that homogeneous solution. The initiator ceric ammonium nitrate prepared in the above manner (10ml) was then added to the above mixture to initiate the polymerization process. After the addition of all the substances is over, the above mixture was heated to 70°C. The stirring of that mixture were performed using a magnetic stirrer simultaneously. Then the above solution was then poured into excess sodium hydroxide solution to precipitate the binary graft copolymer. The precipitated binary graft copolymer was then filtered, dried and weighed. The graft copolymerization was done by changing the conditions like different monomer to polyamide ratios, initiator concentration and various temperatures. The yield of the binary graft copolymer was noted.

The grafting percentage, grafting efficiency, grafting yield and the percentage conversion of monomer was calculated by weighing the original polyamide nylon6 and the grafted product. The synthetic grafting parameters including grafting yield (GY) and grafting percentage (GP) were systematically evaluated as a function of various temperature, initiator, N6-g-MAH and monomer concentration [6] [20 – 22].

$$GY(\%) = \frac{\text{Wt of binary graft copolymer} - \text{Wt of N6-g-MAH}}{\text{Wt of N6-g-MAH}} \times 100 \quad (1)$$

$$GP(\%) = \frac{\text{Weight of binary graft copolymer}}{\text{Weight of N6-g-MAH}} \times 100 \quad (2)$$

### **FT-IR Spectral analysis**

The FT-IR spectra of grafted polyamide nylon6 were recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FTIR Spectrophotometer. The FTIR spectra were obtained in the wave number range from 4000 to 450  $\text{cm}^{-1}$  during 64 scans, with 2  $\text{cm}^{-1}$  resolution.

### **Differential scanning calorimetry (DSC)**

DSC thermogram of N6-g MAH copolymer and binary graft copolymeric samples were measured using a DSC Q200 V24.4Build instrument. The temperature range was varied from room temperature 30°C to 350°C with the heating rate of 10°C/min.

### **Thermogravimetric Analysis (TGA)**

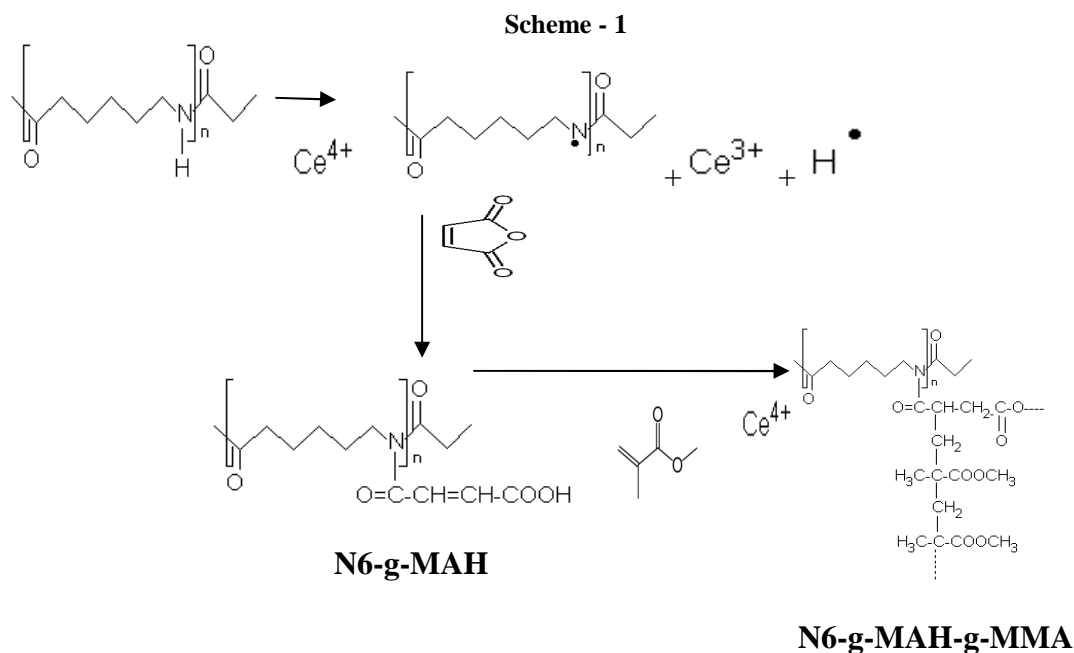
The N6-g-MAH copolymer and binary graft copolymeric samples prepared under different conditions were tested in a TGA Q500 V20.10 Build 36 instrument. The temperature range was varied from room temperature to 850° C with the heating rate of 20°C/min.

### X – Ray Diffraction

The X-ray diffraction patterns of the PA6-g-MAH and binary graft copolymers of nylon6 were tested by an X-ray scattering SHIMADUZ XD-DI Diffractometer using Ni filter Cu K $\alpha$  radiation source ( $\lambda=0.154\text{nm}$ ), set at scan rate =  $10^\circ/\text{min}$ , using a voltage of 40kV and a current of 30 mA.

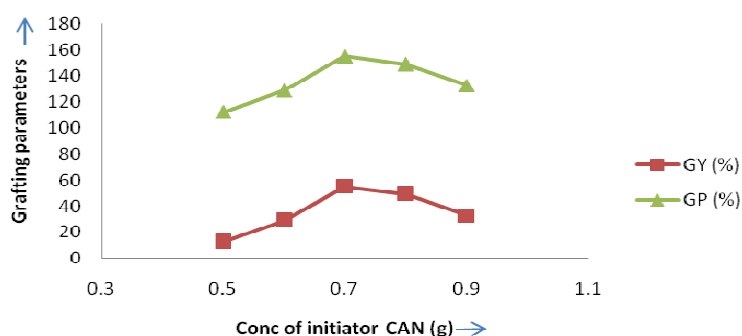
## RESULTS AND DISCUSSION

The mechanism of the graft copolymerization of maleic anhydride onto nylon6 and the methyl methacrylate onto nylon6-g-maleic anhydride was represented in scheme-1 [23]



### Effect of Initiator

The grafting of N6-g-MMA copolymer with methyl methacrylate monomer was carried out at various initiator concentrations between 0.5g to 0.9g keeping the other variables such as temperature, monomer, solvent, and Nylon 6 graft maleic anhydride (MAH) concentrations as constant [24].



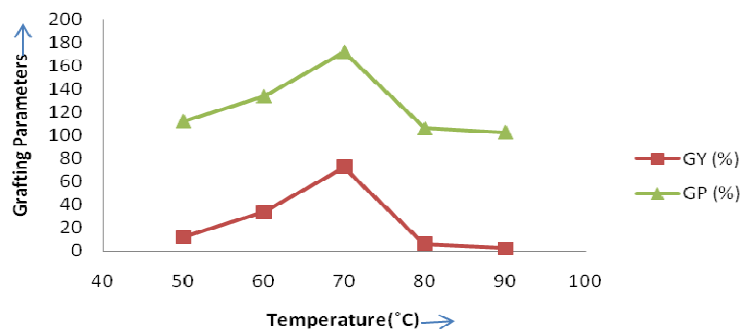
**Figure 1: Effect of initiator concentration**

Figure -1 shows the effect of ceric ammonium nitrate concentration on the grafting parameters of binary graft copolymer of nylon 6. The observed result shows that the grafting parameters sharply rises with increasing initiator concentration up to 0.7g achieves 55% grafting yield and

then decreases with further increase in the initiator concentration. In a grafting point of view, the initial increase is due the availability of more number of free radicals generated for grafting of the monomer but after reaching optimum initiator concentration the grafting parameters shows a decrease. This may be due to the fact that when the concentration of the initiator exceeds a certain value, increased free radical concentration results in serious homopolymerization. This will lead to the decrease in the grafting parameters [25].

### Effect of Temperature

The effects of reaction temperature on the synthetic parameters has been investigated in the range of 50°C- 90°C keeping the monomer, initiator and N6-g-MAH concentrations as constant [22].



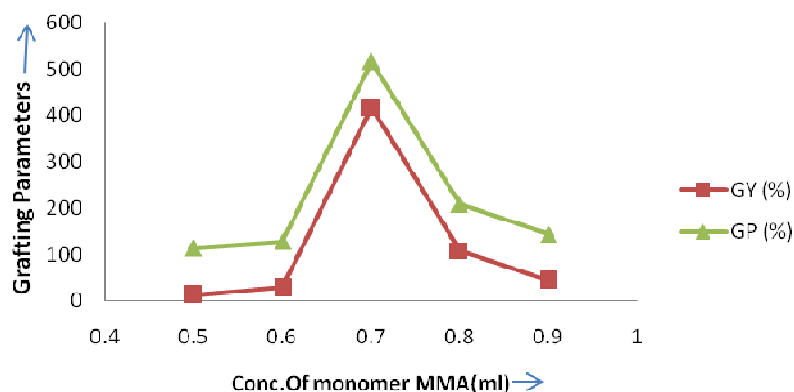
**Figure 2: Effect of temperature**

Figure-2 shows that the effect of temperature on the grafting parameters of binary graft copolymer of Nylon6. The temperature of grafting medium is one of the most important reaction parameters that have a strong effect on the grafting yield during grafted polymer preparation. The increase in temperature of the grafting mixture upto 70°C initially increases the degree of grafting as shown in figure-2.

The enhancement in the grafting yield with increasing temperature may be attributed to the (i) an increase in the mobility of the initiator and monomer (ii) an increased rate of diffusion of the initiator and monomer from the solution phase to the N6-g-MAH backbone (iii) an increased number of active sites in the reaction medium (iv) an increased rate of initiation and propagation step (v) enhancement of N6-g-MAH swellability [25] [26]. But beyond 70°C, the grafting rate decreases. This is because at higher temperature, higher combination rates of monomer are obtained increasing homopolymerisation reaction, which results in a decreased grafting rate [27, 28]. Decrease in percentage of grafting beyond optimum temperature may also be attributed to premature termination of the growing polymeric chains and to the occurrence of the chain transfer reactions. Similar observations have been noted by Somanathan et al., [29] with grafting methacrylic acid into PET using benzoyl peroxide initiator

### Effect of Monomer

The variation of grafting parameters of the binary graft copolymer of nylon6 with maleic anhydride and methyl methacrylate was investigated by carrying out the polymerization at five different monomer concentrations.



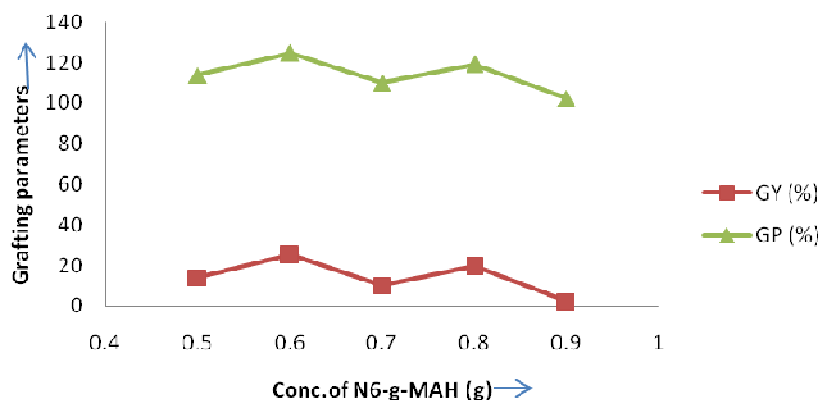
**Figure 3: Effect of monomer concentration**

Figure-3 shows that effect of monomer concentration on the grafting parameters of binary graft copolymer of Nylon6. As is evident, the grafting parameters sharply rises with increasing monomer concentration upto 0.7 ml achieves 416% grafting yield and then decreases with further increase in the monomer concentration. The initial increase in grafting may be due to the reason that most of the monomer is utilized by the available free radical sites on the PA6-g-MAH. As the methyl methacrylate concentration rises the diffusion of monomer onto N6-g-MAH phase increases.

This will lead to the increment in the grafting parameters. But the grafting rate does not exceed beyond the optimum monomer concentration. This may be due to the formation of more homopolymers as compared to the graft copolymer at higher monomer concentration. Moreover, due to homopolymerisation, viscosity of the reaction medium increases which creates hindrance in the movement of the free radicals towards active sites, thereby resulting in less graft yield [30] (Sinha et al., 2008). The number of free radical sites available on the N6-g-MAH backbone becomes a limiting factor, and the rate of diffusion is progressively effected by deposition on the polymer backbone [27, 31].

### Effect of Nylon 6 –G-MAH

The variation of grafting parameters of the binary graft copolymer of nylon6 with maleic anhydride and methyl methacrylate was investigated by carrying out the polymerization at five different N6-g-MAH concentrations.



**Figure 4: Effect of Nylon 6-g-MAH**

Figure-4 shows the effect of N6-g-MAH concentration on grafting yield, grafting efficiency, grafting percentage and monomer conversion of the binary graft copolymer of polyamide6. From

the results it is evident that the grafting parameters mainly depend upon the nylon6-graft-maleic anhydride backbone concentration. The observed results indicate that the grafting percentage increase first and thereafter declines. It may be explained that an increase in backbone concentration can make more monomers and initiators easily approachable to the surface of N6-g-MAH and produce more grafted side chains which cause grafting percentage to increase.

The reason for the decreasing trend of all the parameters after a certain N6-g-MAH concentration may be due to the high viscosity. The high viscosity of the reaction system makes the diffusion of both monomer and CAN diffusion. This leads to the higher local CAN concentration, which makes the rate of termination accelerate due to the reaction between the propagating chain radicals and primary radicals [24]. Similar observations have also been reported in the case of ceric induced grafting of ethyl acrylate onto sodium alginate [32].

### Effect of Solvent

The grafting reactions were carried out using different amounts of solvent. The results are presented in the figure-5. The effect of solvent on the synthetic grafting parameters has been investigated in the range of 20ml to 60ml keeping the other variables such as temperature, monomer and homopolymer concentrations are constant.

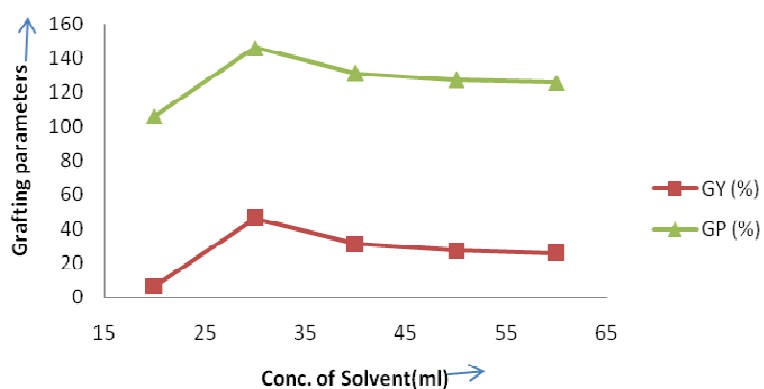


Figure 5: Effect of solvent

From the above figure, it was observed that the grafting parameters sharply raised with increasing the concentration of the solvent at first and thereafter the grafting yield decreases with increase in the amount of solvent. This probably occurs due to the dilution of reaction medium. As a result of this dilution the monomer radical concentration per unit volume decreases. As a result of this lowering of the monomer concentration, lesser amount of grafting takes place [30]

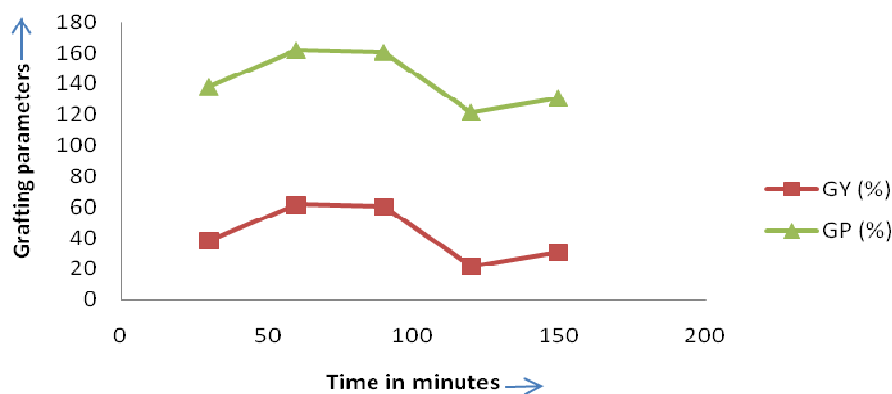


Figure 6: Effect of time

### Effect of Time

The grafting reactions were carried out at different time intervals between 30 mins to 150 mins keeping the other variables such as conc. of initiator, monomer, N6 -g-MAH, solvent and temp as constant.

Figure - 6 shows the effect of time on the grafting parameters of binary graft copolymer of Nylon6. With an increase in reaction time, the free radicals have more time for reaction and therefore results in higher level of grafting. After some time, all the initiators and monomers are used up. Thus no further change in grafting level was observed with increasing reaction time. The decrease in grafting may be due to the induced decomposition of the initiator leading to decrease in the concentration of initiator and hence decrease in the active radicals required to generate active sites on polymeric backbone [30]. Similar observations were reported with grafting acrylic monomer such as acrylamide and glycidyl methacrylate on polyamide fibres using other initiators. With further increase in time, a decline in percentage of grafting has been observed. This probably happens due to the occurrence of various hydrogen abstraction reactions along with some other side chain reactions as well as excessive homopolymerization.

### FT-IR spectral analysis - Evidence of grafting

The grafting of maleic anhydride and methyl methacrylate onto nylon6 was confirmed through FT-IR analysis. The FT-IR spectra of pure nylon6, N6-g-MAH and N6-g-MAH-g-MMA was shown in the figures - (7)-(9). The FT-IR spectrum of pure nylon6 (figure-7) showed a broad peak at  $3350\text{ cm}^{-1}$  due to hydrogen bonded N-H group [33],  $2987\text{ cm}^{-1}$ ,  $1670\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  due to  $\text{CH}_2$ ,  $\text{C}=\text{O}$  in secondary amide and C-C stretching whereas the FT-IR spectra of N6-g-MAH (Figure-8) shows a strong absorption at  $1632\text{ cm}^{-1}$ ,  $1536.68\text{ cm}^{-1}$  and  $1265.67\text{ cm}^{-1}$  corresponding to tertiary amide carbonyl group, C-O-H bending (in acids) and C=C stretching in alkenes. These obtained additional peaks confirm the formation of N6-g-MAH which is an evidence for grafting.

The FT-IR spectrum of binary graft copolymer(N6-g-MAH-g-MMA)(Figure-9) shows a strong absorption at  $1362.5\text{ cm}^{-1}$ ,  $1263.4\text{ cm}^{-1}$  which was attributed to the symmetrical bending of C-H bond in the methyl group and CH (twisting and wagging) in  $\text{CH}_2$ . On comparing the FT-IR spectra of N6-g-MAH(Figure-8) with the N6-g-MAH-g-MMA(Figure-9), it was observed that the binary graft copolymer shows an additional band at  $1201.5\text{ cm}^{-1}$  corresponding to C-O stretching in esters respectively This obtained additional peak confirm the grafting of methyl methacrylate onto N6-g-MAH.

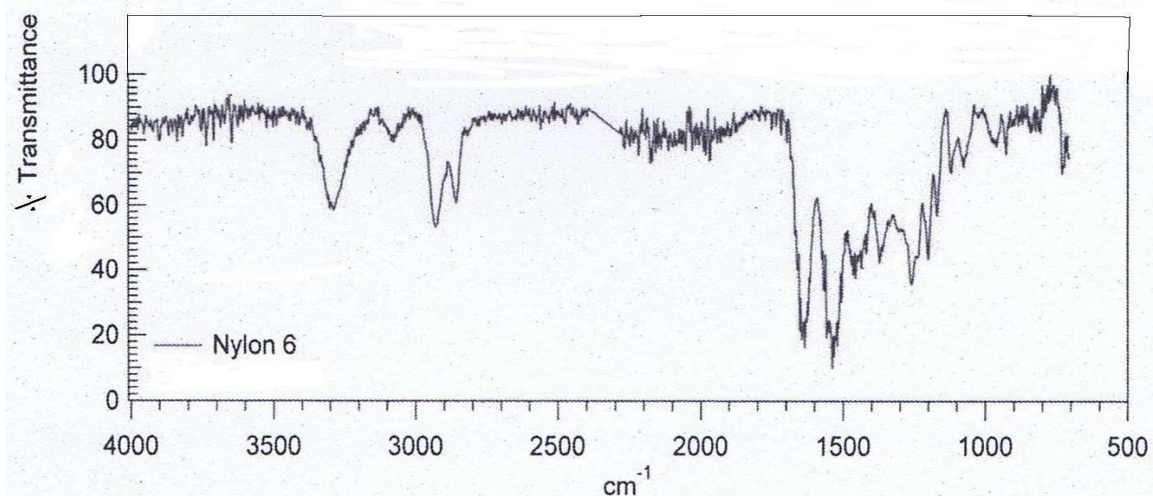


Figure-7: FT-IR srectrum of pure nylon6



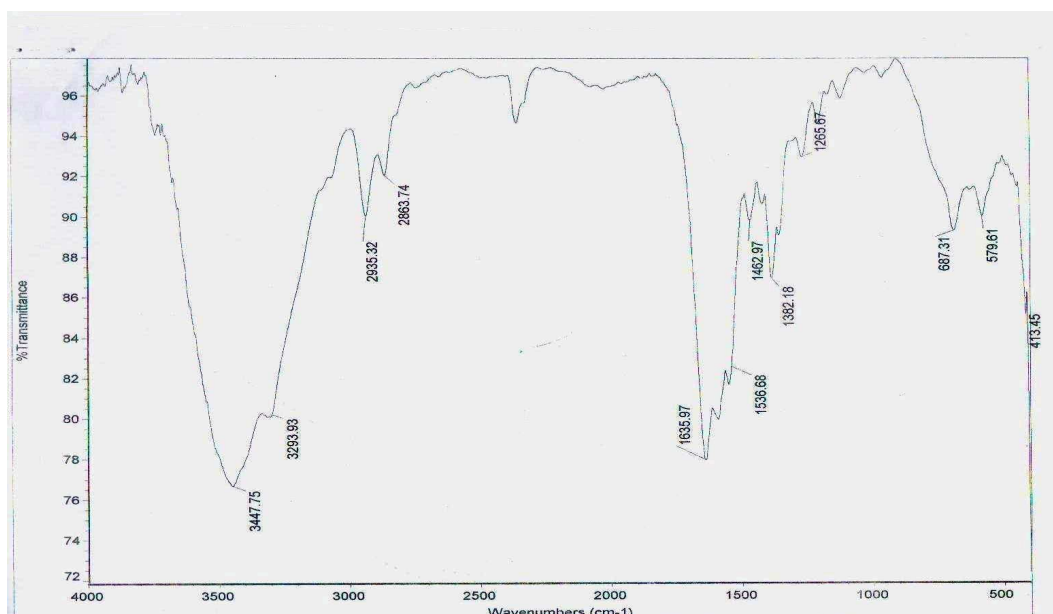


Figure 8: FT-IR spectrum of N6-g-MAH

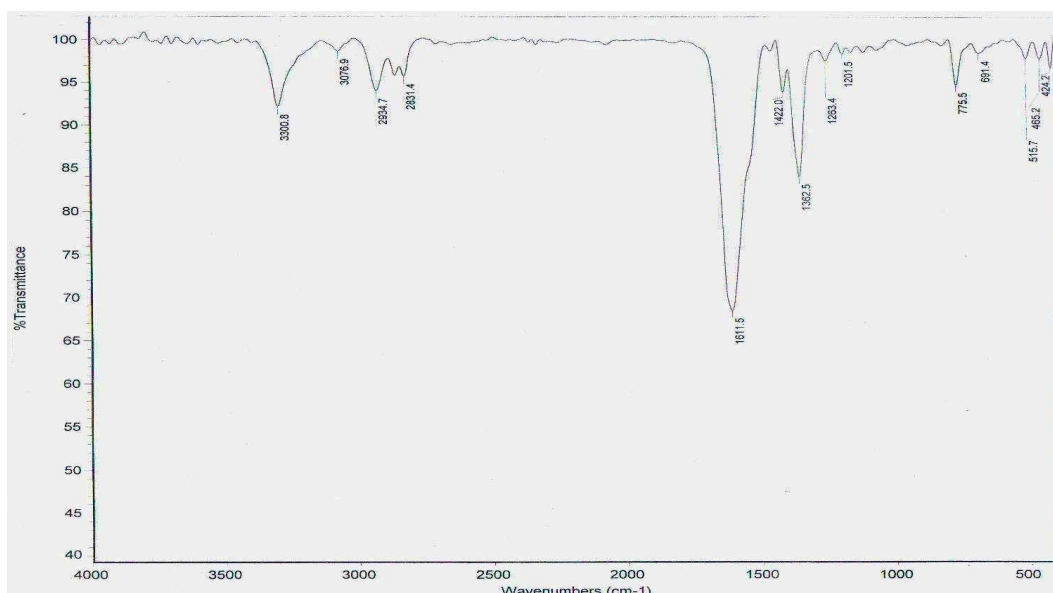
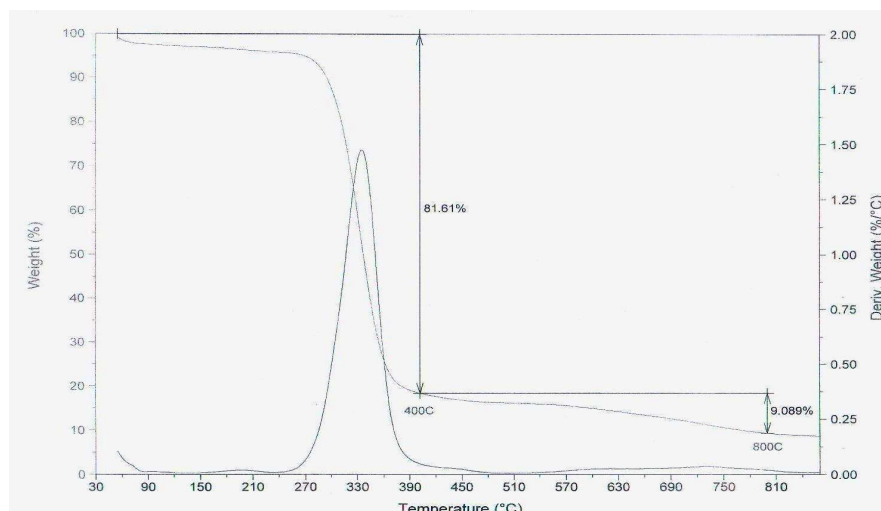


Figure 9: FT-IR spectrum of N6-g-MAH-g-MMA

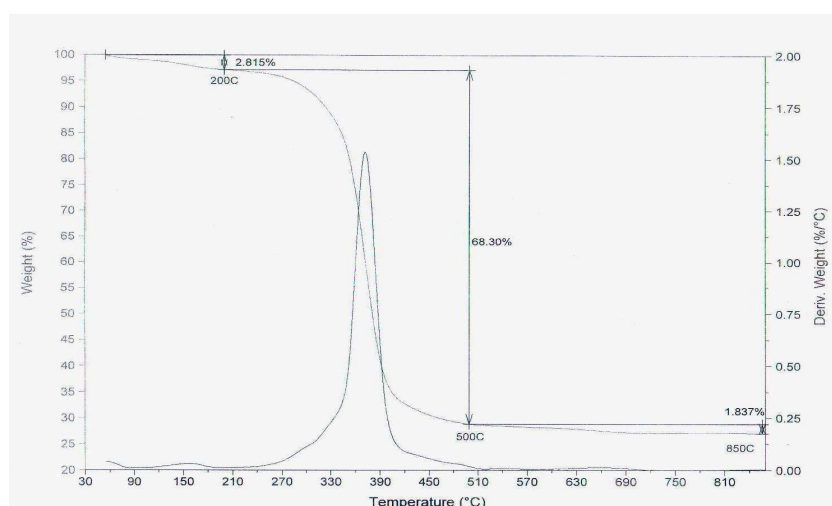
### Thermo Gravimetric Analysis

The TGA thermogram details of Nylon 6-G-maleic anhydride copolymer and binary graft copolymer were represented in the Figures-(10)-(11). The N6-g-MAH copolymer (Figure-10) shows that the residual temperature of the sample was found to be 850°C. Around 81% of the sample had disintegrated at the end of the experiment leaving behind 9.301 % of the blend remained as a residue at 800°C. The TGA thermogram details of the binary graft copolymer (Figure-11) prepared using the 0.9 ml of methyl methacrylate monomer shows that the maximum weight loss occurs at the temperature range of 330° C to 420°C. Around 72.95% of the sample is disintegrated in 850°C leaving behind 27.048% of the sample as a residue

On comparing Figure -11 with Figure-10, it was concluded that the binary graft copolymer was found to be highly thermally stable. This was confirmed from the amount of graft copolymer remained as residue at the end of the experiment, and the various decomposition temperatures.



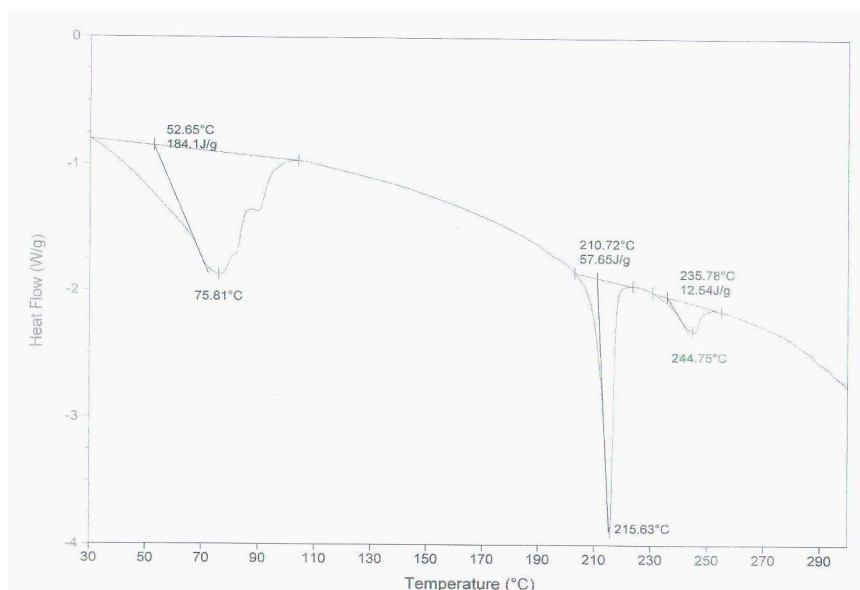
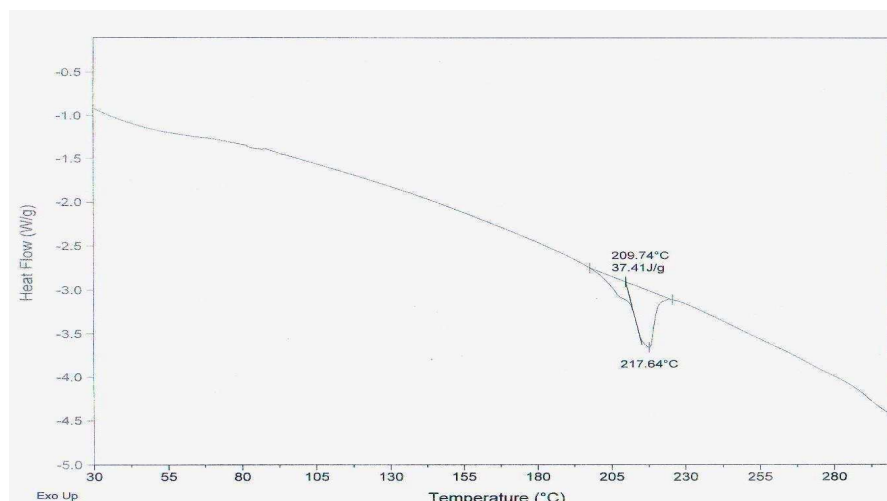
**Figure -10: TGA details of N6-g-MAH**



**Figure 11: TGA details of Binary graft copolymer of N6 (PM3-0.7ml)**

### Differential scanning calorimetry

Figures 12 - 13 represents the DSC curve of Nylon 6-graft-maleic anhydride graft copolymer and binary graft copolymer respectively. Broad endothermic peaks are observed at various temperatures indicating the crystallization of the blend polymers. Figure-12 shows that the glass transition temperature was observed at 150°C. Two sharp and broad endothermic peaks are obtained at 215.63°C, 244.75°C showing the recrystallization process of N6-g-MAH at different temperatures. The DSC curve of binary graft copolymer of nylon 6 prepared using maleic anhydride and methyl methacrylate monomer (Figure -13) shows that the glass transition temperature was found to be 160°C respectively. A broad endothermic peak was observed at 217.64°C

**Figure 12: DSC of N6-g-MAH****Figure 13: DSC of Binary graft copolymer of N6**

On comparing the DSC curve of N6-g-MAH sample with binary graft copolymer of nylon6 it was observed that the endothermic peaks are shifted to higher values. In addition to this the glass transition temperature was also shifted to a higher value for the binary graft copolymer of nylon6 with MAH and MMA. From the above results it was concluded that the addition of the monomer to PA6-gMAH increases the thermal stability.

### **XRD Diffraction Studies**

The XRD spectrum of nylon6-graft maleic anhydride was represented in the Figure-14. Figure-14 shows two distinct sharp peaks at  $2\theta=20^\circ$  &  $2\theta=24^\circ$ . Semi crystalline nature of polymers was indicated by these peaks.

Figures-15 shows the XRD spectral details of binary graft copolymer of nylon6 prepared under different conditions. The binary graft copolymer of nylon6 shows two distinct sharp peaks ( $2\theta=20^\circ$  &  $2\theta=24^\circ$ ) similar to the ones seen for nylon6-graft maleic anhydride. But in addition to this some more sharp peaks are observed at  $2\theta=16^\circ, 28^\circ, 33^\circ, 41^\circ, 45^\circ$  and so on. From the increase in the number of peaks observed for the binary graft copolymer of nylon6, it was concluded that

the crystallinity of nylon6-graft-maleic anhydride was found to be increased. The addition of methyl methacrylate monomer to the nylon6-graft-maleic anhydride copolymer increases the crystalline nature of nylon6-graft-maleic anhydride.

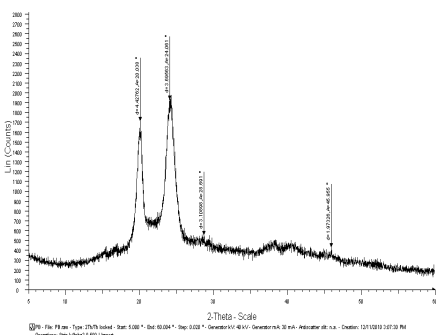


Figure 14: XRD of N6-g-MAH

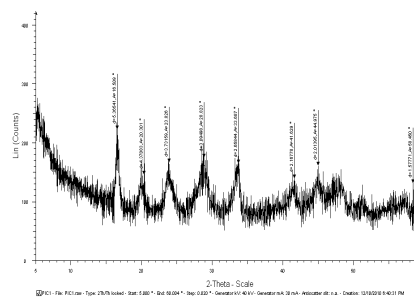


Figure 15: XRD of Binary graft copolymer of N6

## CONCLUSION

Based on the results presented in this paper, we conclude that ceric ammonium nitrate was an efficient initiator for grafting of MAH and MMA onto nylon6 under a wide range of experimental conditions. Grafting parameters such as conversion of monomer to polymer, graft yield can be varied substantially by varying the concentration ratio of initiator ( $Ce^{4+}$ ) to nylon6 and monomer to nylon6. The optimum synthetic conditions may be given as follows: CAN concentration-0.7g; Temperature-70°C; methyl methacrylate-0.7ml, solvent-30ml and time-60 minutes. The proof of grafting was obtained from the FT-IR results. The changes in crystalline nature of the polyamide nylon6 due to polymerization were confirmed using X-ray diffraction patterns. This type of work could encourage the synthesis of new grafted polymers, where some functionality is required, for specific purposes.

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