Applicability and Synthesis of Thermal Resistive Material for Rural Development

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Abstract: The utility of thermal resistive polymeric materials for rural development is of great importance in various constructional and tool development field. Therefore, the synthesis of such usable materials is of great interest. So the focus on facile free radical copolymerization of n- chloro- substituted of N-phenyl maleimide monomer with methyl methacrylate (MMA) were performed at 70°C in DMF using Benzoyl Peroxide (BPO) as a free radical initiator is emphasized so that a thermal resistive usable polymers material can be obtained. These copolymers are characterized by FT-IR, ^{1}H-NMR, GPC, TGA. The average molecular weight achieved by GPC viz. for copolymer, C-PCPMI has the highest molecular weight 9510 with PDI close to 1.6. Thermal analysis reveals copolymer show multistep degradation. The TGA and DTA curves explain its percentage weight loss with temperature at different heating rate 5°C, 10°C and 20°C. The Kissinger method is used for non-isothermal kinetic parameters value. The highest thermal stability is obtained for copolymer of 4- chloro- substituted poly phenyl maleimides polymer with MMA (C-PCPMI). On comparison of the behavior of para, meta and ortho chloro substituted copolymers, the faster weight loss on DTA curve was observed for ortho substituted chloro molecule at the same temperature and heating rate. The activation energy of para chloro substituted N-(phenyl) maleimides of polymer is highest among the all three polymers.

Keywords: Thermal resistive polymeric materials, TGA/DTA, Activation parameters

Introduction

The application of high thermal responsive polymeric materials for rural development is of great importance in various modernized constructional and smart tool development. Therefore, the synthesis of such usable materials is of great interest. So the attention on the aromatic polyimides as thermal stable high-performance polymers are considered as the most important class in development of smart cities construction and equipment development process[1-5]. The vast application of Poly methyl methacrylates as resin applications is modified by the introduction of functional maleimide moiety, may result in the better thermal stable polymers [6]. Free radical polymerization is used for the preparation of thermally stable polymers [7-17]. TGA and GPC techniques were carried out to study the thermal stability and molecular weight determination. The kinetic data processing was performed by applying Kissinger method and [18] gives activation energy for these antimicrobial copolymers. It is also possible to establish a rapid comparison of thermal stabilities and decomposition temperatures of different polymers [19-26]. Thus, thermal analysis could solve selection of thermally stable smart polymeric materials. Hence, in the present communication, we are discussing the kinetics of thermal degradation behaviour of copolymerization of chloro substituted N-phenyl maleimide with vinylic monomer, methyl methacrylate [27].

Experiment

Experimental

Materials

Ortho-, *meta-* and *para-* chloro (phenyl) maleimide, were purchased from SRL, Pure. Maleic anhydride (SRL, Mumbai) recrystallized from chloroform. Methylmethacrylate (MMA) (SRL, Mumbai) distilled prior to use.Benzoyl peroxide (BPO) purchased from (Merck, Mumbai). Phosphorus pentoxide (P_2O_5), sulphuric acid, methanol, acetone were purchased from Merck India.

**Synthesis of N-(chloro phenyl) maleimide monomer**

Substituted aniline in DMF and maleic anhydride (ME) mixed at room temperature to yield   *Ortho/meta/para* chloro substituted N-phenyl maleimide monomers, under following scheme-1.
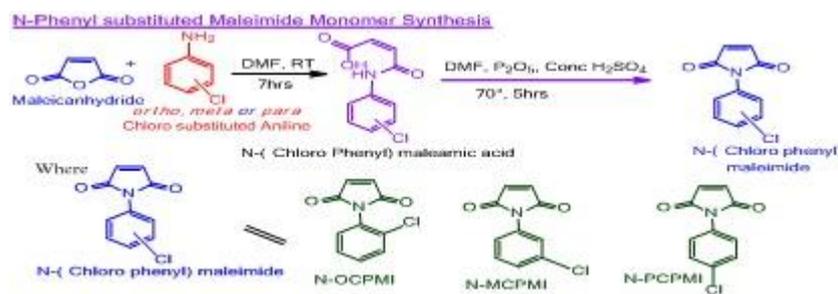
Scheme 1: The synthetic route of chloro- substituted N- phenyl maleimides

Polymerization of N-(chlorophenyl) maleimide monomers with MMA

 80 ml solution of Chloro substituted monomers in THF was mixed well with methyl methacrylate (MMA) (1.00 ml) into the flask at a low temperature followed by the addition of a free radical initiator (BPO, 0.003 g) in an nitrogen atmosphere, refluxed at 70°C for 48 hrs.(Scheme2) to give copolymers as shown in the following scheme 3:
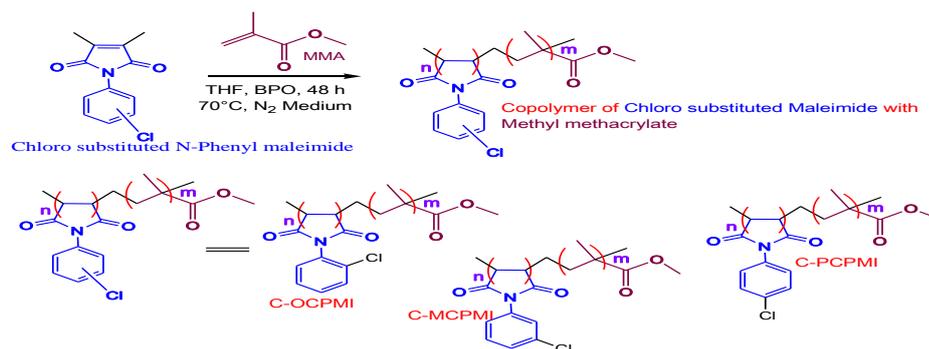
Scheme 2: Co-polymerization of chloro- substituted N- phenyl maleimides with MMA

Results and Discussion

Spectral Characterization of monomers

In **N-OCPMI** monomer, peak at 1634.9 cm^{-1} of hetereo C=C stretching, at 958.4 cm^{-1} of hetero Bending H-C=C-H suggest imide bond intact in monomer with 1781.5 and 1710.2 cm^{-1} of symmetric and asymmetric stretch of C=O in a five member imide ring and 1589.1, 1546.8 and 1482.4 cm^{-1} of C=C aromatic stretching of phenyl ring and 1391.1 aromatic C-N stretching, 697.4 cm^{-1} aromatic C-Cl in 1, 2- disubstituted benzene, 759.1 cm^{-1} ortho \aromatic C-Cl stretching). **^{1}H NMR (300 MHz, TMS, CDCl$_3$, δ ppm)** : δ 7.32-7.41 ppm (4H, phenyl), δ 6.57 ppm Singlet, CH=CH proton of imide.In **N-MCPMI** monomer, peak at 1634.9 cm^{-1} of hetereo C=C stretching,

at 969.5 cm^{-1} of hetero Bending H-C=C-H of imide suggest imide bond intact in monomer with 1780.3 and 1716.0 cm^{-1} of symmetric and asymmetric stretch of C=O in a five member imide ring and 1578.3, 1543.6 and 1435.6 cm^{-1} of C=C aromatic stretching of phenyl ring and 1405.3 of aromatic C-N stretching, 669.9 cm^{-1} of aromatic C-Cl in 1, 3- disubstituted benzene, 765.5 cm^{-1} of meta aromatic C-Cl stretching.**^{1}H NMR (300 MHz, TMS, CDCl$_3$, δ ppm)** δ 7.28-7.50ppm (4H, phenyl), δ 6.76 ppm Singlet, CH=CH proton of imide. In **N-PCPMI** monomer**,** peak at 1630.0 cm^{-1} of -CH=CH imide stretching are consisted with the structure of N-PCPMI and 953 cm^{-1} of hetero bending H-C=C-H of imide and 1780, 1708.2 cm^{-1} of symmetric and asymmetric C=O stretching in hetero ring and 1127.8 of C-N-C stretching and 1396 cm^{-1} of aromatic –CN stretching. 1586.9, 1531.9, 1490.8 cm^{-1} of aromatic HC=CH stretching of benzene, 1630 cm^{-1} of hetero C=C stretching, 828.7, 695.0 cm^{-1} of aromatic C-Cl in 1, 4 disubstituted benzene, 768.9 cm^{-1} of para aromatic C-Cl stretching and **^{1}H NMR (300 MHz, TMS, CDCl$_3$, ppm)**δ 7.260-7.271 ppm doublet, two aromatic proton, ortho to phenyl ring and δ 7.44-7.50 ppm doublet, two aromatic proton in m-group in phenyl ring), δ 6.88 ppm Singlet, CH=CH proton of imide.

Spectral Characterization of Copolymers

FT-IR spectra of C-OCPMI, *C-MCPMI and C-PCPMI* **IR spectra (cm^{-1})** 3077.7 (aromatic C-H stretching), 3118.3 –CH stretching for hetero aromatic, 3121.1 (alkene C-H stretching), 1783.1 and 1720.4 (C=O stretching in a five membered imide ring), 1590.5, 1529.2 and 1486.7 for aromatic C=C stretching, 1442.5 (aromatic C-N stretching), 1194.4 (C-N-C). 2962.3 and 2954.3 (C-H stretching in CH$_3$, CH$_2$) and 1442.5(–CH deformation in CH$_2$ of MMA) **C-OCPMI :**759.1 (aromatic C-Cl stretching in di substituted benzene), 687.8 (aromatic CH-CH bending), 617.3 (heteroaromatic C-H deformation)**C-MCPMI:** 852.4 and 780.1 (aromatic C-Cl stretching in di substituted benzene), 698.4 (aromatic CH-CH bending), 607.0 (heteroaromatic C-H deformation) **C-PCPMI:** 852.6cm^{-1} and 766.5 cm$^-$ (aromatic C-Cl stretching in di substituted benzene), and 677.0 (aromatic CH-CH bending) 604.2 cm^{-1} (heteroaromatic C-H deformation) **^{1}H NMR of copolymers (300 MHz, TMS, CDCl$_3$, ppm) δ:** δ 7.21-8.03 ppm (2d, 4H phenyl). δ 3.70-3.89 ppm appeared for (S, 2H –CH-CH-), δ 0.85-1.12 ppm (T,3H CH$_3$) , δ 1.89-2.04 ppm (2H ,CH$_2$)

Gel permeation chromatography (GPC)

Molecular weight usually decreases while the polydispersity index increases with increasing the maleimide content indicating higher rate of transfer to the maleimide monomer. GPC traces show that the synthesized copolymers contain no impurities. The PDI values indicate that the polymers show narrow molar mass distribution even synthesized by FRP.(Table 1)

Table 1: Molecular weight and PDI values for and Copolymers

COPOLYMERS	C-OCPMI	C-MCPMI	C-PCPMI
Mw	9217	9440	9510
PDI=Mw/Mn	1.21	1.56	1.59

Thermal analysis   and   Evaluation of Activation Thermodynamic Parameters

The thermodynamic activation parameters of decomposition processes for polymers such as activation energy (E*), entropy of activation (ΔS*), enthalpy of activation (ΔH*) and Gibbs free energy (ΔG*), are calculated with the help of DTA and TGA curves for copolymers and homo by using Kissinger method [33].The TG and DTA graph are shown in Figure 1and 2. The method proposed by Kissinger [34] is based on functional dependence of the heating rate (β) and variation of TG and DTA peak temperature (T_{max}) is in proportion to the maximum rate of reaction and equation:

$$\text{Log}(\beta/T^2_{max}) = \log (AR/E_a) – E_a/ (2.302. RT_{max})$$

Plotting the left side of this equation against $1/T_{max}$ should give a straight line of the slope $-E_a/2.303R$ and intercept log AR/E_a. To apply this method several thermal analysis of the same substance at different heating rate is performed. Other non-isothermal parameters are calculated using following equation:

E* = - slope (2.303 R), ΔS* = 2.303[log(Ah/kT)]R , ΔH* =E*- RT , ΔG*= ΔH*- TΔS*,

Where, T_{max} is the peak temperature, h= plank constant=$6.6*10^{-34}$J.s, k= boltzman constant= 1.38×10^{-23}J/K, R= gas constant= 8.314 J/mol. K. A= Arrhenius factor

The data for copolymer degradation in different heating rate at various temperature stages.The high activation energy explains the thermal stability of the polymers. The entropy of activation has negative values indicates The decompositionion reactions proceed with a lower rate than normal ones.

Copolymer: C-PCPMI

About 7.1 % mass loss for *C-PCPMI* was observed up to 190 °C at a heating rate of *5°C/min.* and almost 50.2% copolymer (C-PCPMI) was degraded up to 340 °C, and up to 500 °C about 90 % mass loss was observed (figure 1). The thermo curve of copolymer (C-PCPMI) shows two-step degradation process with and gradual mass loss from copolymer. The first stage of degradation was between 256 to 318 °C with maximum mass loss at 287°C, and the second stage degradation was between 380 to 444 °C with maximum mass loss at 412°C. These two stages are visible from DTA curve. 0.2 % char yield was obtained at 640°C in case of copolymer (C-PCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *5°C/min* was -6171 Jmol^{-1} at the range of 40-170 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -13307 Jmol^{-1} at the range of 460-590°C. The entropy was negative from range -1.4012 to -1.34903Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9854 to -20482 Jmol^{-1} and 9233 to -19318 Jmol^{-1}. About 8.3 % mass loss for *C-PCPMI* was observed up to 180 °C at a heating rate of *10°C/min*. and almost 50 % copolymer was degraded up to 335 °C, and up to 500 °C about 90 % mass loss was observed (figure 1).Thermo curve of copolymer (C-PCPMI) shows two-step degradation process with gradual mass loss. The first stage of degradation was between 257 to 325 °C with maximum mass loss at 303°C, and the second stage degradation was between 379 to 446 °C with maximum mass loss at 421°C. These two stages are visible from DTA curve. 2 % char yield was obtained at 587°C in case of copolymer (C-PCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *10°C/min* was -6102 Jmol^{-1} at the range of 40-160 °C of

decomposition temperature this value decreases as temperature increases gradually in every step to -13141 Jmol^{-1} at the range of 450- 580°C. The entropy was negative from range -1.4026 to -1.3422 Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9785to -20233 Jmol^{-1} and -9164 to- 19087 Jmol^{-1}.

About 5.6 % mass loss for *C-PCPMI* was observed up to 180 °C at a heating rate of ***20°C/min***. and almost 50 % copolymer was degraded up to 345 °C, and up to 490 °C about 90 % mass loss was observed. Thermo curve of copolymer (C-PCPMI) shows two-step degradation process with and gradual mass loss from copolymer. The first stage of degradation was between 273 to 350 °C with maximum mass loss at 320°C, and the second stage degradation was between 381 to 462 °C with maximum mass loss at 420°C. These two stages are visible from DTA curve. 1.1 % char yield was obtained at 585°C in case of copolymer (C-PCPMI). Copolymer loses completely before 587°C. The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *20°C/min* was -6033 Jmol^{-1} at the range of 40-150 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -12773 Jmol^{-1} at the range of 450- 580°C. The entropy was negative from range -1.40602 to - 1.3422 Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9500 to -19889 Jmol^{-1} and -8955 to- 18881.1 Jmol^{-1}. So, by studying the degradation pattern for copolymer (C-PCPMI) at different heating rate it is observed that degradation steps are almost same in this case but their range of degradation is changing and it is increasing slightly towards right side on increasing the heating rate. The activation energy at heating rate of 20°*C/min* of for copolymer C-PCPMI is the highest. Arrhenius factor, A for C-PCPMI also increases from 0.2007 to 0.2132 on increasing the heating rate at 5°*C/min* to 20 °*C/min* while activation energy value decreases.

Copolymer : C-MCPMI

About 1.5 % mass loss for C-MCPMI was observed up to 160 °C at a heating rate of ***5°C/min***. and almost 50.2% copolymer (C-MCPMI) was degraded up to 330 °C, and up to 520 °C about 90 % mass loss was observed (figure 1). The thermo curve of copolymer (C-MCPMI) shows two-step degradation process with and gradual mass loss from copolymer. The first stage of degradation was between 256 to 318 °C with maximum mass loss at 288°C, and the second stage degradation was between 339 to 423 °C with maximum mass loss at 402°C. These two stages are visible from DTA curve. 3 % char yield was obtained at 500°C in case of copolymer (C-MCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *5°C/min* was -6102 Jmol^{-1} at the range of 40-170 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -12974 Jmol^{-1} at the range of 470- 570°C. The entropy was negative from range -1.4486 to - 1.3596 Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9702 to -19982 Jmol^{-1} and -9095 to- 18836 Jmol^{-1}.

About 1.6 % mass loss for C-MCPMI was observed up to 160 °C at a heating rate of ***10°C/min.*** and almost 50 % copolymer was degraded up to 330 °C, and up to 500 °C about 90 % mass loss was observed (figure 1). The thermo curve of copolymer (C-MCPMI) shows two-step degradation process. The first stage of degradation was between 273 to 350 °C with maximum mass loss at 316°C, and the second stage degradation was between 358 to 441°C with maximum mass loss at 405°C. These two stages are visible from DTA curve. 3 % char yield was obtained at 600°C in case of copolymer (C-MCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *10°C/min* was -6094 Jmol^{-1} at the

range of 40-150 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -1293 Jmol[-1] at the range of 450- 580°C. The entropy was negative from range of -1.4026 to -1.1773 Jmol[-1]. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9777 to -20114 Jmol[-1] and -9156 to- 19098 Jmol[-1]. About 1.3 % mass loss for C-MCPMI was observed up to 160 °C at a heating rate of **20 °C/min.** and almost 50 % copolymer was degraded up to 300 °C, and up to 490 °C about 90 % mass loss was observed (figure 2). The thermo curve of copolymer (C-MCPMI) shows two-step degradation process. The first stage of degradation was between 248 to 356 °C with maximum mass loss at 316°C, and the second stage degradation was between 378 to 459 °C with maximum mass loss at 415°C. These two stages are visible from DTA curve. 4.5 % char yield was obtained at 568°C in case of copolymer (C-MCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *15°C/min* was -6102 Jmol[-1] at the range of 40-160 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -12918 Jmol[-1] at the range of 410- 600°C. The entropy was negative from range of -1.4043 to -1.3425 Jmol[-1]. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9702 to -20177 Jmol[-1] and -9094 to- 19005 Jmol[-1].

So, by studying the degradation pattern for copolymer (C-MCPMI) at different heating rate it was observed that degradation steps are almost same in this case but their range of degradation is changing. The Arrhenius factor, A for C-MCPMI is also increases from 0.2030 to 0.1459 on increasing the heating rate at 5°C/min to 20 °C/min while activation energy value decreases. On observing the change in the activation energy and other non-isothermal parameters of C-MCPMI with increase in heating rate, it is concluded that increased heating rate does not affect the degradation of C-MCPMI to a large extent as the increase in activation energy is not much significant.

Copolymer : C-OCPMI

About 7.6 % mass loss for C-OCPMI was observed up to 140 °C and 10 % mass loss for C-OCPMI was observed up to 180 °C at a heating rate of *5°C/min*. and almost 50 % copolymer (C-OCPMI) was degraded up to 290 °C, and up to 510 °C about 90 % mass loss was observed (figure 1). The thermo curve of copolymer (C-OCPMI) shows two-step degradation process. The first stage of degradation was between 235 to 308 °C with maximum mass loss at 297°C, and the second stage degradation was between 360 to 423 °C with maximum mass loss at 381°C. 4.9 % char yield was obtained at 595°C in case of copolymer (C-OCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *5°C/min* was -5843 Jmol[-1] at the range of 40-140 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -13051 Jmol[-1] at the range of 440- 580°C. The entropy was negative from range of -1.4061 to - 1.1768 Jmol[-1]. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -6974 to -17873 Jmol[-1] and -8817 to- 19138 Jmol[-1].

About 8.1 % mass loss for C-OCPMI was observed up to 130 °C and 10 % mass loss for **C-**OCPMI was observed up to 170 °C at a heating rate of ***10°C/min***. and almost 50 % copolymer (C-OCPMI) was degraded up to 260 °C, and up to 500 °C about 90 % mass loss was observed (figure 1). The thermo curve of copolymer (C-OCPMI) shows two-step degradation process. The first stage of degradation was between 243 to 320 °C with maximum mass loss at 299°C, and the second stage degradation was between 323 to 448 °C with maximum

mass loss at 397°C. 4.9 % char yield was obtained at 545°C in case of copolymer (C-OCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *10°C/min* was -5893 Jmol^{-1} at the range of 40-130 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -12845 Jmol^{-1} at the range of 400- 600°C. The entropy was negative from range of -1.4085 to - 1.3425 Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of -9244 to -20021 Jmol^{-1} and -8676 to- 18862 Jmol^{-1} .

About 10.2 % mass loss for C-OCPMI was observed up to 140 °C at a heating rate of *20°C/min* and almost 50 % copolymer was degraded up to 250 °C, and up to 480 °C about 90 % mass loss was observed (figure 1) thermo curve of copolymer (C-OCPMI) shows two-step degradation process. The first stage of degradation was between 248 to 334 °C with maximum mass loss at 309°C, and the second stage degradation was between 334 to 471 °C with maximum mass loss at 403°C. These two stages are visible from DTA curve. 5.5 % char. The yield was obtained at 530°C in case of copolymer (C-OCPMI). The activation energy value shows the decomposition proceeds with an exothermic process and activation energy at a heating rate of *20°C/min* was - 5964 Jmol^{-1} at the range of 40-140 °C of decomposition temperature this value decreases as temperature increases gradually in every step to -12729 Jmol^{-1} at the range of 440- 580°C. The entropy was negative from range of -1.4581 to - 1.3432 Jmol^{-1}. Here negative value of entropy suggests the stability of the copolymer and enthalpy and gibbs free energy values were also negative in the range of - 9398 to - 19987 Jmol^{-1} and – 8816 to – 18815 Jmol^{-1} .

So, by studying the degradation pattern for copolymer (C-OCPMI) at different heating rate it was observed that degradation steps are almost same in this case but their range of degradation is changing. It was observed that on increasing the heating rate from 5° C/min to 20°C/min , the copolymer C-OCPMI activation energy and other non-isothermal parameters are not almost same but at higher heating rate at *20°C/min* the activation energy decreases for the degradation of copolymer, C-OCPMI. Arrhenius factor, A for C-OCPMI decreases from 0.2191 to 0.2161 for first stage and increases for last stage from 0.0956 to 0.1014 with increase in temperature and heating rate at 5°*C/min* to 20 °*C/min* while activation energy value decreases. This is suggesting that first degradation was not faster later at higher temperature the degradation increases in C-OCPMI copolymer. Even the activation energy at 5°*C/min* and 10°*C/min* is almost same and higher than that of at 20°*C/min*   suggesting faster degradation of C-OCPMI at higher heating rate and therefore, less activation energy is required for its degradation.

The degradation of copolymers is gradual. In general, the polymer chain of polyimide was begun to decompose gradually as the temperature increased continuously. From all the DTA curves, the decomposition rates of the copolymers showed two clear minimum values, indicating two distinguishing decomposition stages. On further increase in Ti value degradation process also increases in copolymers since two units are attached one is maleimide unit and other methylmetha acrylate so the polymeric chain fragmentation and degradation occur at multiple step degradation temperature range. Since it involves the breaking of carbon-carbon single bond between two polymerizing unit and thus require energy to degrade at higher temperature value at the second stage degradation in copolymers. On comparison of the behavior of para, meta and ortho chloro substituted copolymers, the greater or faster weight loss on DTA curve was observed for ortho substituted chloro molecule at the same temperature and heating rate. It is due to greater steric hindrance imposed by ortho position resulting in poor stacking of molecule.

Figure 1 : TG and DTA curve for copolymers at 5K/min, 10K/min and 20K/min
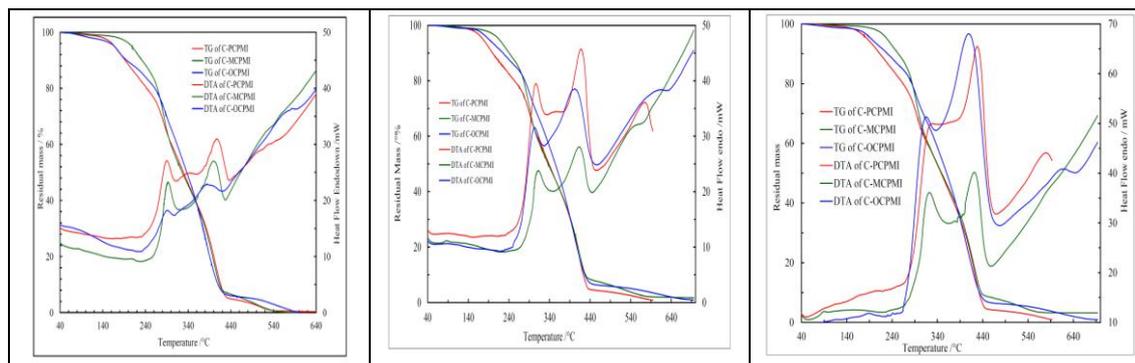
Figure 1: TGA and DTA curve for Homopolymers at 5K/min, 10K/min and 20K/min

Conclusion

Free radical polymerization method is used for the synthesis of halogen substituted homopolymer and copolymers using BPO as free radical initiator and DMF as a solvent at $70°C$ for 48 hours. As such moieties are used in development and synthesis of novel highly efficient thermal responsive materials for a smart material production therefore the above work applicability increases and in high demand as it supports heat contact resistance, the heat losses from the free sample surfaces. The GPC results shows the copolymer, C-PCPMI has the highest molecular weight of 9510 among copolymers. The polymers synthesized using *para* substituted phenyl maleimide are comparatively more stable. Among copolymers para chloro substituted copolymer, C-PCPMI is more stable at higher temperature as the percentage weight loss is less at higher temperatures and its activation energy is more negative than meta and ortho chloro substituted ccopolymers and is in the range of -6171 to -12773 Jmol $^{-1}$. The activation energy require for degradation of C-PCPMI is the highest among all the synthesized copolymers. The GPC results shows the homopolymer, C-PCPMI has the highest molecular weight (9510) among the all. Among the three copolymers viz. H-PCPMI, H-MCPMI & H-OCPMI, para chloro substituted N-(phenyl) maleimide was found thermally more stable due to good stacking of molecules and less steric hindrance at para position assuring the more intermolecular hydrogen bonding in the H-PCPMI homopolymer chains. Furthermore, the activation energy of para chloro substituted N-(phenyl) maleimide polymer is highest among the all three polymers, which clearly indicates that the stability of this polymer is more compared to ortho or meta substituted polymers. Thus due to its thermal resistive properties, it benefits modern tool development in larger aspects.

Acknowledgements

REFERENCES

1. Al‑Sagheer FA, Ali AA, Reyad MA, Elsabee MZ. Preparation and polymerization of vinyl monomers containing a heterocyclic pendant group. Polymer international. 1997 Sep 1;44(1):88-94.

2. Erceg A, Vukovic R, Bogdanic G, Pilizota V, Fles D. synthesis and polymerization of n-acryl-dicyclohexylurea and n-methacryl-dicyclohexylurea and copolymerization with α-methylstyrene. Journal of Macromolecular Science, Part A Pure and Applied Chemistry, A37 11 (2000) 1363 -1375.

3. Sabaa, M.S.; Mikhael, M.G.; Elsabeé, M.Z. Effect of ZnCl2 on the copolymerization of acrylonitrile with N-phenylmaleimide. Polym. Bull. 1987, 18, 9

4. Elsabee MZ, Sabaa MW, Mokhtar S. Copolymerization of N-arylmaleimides with vinyl acetate. Polymer journal. 1983 Jun;15(6):429.

5. Patel CB, Malek NI, Oswal SL. Synthesis and radical polymerization of N‑[4‑N′‑(phenylamino‑carbonyl) phenyl] maleimide and its copolymerization with methyl methacrylate. Journal of Macromolecular Science, Part A. 2006 Feb 1;43(2):289-303.

6. Elsabee MZ, Sabaa MW, Mokhtar S. Copolymerization of N-Arylmaleimide with Vinyl Acetate—Effect of the Total Monomer Concentration on the Reactivity Ratios of the Copolymerization. Polymer journal. 1985 Jun;17(6):737.

7. Mohamed AA, Jebrael FH, Elsabee MZ. Copolymerization of styrene with N-arylmaleimides. Macromolecules. 1986 Jan;19(1):32-7.

8. Al-Awadi NA, Elsabee MZ. Pyrolysis of some acrylamido derivatives bearing a heterocyclic group. Polymer degradation and stability. 1998 Apr 1;60(1):71-8.

9. Oswal SL, Sarkar NS, Bhandari VK, Oza HB, Patel CB. Synthesis, characterization and thermal properties of copoly (maleimide-methylmethacrylate), terpoly (maleimide-methylmethacrylate-acrylic acid), and terpoly (maleimide-methylmethacrylate-methylacrylic acid). Iranian Polymer Journal,13 4 (2004): 297-305.

10. Naguib HF, Saad GR, Elsabeé MZ. Copolymerization of bromophenylmaleimide with ethyl or butyl methacrylate. Polymer international. 2003 Jul 1;52(7):1217-1221.

11. Scroog, CE. Polyimides. J. Polym. Sci. 1976; 2(1:, 161–208.

12. Hiran BL, Paliwal SN. Synthesis and Free Radical Copolymerization of N-[4-N-(Benzyl aminocarbonyl) phenyl] Maleimide with Methyl Methacrylate. Malaysian Polymer Journal. 2008;3(2):1-2.

13. Hiran BL, Chadhary J, Paliwal SN, Meena S, Chaudhary PR. Synthesis and characterization of some new thermal stable polymers-polymerization of N-[4-N-(benzylamino-carbonyl) phenyl] maleimide. Journal of Chemistry. 2007;4(2):222-31.

14. Sabaa MW, Mikhael MG, Yassin AA, Elsabee MZ. Effect of ZnCl 2 on the copolymerization of acrylonitrile with N-2-chlorophenylmaleimide. Polymer Bulletin. 1987 Jul 1;18(1):9-12.

15. El Sabee MZ, Mokhtar S. Polymerization of n-aryl maleimides. European Polymer Journal. 1983 Jan 1;19(5):451-6.

16. Salman IA, Al-Sagheer FA, Elsabee MZ. Copolymerization of maleimide monomers containing heterocyclic groups. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry. 1997 Jul 1;34(7):1207-20.

17. Yılmaz Baran N, Demir HÖ, Kostekçi S, Sacak M. Poly‑2‑[(4‑methylbenzylidene) amino] phenol: Investigation of thermal degradation and antimicrobial properties. Journal of Applied Polymer Science. 2015 Apr 10;132(14).

18. Konsulov V, Grozeva Z, Tacheva J, Tachev K. Copolymerization of N-(Dichlorophenyl) maleimides with Methyl Methacrylate. Journal of the University of Chemical Technology and Metallurgy. 2008;43(2):205-12.

19. Borbely J, Kelen T, Konsulov VB, Grozeva Z. Synthesis and characterization of poly-(methyl methacrylate-co-N-4-bromophenyl maleimide). Polymer bulletin. 1991 Aug 1;26(3):253.

20. Yukawa S, Omayu A, Matsumoto A. Thermally stable fluorescent maleimide/isobutene alternating copolymers containing pyrenyl and alkynylpyrenyl moieties in the side chain. Macromolecular Chemistry and Physics. 2009 Nov 6;210(21):1776-84.

21.   Omayu A, Matsumoto A. Thermal Properties of N-Phenylmaleimide-Isobutene Alternating Copolymers Containing Polar Groups to Form Intermolecular and Intramolecular Hydrogen Bonding. Polymer journal. 2008 Aug;40(8):736

22.   Shi L, Wan D, Huang J. Aggregation of 2-ethylacrylic acid in dioxane and its effect on the radical copolymerization of maleimide with 2-ethylacrylic acid. Macromolecular Chemistry and Physics. 2000 Jun 1;201(9):941-948.

23.   L. Shi, D. Wan and J. Huang, Macromolecular Chemistry and Physics, 201 (2000) 941–948.

24.   Sortino M, Cechinel Filho V, Corrêa R, Zacchino S. N-Phenyl and N-phenylalkyl-maleimides acting against Candida spp.: Time-to-kill, stability, interaction with maleamic acids. Bioorganic & medicinal chemistry. 2008 Jan 1;16(1):560-568.

25.   Shukla S, Mishra AP. Non-isothermal degradation-based solid state kinetics study of copper (II) Schiff base complex, at different heating rates. Journal of thermal analysis and calorimetry. 2011 May 11;107(1):111-117.

26.   Nie S, Zhou C, Peng C, Liu L, Zhang C, Dong X, Wang DY. Thermal oxidative degradation kinetics of novel intumescent flame-retardant polypropylene composites. Journal of Thermal Analysis and Calorimetry. 2015 May 1;120(2):1183-91.

27.   Chauhan NP. Structural and thermal characterization of macro-branched functional terpolymer containing 8-hydroxyquinoline moieties with enhancing biocidal properties. Journal of Industrial and Engineering Chemistry. 2013 May 25;19(3):1014-23.

28.   Sang TO, Chang SH, Won JC. Synthesis and antimicrobial activity of polymer containing chloro substituted diphenyl ether. Pollimo. 1994;18:309-15.

29.   Chauhan NP. Terpolymerization of p-acetylpyridine oxime, p-methylacetophenone and formaldehyde, and its thermal studies. Journal of thermal analysis and calorimetry. 2012 Dec 1;110(3):1377-88.

30.   Bauer AW, Kirby WM, Sherris JC, Turck M. Antibiotic susceptibility testing by a standardized single disk method. American journal of clinical pathology. 1966 Apr;45(4):493-496.

31.   Brahmeshwari G, Surekha M, Saini K. antibacterial activity of naphthothiazoles derived from lawsone. Journal of Pharmaceutical and Biomedical Sciences (JPBMS). 2012;14(14).

32.   M.E. Browna, M. Maciejewskib S. Vyazovkinc, R. Nomend, J.Sempered, A. Burnhame, J. Opfermannf, R. Streyg, H.L. Andersong, A. Kemmlerg, R. Keuleersh, J. Janssensh, H.O. Desseynh, C.R. Lii, T.B. Tangi, B. Roduitj, J. Malekk and T. Mitsuhashi, Thermochimica Acta, 355 (2000) 125-143.

33.   Kissinger HE. Reaction kinetics in differential thermal analysis. Analytical chemistry. 1957 Nov 1;29(11):1702-6.