PART-A

THERMAL ANALYSIS

4.1.[A]. INTRODUCTION:

Thermal analysis is a term used to cover a group of techniques in which a physical property of a substance and/or its reaction product(s) is measured as a function of temperature, while the material is subjected to a controlled temperature programmed [1]. Thermal analysis includes a group of methods by which the physical and chemical properties of a substance, a mixture and/or reaction mixtures are determined as a function of temperature or time, while the sample is subjected to a controlled heating program. The program may involve heating or cooling (dynamic), or holding the temperature constant (isothermal), or any combination of these [2,3]. A group of techniques are concerned with the detection, estimation and analysis of volatile materials released as a result of chemical reactions or desorption on heating the sample. Thermal analysis methods are rapid, sensitive and precise. The instrument is sophisticated and versatile, yet reliable and easy to use. The basic techniques of thermal analysis involve the measurement of specific physical properties as a function of temperature.

There are several thermal analysis techniques namely: Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermo-mechanical Analysis (TMA), whereas other techniques are: Melt Elasticity Index, Dielectric Analysis, Thermally Stimulated Current Analysis, Free Volume Microprobe, Differential Photo Calorimetry and Thermal Conductivity Analysis. The chief methods used in present investigations are TGA and DTA.

In Thermo Gravimetric Analysis, a small but accurately known sample mass (2 – 50 milligram) is heated in a crucible on an analytical balance with controlled heating. In general an inert gas atmosphere (e.g. N₂) can be chosen. Any change in weight of the sample is recorded versus temperature during controlled heating. This may be related to reaction(s) taking place in a sample, such as oxidation, reduction, dehydration or dehydroxylation etc. The technique is suited to many solid materials, although limitations may arise with respect to possible reactions with the crucible material, or corrosive gases emitted by the sample. TGA is commonly employed in
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research and testing to determine characteristics of materials such as polymers, to determine decomposition temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues [4-9]. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

There are basically two types of TGA methods: Isothermal and non-isothermal or dynamic. In isothermal method the weight loss is recorded with time at a fixed temperature, while in non-isothermal or dynamic method the sample temperature is increased at uniform heating rate and weight loss is recorded as a function of temperature. The equipment used in TGA is thermo-balance, which permits the continuous weighing of a sample as a function of temperature or time. Usually the most common mode of operation in determining the thermal stability of polymer is heating the sample in a furnace at the heating rate from $50^\circ C$ to $100^\circ C$ per minutes.

Differential Thermal Analysis (DTA) : In DTA, the material under study and an inert reference are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting, sublimation and decomposition. The area under a DTA peak can be due to the enthalpy change and it is not affected by the heat capacity of the sample. Various application of DTA is in pharmaceutical industry, food industry, cement chemistry, mineralogical research and environmental studies as well as to study archaeological materials [10-14].

In the study of thermosetting polymers, copolymers, blends and resins. Number of researchers have reported the application of TGA and DTA.

Mehmet and co-workers [15] investigated the effect of acrylonitrile (AN) on thermal stability of poly-2,3-(mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate (poly-MCHEMA) by TGA. The thermal data shows that initial decomposition temperature (IDT) increases with the introduction of a unit. The IDT of poly-MCHEMA and poly-AN are at $235^\circ C$ and $300^\circ C$ respectively. The IDT of poly (MCHEMA-co-66%AN) is $285^\circ C$ and that of poly(MCHEMA-co-23% AN) is
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270°C. Erol Ibrahim and Soykan [16] prepared aryl-oxycarbonyl methyl methacrylate monomers and its polymers. The glass transition temperature and thermal decomposition temperature of the polymers were investigated by DSC and TGA thermobalance, respectively. They determined the activation energy of these polymers by using multiple heating rate kinetics (MHRK) [17] method. Marin and co-workers [18] shows that ethylene vinylacetate (EVA) polymers are thermally degradable at high temperature with acetic acid release at ~ 620°C. This release can be studied using thermal analysis. They have calculated the activation energy of the overall deacetylation process of four different EVA samples.

S.Liang and co-workers [19] synthesized homo and copolymers (PAG) using alpha methyl styrene (AMS) and Glycidyl methacrylate (GMA) which shows that the thermal stability of copolymers decreases with increases AMS content. Generally, side groups on the main chain of any polymer are important to understand how decomposition takes place in its thermal degradation. Poly(methacrylic esters) show different behavior in thermal degradation depending on the alkyl side chain of the ester. Some poly(methacrylates) degrade relatively easily to the monomer on heating [20, 21]. In contrast, some undergo ester decomposition without giving the corresponding monomer [22, 23]. Satapathy and Banthia [24] synthesized homo and copolymer of 4-nonylphenyl methacrylate (NPMA) and styrene and studied TGA of the polymer in nitrogen atmosphere. The TGA curve reveals that copolymers possess very good thermal stability in comparison to alkyl acrylates due to presence of pendant nonylphenyl group. Subramanian and co-workers [25] synthesized 4-acryloyloxy phenyl-4’-methoxystyrylketone (APMSK) and its polymer, where APMSK was copolymerized with glycidyl methacrylate (GMA). The copolymers were investigated by TGA in air. The TGA trace of poly(APMSK) is that of a thermo-oxidative decomposing polymer with a weight loss of 46% in the first stage (i.e 281-459°C) and weight loss of 53% in the second stage (470-675°C). Poly(GMA) is a single stage decomposing polymer (i.e. 200-416°C) with weight loss of about 96%. Patel and co-workers [26] prepared copolymers of 2,4-dichlorophenyl methacrylate with styrene in different feed ratios in DMF solvent using AIBN as an initiator. The copolymers were characterized by TGA and DSC at a heating rate of 10°C/min in a nitrogen atmosphere. Fuente and coworkers [27] synthesized copolymers of Acrylic acid with Styrene and copolymers of Butyl acrylate with Styrene. They determined
the thermal characterization of these copolymers by TGA and DSC and found that the thermal stability of poly(Acrylic acid-co-Styrene) is higher. Erol and co-workers [28] prepared copolymers using coumarine and sulfonamide which gives good thermal stability.

Ghaitan and co-workers [29] investigated hydrolysis and thermal decomposition of polyacrylamide/tert-butyl acrylate (PAtBA) copolymer. $^{13}$C-NMR spectroscopy was used to monitor the structural changes of the PAtBA. Activation energy for the amide groups of the PAtBA was found to be 86.4 KJ.mol$^{-1}$. Gas chromatography was used to identify gas products of the thermal decomposition of PAtBA. Kaith[30] analyzed binary vinyl mixture such as methyl methacrylate(MMA) + vinyl acetate(VA), MMA + acrylamide and MMA + styrene have been graft copolymerized onto flax fiber. Graft copolymers thus prepared were characterized with TGA and DTA. Jalili and co-workers [31] prepared a copolymer of styrene and methyl methacrylate in presence of n-pentane and studied the thermal behavior. Combustion and thermal behavior of polyurethane acrylate modified with phosphorous monomer were studied by Chen and co-workers [32]. There are several reports on thermal analysis of acrylate copolymers by Patel et al. [33-35].

Meysam and co-workers [36] synthesized 4- chloromethyl styrene(CMS) with different monomers by free radical polymerization method. The glass transition temperature of all copolymers was determined by dynamic mechanical thermal analysis showed that the chemical modification of 4-CMS copolymers with phthalimide substituent leads to an increase in the rigidity. Hossein and co-workers [37] synthesized and thermal behavior of methacrylic and acrylic copolymers of glycidyl methacrylate without and with indole groups are reported. They reported the T(\text{g}) value of methacrylate copolymers containing indole groups was found to be decreased with incorporation of indole goup in polymer structure, while it increased in indole-incorporated acrylate copolymer. P. S. Vijayanand and co-workers [38] prepared novel methacrylic monomer, 4-nitro-3-methylphenyl methacrylate (NMPM) was synthesized by reacting 4-nitro-3-methylphenol dissolved in MEK with methacryloyl chloride in the presence of triethylamine as a catalyst. The homopolymer and copolymer was characterized by spectroscopic technique and thermogravimetric method. The thermogravimetric analysis of the polymers performed in air showed that the thermal stability of the copolymer increase with
NMPM content increase. Bozkurt and Karadedeli [39] prepared copolymers of 4(5)-vinylimidazole and ethyleneglycol methacrylate phosphate. Thermal properties of the dry copolymers were investigated via thermogravimetric analysis (TGA).

Dharmalingam and co-workers [40] have synthesized copolymers of styrene with methyl methacrylate by Ziegler-Natta polymerization and carried out thermal analysis. From TGA curve, the decomposition of both the homo polymers occurred in single stage, while that of the copolymer occurred in two stages. The first stage was observed from 363 to 414 °C. The second stage of degradation was found from 419 to 474 °C. Jayakumar and co-workers [41] synthesized 2-(N-phthalimido) ethyl methacrylate monomer and copolymerized the monomer with MMA. These copolymers were characterized by thermal analyses like DSC, DTA, and TGA. The TGA curves for poly(NPEMA), poly(MMA) showed single stage decomposition, whereas poly(NPEMA-co-MMA) decomposes in two different stages. The initial decomposition temperature for homo polymer poly(NPEMA) was 188 °C and for copolymer it was 213 °C, whereas IDT for poly(MMA) was 264 °C. Increase in MMA contents increases the stability of the polymer. Ceylan and co-workers [42] prepared the copolymers of (2-phenyl-1,3-dioxolane-4-yl) methyl methacrylate with 2-hydroxyethyl methacrylate and investigated kinetics study of thermal decomposition for these copolymers by TGA and DTA. They determined activation energy of these copolymers and they were in the range of 65-95 KJ. mol⁻¹. Senthilkumar and others [43,44] prepared new methacrylate monomer and copolymerized it with different feed ratios of styrene/methyl acrylate/N-vinyl pyrrolidone. The copolymers were characterized by TGA in air. E. Kaya [45] reported thermal study of copolymers, prepared using 4-methoxybenzylmethacrylate (MBMA) and Isobornyl methacrylate (IBMA) which indicates that the thermal stability of copolymer increases with rising IBMA content.

The present part of this chapter describes thermal characterization of homo and copolymers of VMA by Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA).
4.2. [A]. EXPERIMENTAL

a. Characterization

TA instrument (U.S.A.) – 2960 thermogravimetric analyzer and differential thermal analyzer was used in the present study to record the thermograms of polymer samples. About 5 to 10 mg of the polymer sample was weighed in the boat of a thermo-balance and was subjected to heating of 10°C/min heating rate in nitrogen atmosphere. The continuous loss in weight of a sample as a function of temperature gave a TG thermogram, whereas in DTA the difference in temperature between a sample and a reference material against temperature was measured.

b. Calculations from TGA and DTA

Several methods [46-48] have been proposed for estimating kinetic parameters from TGA curve, depending upon the nature of experimentation. Among these methods, the methods proposed by Broido [49] and Doyle [50] have been used in the present work for the analysis of TGA data whereas the expression reported by Reich [51] has been used to estimate the kinetic parameters from single DTA trace.

i. Broido’s method for the analysis of TGA data

When a polymeric substance is heated beyond some limit, it undergoes degradation. It is assumed that degradation products are volatile. The fraction (Y) of the number of initial molecules not yet decomposed is defined by the following relation:

\[ Y = \frac{N}{N_0} = \frac{(W_i - W_\alpha)}{(W_o - W_\alpha)} \]  

---------(4.1)

Where,

- \( W_o \) = initial weight of the sample
- \( W_i \) = weight of the sample at temperature T °C
- \( W_\alpha \) = weight of the residue at completion of the reaction

If the degradation is carried out isothermally, the rate of reaction is given by

\[ \frac{dY}{dt} = - K Y^n \]  

---------(4.2)

Where, \( n \) = order of the reaction

The rate constant changes with absolute temperature according to the Arrhenius equation
\[ K = Ae^{-E/RT} \]  

\[ \text{From Eq. (4.2) and (4.3), it follows} \]

\[ \frac{dY}{Y^n} = -K \, dt \]  

\[ \frac{dY}{dt} = -Ae^{-E/RT}Y^n \]  

Instead of operating the reaction isothermally, the reaction is operated at increasing temperature and if temperature (T) is a linear function of a time (t) and the rate of heating is \( \beta \), then

\[ T = T_0 + \beta t \]  

\[ dT = \beta \, dt \]  

From Eq. (4.5) and (4.7), it follows

\[ \frac{dY}{Y^n} = -\left( \frac{A}{\beta} \right) e^{-E/RT} \, dT \]  

The thermogravimetric curve of such a relation represents this rate equation integrated from a temperature \( T_0 \) at which \( Y = 1 \). Thus,

\[ \int_{1}^{Y} \frac{dY}{Y^n} = \frac{A}{\beta} \int_{T_0}^{T} e^{-E/RT} \, dT \]  

A large number of degradation processes are known to be first order reaction. As \( n = 1 \), the integration of L.H.S. part is simple,

\[ \int_{1}^{Y} \frac{dY}{Y^n} = \frac{1}{Y} = -\ln \frac{1}{Y} \]  

Conversely, the integration of the R.H.S. part of equation 4.7 is not simple. Vallet [52] has reported the values of integration of the terms like that involved in Eq. (4.9). From these data, the value of integration of the L.H.S. term was obtained by Broido.

Krevelen and co-workers [53] revealed that the entire measurable reaction usually occur within 10% of the temperature of maximum reaction velocity (\( T_{\text{max}} \)). They applied a certain approximation and obtained the following relation.
\[ \ln \ln \left( \frac{1}{Y} \right) = \left( \frac{E}{R} \cdot T_m^2 \right) \ln T + \text{Constant} \quad \text{---------(4.11)} \]

According to Eq. (4.11) a plot of \( \ln \ln \left( \frac{1}{Y} \right) \) Vs \( \ln T \) yields a straight line whose slope is related to the energy of activation. Horowitz and Metzger [54] introduced two alternate approximations and developed relation (4.12) and (4.13).

\[ \ln \ln \left( \frac{1}{Y} \right) = \left( \frac{E}{R} \cdot T_m^2 \right) T + \text{Constant} \quad \text{---------(4.12)} \]

\[ \ln \ln \left( \frac{1}{Y} \right) = -\left( \frac{E}{R} \right) \left( \frac{1}{T} \right) + \text{Constant} \quad \text{---------(4.13)} \]

The expression (4.13), which found to be more accurate than Eq. (4.11) and (4.12), was employed in the present work to calculate the activation energy \( (E_a) \) of thermal degradation of the polymers from TG thermograms.

**ii. Doyle’s method for calculation of IPDT from TGA**

Two general types of procedural decomposition temperature have so far been defined for thermogravimetric analysis in an inert atmosphere.

1. Differential procedural decomposition temperature (DPDT) was devised as a means of defining the locations of knees in normalized data records. But, DPDT is neither consistently available nor unique and is not considered further here.

2. Integral procedural decomposition temperature (IPDT) was devised as a means of summing up the whole shape of the normalized data curve. As such, it is consistently available from the cumulative data record of thermogravimetric analysis in an inert atmosphere.

The IPDT values are determined from a weight loss curve as follows. The curve, as shown in Figure 4.1, is divided into small squares. The area under the curve is integrated by weighing a paper cutout of the curve on an analytical balance. The weight of crosshatched region in Figure 4.1 divided by the weight of the total rectangular plotting area is the total curve area \( A^* \), normalized with respect to both residual weight and temperature.

The quantity \( A^* \) is converted to a temperature \( T_{A^*} \), by

\[ T_{A^*} = 875 A^* + 25 \quad \text{---------(4.14)} \]

It is presumed that all materials volatilize below 900°C and do so at a single temperature. Thus, \( T_{A^*} \) represents a characteristic end-of-volatilization temperature. However, it does serve as a measure of refractoriness, but is not very satisfactory.
To put all materials on an equal basis with respect to experimental temperature range, as in $A^*$, but also with respect to their individual refractory contents, a second curve area, $K^*$, was defined as illustrated by the double crosshatched region given in Figure 4.1. In value, the lesser area, $K^*$, is the ratio between the doubly crosshatched area and the rectangular area bounded by the characteristic end-of volatilization temperature, $T_A^*$ and the residual weight fraction at the fixed end-of-test temperature of 900°C.

![Figure 4.1](image)

Doyle showed that the product $A^*K^*$ represented a comprehensive index of intrinsic thermal stability for 54 polymers of widely different basis types. It was also shown that by substituting $A^*K^*$ for $A^*$ in equation (4.14) the IPDT obtained had a practical meaning as a half-volatilization temperature.

iii. Reich’s method for the analysis of DTA data

The estimation of kinetic parameters ($E^*$ and $n$ from thermal decomposition) according to Borchardt & Daniels [55] and Wendlandt [56] by means of DTA technique involved trial and error procedures.

Assuming the Arrhenius equation to be valid for pyrolysis, Reich utilized following expressions to estimate kinetic data from DTA traces.
\[
\frac{E^*}{R} = \frac{S}{Wc \ln \left( \frac{W_o.c}{Wc} \right)}
\]  
----------(4.15)

Where, \(Wc = W - Wr, W = \) Weight or weight fraction of material remaining after pyrolysis, \(Wr = \) Weight or weight fraction of inactive material remaining after pyrolysis, \(S = \frac{dWc}{d(1/T)}, W_o.c = W_o - Wr, W_o = \) Weight of the material taken initially.

By assuming that the heat capacity terms are negligible in comparison with other terms such as particle size, effect of diluent, amount of sample etc. and that the cell constants for the sample and reference cells are almost equal, it has been shown that:

\[
-\frac{dWc}{dT} = W_o.c \left( \frac{\Delta T}{A} \right)
\]  
----------(4.16)

\[
Wc = W_o c (a/A)
\]  
----------(4.17)

Where, \[a = \int_{T_1}^{T} \Delta T dT - \int_{T_i}^{T} \Delta T dT \] and \[A = \int_{T_1}^{T} \Delta T dT\]  
----------(4.18)

Where, \(\Delta T\) is the height of the DTA trace.

By inserting Eqs. (4.16) and (4.17) in Eq. (4.15) Reich obtained the following expression,

\[
\frac{E^*}{R} = \frac{T^2 \Delta T}{a \ln(A/a)} \quad \text{and} \quad F(T) = \frac{a_1}{a_2} \times \frac{\log(A/a_1)}{\log(A/a_2)}
\]  
----------(4.19)

Where, \(a_1\) and \(a_2\) are the values of “a” at \(T_1\) and \(T_2\) respectively. e.g. (4.19) and have been shown to be the most reliable for obtaining the values of \(E^*\) and \(n\).

The kinetic parameters estimated by means of single DTA trace using the theories [57] represented overall values because it was difficult to as certain whether or not any change in mechanism occurred during polymer pyrolysis.

Reich has reported an expression which is relatively simple and with the help of that, kinetic parameters could be estimated from a single DTA trace. The expression has been shown to be independent of the type of the material undergoing the pyrolysis. Reich obtained the following expression.
\[ \log \Delta T = \log C + n \log a - \frac{E^*}{4.6T} \]  \hspace{1cm} \text{(4.20)}

For, any two temperatures prior to and after the DTA peak, \( T_1 \) and \( T_2 \), respectively, which possess the same value of \( T \), Reich obtained the following expression,

\[ n \Delta \ln a = - \left( \frac{E^*}{R} \right) \times \Delta \left( \frac{1}{T} \right) \]  \hspace{1cm} \text{(4.21)}

Where,

\[ \Delta \ln a = \ln \left( \frac{a_1}{a_2} \right) \text{ and } \Delta \left( \frac{1}{T} \right) = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]  \hspace{1cm} \text{(4.22)}

By substituting Eq. (4.21) in Eq. (4.22), Reich obtained finally,

\[ \log \Delta T \log C - \frac{E^* V}{4.6} \]  \hspace{1cm} \text{(4.23)}

Where,

\[ V = \frac{1}{T} \Delta \left( \frac{1}{T} \right) \log a \]  \hspace{1cm} \text{(4.24)}

\[ a = A - \int_{T_o}^{T} \Delta T \, dT \]  \hspace{1cm} \text{(4.25)}

\( \Delta T \) = The height of the peak from its base line at temperature \( T_1 \) and \( T_2 \). \( T_o \) = The starting temperature of the reaction. \( A \) = Represents the total area under the DTA trace, \( C \) = Constant under the given experimental conditions.

The activation energy, \( E^* \) is calculated from the slope of the plot of \( \log \Delta T \) vs \( V \). The order of reaction can be obtained from the slope of the plot of \( \ln a \) vs \( \Delta \left( \frac{1}{T} \right) \) by substituting the value of energy.
Figure 4.2: TG thermograms of poly(VMA), poly(MA) and poly(VMA-co-MA)
Table 4.1: TGA data for homo and copolymers of VMA with MA:

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>$T_{\text{max}}^a$ (°C)</th>
<th>$T_{50}^b$ (°C)</th>
<th>IPDT$^c$ (°C)</th>
<th>Activation Energy$^d$ ($E_a$) (KJ.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>190-288 288-410</td>
<td>330</td>
<td>340</td>
<td>306</td>
<td>15</td>
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<tr>
<td>2</td>
<td>200</td>
<td>175-295 295-405</td>
<td>310</td>
<td>315</td>
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<td>180-250 250-375</td>
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<td>310</td>
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<td>155-290 290-390</td>
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<td>345</td>
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$^a$ Temperature for maximum rate of decomposition, $^b$ Temperature for 50% weight loss,

$^c$ Integral procedural decomposition temperature by Doyle’s method, $^d$ By Broido's method
Figure 4.3: TG thermograms of poly(VMA), poly(MCMA) and poly(VMA-co-MCMA)
Table 4.2: TGA data for homo and copolymers of VMA with MCMA:

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>$T_{max}^a$ (°C)</th>
<th>$T_{50}^b$ (°C)</th>
<th>IPDT$^c$ (°C)</th>
<th>Activation Energy$^d$ ($E_a$) (K.J.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 5 25 85 93</td>
<td>190-288 288-410</td>
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<td>340</td>
<td>306</td>
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<td>260</td>
<td>270</td>
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$^a$ Temperature for maximum rate of decomposition, $^b$ Temperature for 50% weight loss, $^c$ Integral procedural decomposition temperature by Doyle’s method, $^d$ By Broido's method
Figure 4.4: TG thermograms of poly(VMA), poly(4-CMA) and poly(VMA-co-4-CMA)
**Table 4.3:** TGA data for homo and copolymers of VMA with 4CMA:

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>( T_{\text{max}}^a ) (°C)</th>
<th>( T_{50}^b ) (°C)</th>
<th>IPDT(^c) (°C)</th>
<th>Activation Energy(^d) (( E_a )) (K.J.mole(^{-1}))</th>
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</thead>
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<tr>
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<td>1 5 25 85 93 -</td>
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<td>340</td>
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<td>395</td>
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<td>170-320 320-425</td>
<td>400</td>
<td>340</td>
<td>273</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^a\) Temperature for maximum rate of decomposition, \(^b\) Temperature for 50% weight loss,
\(^c\) Integral procedural decomposition temperature by Doyle’s method, \(^d\) By Broido's method
Figure 4.5: TG thermograms of poly(VMA), poly(PCPMA) and poly(VMA-co-PCPMA)
Table 4.4: TGA data for homo and copolymers of VMA with PCPMA:

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<th>( T_{50}^b ) (°C)</th>
<th>IPDT(^c) (°C)</th>
<th>Activation Energy(^d) (E(_a)) (K.J.mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 2 5 25 85 93 --</td>
<td>190-288</td>
<td>330</td>
<td>340</td>
<td>306</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
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<td>200-300</td>
<td>340</td>
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<td>316</td>
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</tr>
<tr>
<td>22</td>
<td>2 8 23 85 92 --</td>
<td>180-320</td>
<td>340</td>
<td>340</td>
<td>311</td>
<td>42</td>
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<td>24</td>
<td>3 5 27 82 90 --</td>
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<td>360</td>
<td>360</td>
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<td>33</td>
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<tr>
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<td>5 9 26 95 --</td>
<td>225-390</td>
<td>360</td>
<td>355</td>
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</tr>
</tbody>
</table>

\(^a\) Temperature for maximum rate of decomposition, \(^b\) Temperature for 50% weight loss, \(^c\) Integral procedural decomposition temperature by Doyle’s method, \(^d\) By Broido's method
Figure 4.6: TG thermograms of poly(VMA), poly(GMA) and poly(VMA-co-GMA)
Table 4.5: TGA data for homo and copolymers of VMA with GMA:

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;50&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (°C)</th>
<th>IPDT&lt;sup&gt;c&lt;/sup&gt; (°C)</th>
<th>Activation Energy&lt;sup&gt;d&lt;/sup&gt; (E&lt;sub&gt;a&lt;/sub&gt;) (K.J.mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>190-288 288-410</td>
<td>330</td>
<td>340</td>
<td>306</td>
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<tr>
<td>28</td>
<td>6</td>
<td>175-420</td>
<td>380</td>
<td>370</td>
<td>291</td>
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<tr>
<td>30</td>
<td>5</td>
<td>190-430</td>
<td>390</td>
<td>385</td>
<td>301</td>
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</tr>
<tr>
<td>31</td>
<td>9</td>
<td>170-420</td>
<td>380</td>
<td>370</td>
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<td>31</td>
</tr>
</tbody>
</table>

<sup>a</sup> Temperature for maximum rate of decomposition, <sup>b</sup> Temperature for 50% weight loss,  
<sup>c</sup> Integral procedural decomposition temperature by Doyle’s method,  
<sup>d</sup> By Broido’s method
Figure 4.7: TG thermograms of poly(VMA), poly(8-QMA) and poly(VMA-co-8-QMA)
Table 4.6: TGA data for homo and copolymers of VMA with 8-QMA:

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>$T_{max}^a$ (°C)</th>
<th>$T_{50}^b$ (°C)</th>
<th>IPDT$^c$ (°C)</th>
<th>Activation Energy$^d$ ($E_a$) (K.J.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 5 25 93 -</td>
<td>190-288 288-410</td>
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<td>340</td>
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<td>160-430</td>
<td>330</td>
<td>340</td>
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<td>34</td>
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<td>37</td>
<td>11 60 85 90 93</td>
<td>150-420</td>
<td>400</td>
<td>220</td>
<td>290</td>
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</table>

$^a$ Temperature for maximum rate of decomposition, $^b$ Temperature for 50% weight loss,

$^c$ Integral procedural decomposition temperature by Doyle’s method, $^d$ By Broido's method
Figure 4.8: DTA traces for poly(VMA), poly(4-CMA) and poly(VMA-co-4-CMA)
### Table 4.7: DTA data for homo- and copolymers of VMA with MA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>( T_1^a ) (°C)</th>
<th>( T_2^b ) (°C)</th>
<th>( T_b^c ) (°C)</th>
<th>Activation Energy(^d) (E(_A)) (KJ.mole(^{-1}))</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
<td>445</td>
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<td>2</td>
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<td>7</td>
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</tbody>
</table>

\(^a\) Starting Temperature of DTA trace, \(^b\) Ending Temperature of DTA trace

\(^c\) Peak maxima Temperature of DTA trace, \(^d\) Activation Energy by Reich's method

### Table 4.8: DTA data for homo- and copolymers of VMA with MCMA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>( T_1^a ) (°C)</th>
<th>( T_2^b ) (°C)</th>
<th>( T_b^c ) (°C)</th>
<th>Activation Energy(^d) (E(_A)) (KJ.mole(^{-1}))</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>445</td>
<td>400</td>
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</table>

\(^a\) Starting Temperature of DTA trace, \(^b\) Ending Temperature of DTA trace

\(^c\) Peak maxima Temperature of DTA trace, \(^d\) Activation Energy by Reich's method
Table 4.9: DTA data for homo- and copolymers of VMA with 4-CMA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$T_1$ a (°C)</th>
<th>$T_2$ b (°C)</th>
<th>$T_b$ c (°C)</th>
<th>Activation Energy d ($E_A$) (KJ.mole$^{-1}$)</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
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<td>385</td>
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</table>

a Starting Temperature of DTA trace, b Ending Temperature of DTA trace

c Peak maxima Temperature of DTA trace, d Activation Energy by Reich's method

Table 4.10: DTA data for homo- and copolymers of VMA with PCPMA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$T_1$ a (°C)</th>
<th>$T_2$ b (°C)</th>
<th>$T_b$ c (°C)</th>
<th>Activation Energy d ($E_A$) (KJ.mole$^{-1}$)</th>
<th>Reaction Order</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>365</td>
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<td>22</td>
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<td>376</td>
<td>500</td>
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</table>

a Starting Temperature of DTA trace, b Ending Temperature of DTA trace

c Peak maxima Temperature of DTA trace, d Activation Energy by Reich's method
Table 4.11: DTA data for homo- and copolymers of VMA with GMA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$T_1^a$ ($^\circ$C)</th>
<th>$T_2^b$ ($^\circ$C)</th>
<th>$T_b^c$ ($^\circ$C)</th>
<th>Activation Energy$^d$ ($E_A$) (KJ.mole$^{-1}$)</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
<td>445</td>
<td>400</td>
<td>17</td>
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</tr>
<tr>
<td>28</td>
<td>310</td>
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<tr>
<td>30</td>
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<tr>
<td>31</td>
<td>338</td>
<td>410</td>
<td>375</td>
<td>34</td>
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</tbody>
</table>

$^a$ Starting Temperature of DTA trace, $^b$ Ending Temperature of DTA trace

$^c$ Peak maxima Temperature of DTA trace, $^d$ Activation Energy by Reich's method

Table 4.12: DTA data for homo- and copolymers of VMA with 8-QMA.

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$T_1^a$ ($^\circ$C)</th>
<th>$T_2^b$ ($^\circ$C)</th>
<th>$T_b^c$ ($^\circ$C)</th>
<th>Activation Energy$^d$ ($E_A$) (KJ.mole$^{-1}$)</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
<td>445</td>
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</tr>
<tr>
<td>32</td>
<td>360</td>
<td>428</td>
<td>408</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>287</td>
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<td>315</td>
<td>26</td>
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</tr>
<tr>
<td>36</td>
<td>345</td>
<td>440</td>
<td>390</td>
<td>36</td>
<td>1</td>
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<tr>
<td>37</td>
<td>235</td>
<td>323</td>
<td>290</td>
<td>41</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ Starting Temperature of DTA trace, $^b$ Ending Temperature of DTA trace

$^c$ Peak maxima Temperature of DTA trace, $^d$ Activation Energy by Reich's method
4.3 [A] RESULTS AND DISCUSSION:

Tables 4.1 to 4.6 shows the characteristic temperature and kinetic parameters for the thermal degradation of the homopolymers of VMA, MCMA, 4-CMA, PCPMA, GMA and 8-QMA and the copolymers of VMA with other monomers, whereas Figures 4.2 to 4.7 shows the TGA thermograms of the homopolymers of VMA, MCMA, 4-CMA, PCPMA, GMA and 8-QMA as well as the copolymers of VMA with other monomers.

Poly(VMA) shows two step decomposition, the first step occurs between 190-288°C, while second decomposition takes place in the range of 288-410°C. All the copolymers of poly(VMA-co-MA), poly(VMA-co-4-CMA) and poly(VMA-co-PCPMA) undergo two step decomposition, the first step occurs between ranges from 150-325°C, while second step decomposition range from 250-460°C. Also the poly(MCMA) shows the two step decomposition range from 150-340°C. Poly(4-CMA) shows the two step decomposition ranges from 170-425°C. The first step for all the copolymers i.e. poly(VMA-co-MA), poly(VMA-co-4-CMA) and poly(VMA-co-PCPMA) containing different feed ratio ranges from 150-325°C whereas second step ranges from 300-430°C. Poly(MA) which undergoes single step decomposition ranges from 280-380°C, poly(PCPMA) which undergoes single step decomposition ranges from 225-405°C, while poly(GMA) undergoes single step decomposition ranges from 170-420°C. POLY(8-QMA) which undergoes single step decomposition ranges from 150-420°C and copolymers of poly(VMA-co-MCMA), poly(VMA-co-GMA), poly(VMA-co-8-QMA) which undergoes single step decomposition ranges from 150-440°C.

The values of $T_{\text{max}}$ and $T_{50}$ for poly(VMA) obtained from the thermogram are 330°C and 340°C respectively, whereas $T_{\text{max}}$ and $T_{50}$ for its copolymers with MA, MCMA, 4-CMA, PCPMA, GMA and 8-QMA are in the range of 300-360°C and 310-345°C, 280-310°C and 300-345°C, 390°C and 360-395°C, 340-360°C and 330-360°C, 380-390°C and 370-385°C and 330-390°C, 295-340°C respectively.

The values of integral procedural decomposition temperature (IPDT) calculated by Doyle’s method for poly(VMA) is 306°C and for its copolymers with MA, MCMA, 4-CMA, PCPMA, GMA and 8-QMA are in the range of 265-280°C, 260-290°C, 290-325°C, 295-320°C, 275-300°C and 230-285°C respectively. As the
VMA content increases in poly(VMA-co-4-CMA), poly(VMA-co-PCPMA), and poly(VMA-co-8-QMA) the IPDT also increases whereas in poly(VMA-co-MA), poly(VMA-co-MCMA) and poly(VMA-co-GMA) the IPDT decreases. The value of IPDT represents an overall thermal stability of the polymers.

Broido’s method was employed to obtained activation energies (Ea) which are 22-25, 28-34, 18-24, 33-42, 23-27 and 26-35 K.J.mole\(^{-1}\) for poly(VMA-co-MA), poly(VMA-co-MCMA), poly(VMA-co-4-CMA), poly(VMA-co-PCPMA), poly(VMA-co-GMA) and poly(VMA-co-8-QMA) respectively.

The characteristic temperature and kinetic parameters for the homo and copolymers have been obtained from DTA traces using Reich’s method. DTA traces for poly(VMA), poly(VMA-co-4-CMA) and poly(4-CMA) shown in figure 4.8. it is observed from the DTA traces of poly(VMA) that the starting temperature (T\(_1\)), ending temperature (T\(_2\)) and peak maxima temperature (T\(_b\)) are 365°C, 445°C and 400°C respectively. The activation energy is 17 K.J.mol\(^{-1}\) and order of reaction is 1 for poly(VMA). The traces clearly indicates that poly(VMA), poly(VMA-co-4-CMA) with different feed composition as well as poly(4-CMA) undergoes single step decomposition. In case of poly(VMA-co-4-CMA) first step decomposition ranges from 310°C to 395°C (for sample 14), 375°C to 455°C (for sample 16), 305°C to 390°C (for sample 18) respectively.

From Tables 4.7 to 4.12, it is observed that all the copolymers of VMA with MA, MCMA, 4-CMA, PCPMA, GMA and 8-QMA shows single step degradation from the DTA data. The activation energy for thermal degradation ranges from 20-28 K.J.mol\(^{-1}\) for poly(VMA-co-MA), 30-37 K.J.mol\(^{-1}\) for (VMA-co-MCMA), 22-30 K.J.mol\(^{-1}\) for poly(VMA-co-4-CMA), 38-44 K.J.mol\(^{-1}\) for poly(VMA-co-PCPMA), 24-34 K.J.mol\(^{-1}\) K.J.mol\(^{-1}\) for poly(VMA-co-GMA) and 23-41 K.J.mol\(^{-1}\) for poly(VMA-co-8-QMA) having different feed composition. The activation energy (Ea) obtained by Broidos method (TGA) and Reich’s method (DTA) compare well. Order of reaction for all the copolymers is one.
PART- B

MELT FLOW INDEX

4.1.[B]. INTRODUCTION

The melt flow rate is an indirect measure of molecular weight, high melt flow rate corresponding to low molecular weight. At the same time, the melt flow rate is a measure of the ability of the materials melt to flow under the pressure. The melt flow rate is inversely proportional to the viscosity of the melt at the condition of the test, though it should be born in mind that the viscosity for any such material depends on the applied force. Ratios between two melt flow rate values for one material at different gravimetric weights is often used as a measure for the broadness of the molecular weight distribution.

The Melt Flow Index (MFI) or Melt Tension Test (MTT) or Melt Index (MI) or Melt Flow Rate (MFR) value in the rheological is the most important. MFI measures the rate of extrusion of thermoplastic material through a specific length diameter under standard condition of temperature and pressure. Extensional properties play an important role in some processes such as melt spinning, blow molding and film blowing. MFI is a simple method for characterization of extensional properties. MFI value is key factor for the product designer who recommended the proper plastic material which is suitable for particular product. Melt Flow Index is an assessment of average molecular mass and is an inverse measure of the melt viscosity; in other words, the higher a MFI, the more polymer flows under test conditions. Knowing the MFI of a polymer is vital to anticipating and controlling its processing. Generally, higher MFI polymers are used in injection molding and lower MFI polymers are used with blow molding or extrusion processes.

MFI provides a means of measuring flow of melted materials which can be used to differentiate grades as with polyethylene, or determine the extent of degradation of the plastic as a result of molding. Degraded materials would generally flow more as a result of reduced molecular weight, and could exhibit reduced physical properties. Shenoy and co-workers[58-61] proposed the method to estimate the rheograms of a melt at temperatures relevant to its processing conditions with the use of a master curve, knowing the melt flow index and glass transition temperature of the
material. Rheograms curves of different grades at various temperatures have been generated and presented for low density polyethylene, high density polyethylene, polypropylene, poly-styrene and styrene-acrylonitrile copolymer. Jan and co-workers [62] studied the steady shear MFI and viscosity of a metallocene ethylene-octene copolymer at temperatures ranging from 110°C to 230°C.

Florentino and co-workers [63] carried out recyclization of high impact polystyrene in coextruded sheet and studied the effect of the molecular weight, grafting degree and morphology of the rubber phase on the MFI. Thompson and co-workers [64] performed a study to examine the process of micropelletization on four different polyethylenes with melt index values between 1 and 5 g/10 min. Gao J and co-workers [65] synthesized terpolymers of methyl methacrylate (MMA), N-phenylmaleimide (PMI) and styrene (STY) synthesized by emulsion copolymerization. The thermal stabilities of terpolymers were studied by thermogravimetric analysis. The terpolymer's apparent viscosity in melt decreases with increasing feed contents of PMI and STY. The terpolymer's flow index increases with the increasing feed content of PMI.

Munari and co-workers [66] synthesized and characterized linear and branched polymeric samples, and measured the intrinsic viscosity and the MFI over a range of shear rates at 250°C. Pfleger and co-workers [67] patented on copolymers of ethylene with acrylates or acrylic acid by copolymerization. The melt flow index of the products is from 0.1 to 30 g/10 min, determined according to ASTM-D 1238-65T at 190°C and with an applied weight of 2.16 kg. The density of the copolymers is from 0.924 to 0.936 g/cm³, measured according to DIN 53,479. Kuriakose et al. [68] studied on the melt flow behavior of thermoplastic elastomers from polypropylene - natural rubber blends. Flow that takes place in a MFI experiment has been simulated for two grades of high molecular weight polyethylene has been studied by Barrera and others [69]. Kuriakose and co-worker [70] studied on the melt flow behavior of thermoplastic elastomers from polypropylene - natural rubber blends.

The acrylic polymer may solely consist of a thermoplastic polymer. Preferably such a polymer is one in which a major proportion is derived from an alkyl ester of acrylic or methacrylic acid and a minor proportion of a copolymerizable unsaturated carboxylic acid. Preferably the acrylic polymer is a multi-phase polymer
comprising elastomeric phase and rigid phase. The thermal properties of such acrylic polymers are modified by introducing some functional groups. Keeping this in mind the present chapter describes the MFI of the prepared homo and copolymers of the VMA with selected vinyl monomers.

Keeping this in mind this part describes the MFI of the prepared homo and copolymers of the VMA with selected vinyl monomers.

4.2. [B]. EXPERIMENTAL

a. Characterization

NOVA Melt Flow Index Tester (Extrusion Plastometer) was employed to measure the MFI of the homo-polymers of MA, MCMA, 4-CMA, PCPMA, GMA and QMA and their copolymers with VMA material.

b. Test procedure

Approximately 7 grams of the material is loaded into the barrel of the melt flow apparatus, which has been heated to a specified temperature and specified load was applied (as per ASTM 1238) to a plunger and the molten material is forced through the die. A timed extrudate is collected and weighed. Melt Flow rate values are calculated in g/10 min as follows:

\[
MFI = \frac{Average\ weight\ of\ cut\ outs\ (extrudate)\ in\ gms \times 600}{Cut\ off\ time\ in\ second}
\]

4.3. [B]. RESULTS AND DISCUSSION

The value of Melt Flow Index for VMA is 1.0315 g/10 min. In case of poly(VMA-co-MA) the experimental data reveals that the values of MFI ranges from 0.9 to 1.3 g/10 min and for poly(MA) the value is 0.956 g/10 min. These copolymers have lowest thermal stability so the flow rate is higher compared to the other copolymers.

For poly(VMA-co-MCMA) the values of MFI are ranges from 0.99 to 1.4 g/10 min, while poly(MCMA) shows MFI of 1.35 g/10 min. The MFI data for poly(VMA-co-4-CMA) is between 1.0 to 1.8 g/10 min, whereas the 1.892 g/10 min
MFI value is observed for the poly(4-CMA). The result reveals that MFI changes randomly as the VMA content decrease in copolymer.

For poly(VMA-co-PCPMA) the values of the MFI ranges from 1.0 to 1.3 g/10 min and for poly(PCPMA) the value of the MFI is 1.36 g/10 min. The MFI values for poly(PAPM-co-GMA) are ranges from 1.0 to 1.8 g/10 min and for the poly(GMA) the MFI is 1.89 g/10 min. The result reveals that the value of MFI increases as the VMA content decrease in copolymer. While in case of poly(VMA-co-QMA) the values ranges between 1.0 to 1.9 g/10 min and for the poly(QMA) the value of MFI is 1.98 g/10 min. These polymers shows very low flow rate which may be attributed to their high molecular weight.

The overall examination of MFI of the copolymers system leads to the conclusion that in most of the samples the values of MFI increase with decrease in VMA content in the copolymer.
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