In Situ Emulsion Polymerization of Terpolymer / Montmorillonite Nanocomposites using redox initiation system

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Abstract: Intercalated modification of MMT clay was carried out using cetyl ammonium bromide (CAB) in the presence of hydrochloric acid to produce modified MMT clay. The modified clays were characterized by XRD and SEM. The data shows an increase in d-spacing of modified clay as a result of cationic exchange. Modified MMT clay was used in the preparation of terpolymer/clay nanocomposites using emulsion polymerization of glycidylmethacrylate (GMA), methylmethacrylate (MMA) and butyl acrylate (BuA) with different monomer composition ratios and constant weight percentage of the modified clay. The structure and properties of the prepared terpolymers and nanocomposites were done by XRD, TGA, and SEM. The results clarified that increasing the MMA monomer content had positive effect for improving the thermal stability of the prepared terpolymers. Moreover, nanocomposites samples were higher thermal stability than its mates prepared in absence of modified clay. It is also obvious that the XRD and SEM show that the clay is more homogenous and produce exfoliated nanocomposite at higher BuA monomer ratio.
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1. Introduction:

The chemical modification of the synthetic polymers provides the control of their properties and expands their applicability [1-2]. Recently, the co-or-ter-polymerization reactions, involving two or three monomers for the synthesis of synthetic polymers, have been commonly used. The properties of available polymers can also be changed by these reactions and novel polymers can be obtained by such polymerization reactions. Thus, several useful co-or-ter-polymers have been synthesized for different purposes [3-12]. Montmorillonite (MMT) clay is considered the common natural layered silicates and the suggested crystallographic structure of it based on pyrophyllite consisting of two fused tetrahedral silica sheets sandwiching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide [13]. Cation exchange procedures are used to modify clay surfaces often with quaternary ammonium surfactants to enhance clay miscibility in organic systems [14. Different clay dispersion states in such polymer systems are commonly observed: an intercalated morphology in which the clay retains its ordered structure with polymer embedded in the interlayers, and complete delamination of the clay platelets to form exfoliated nanocomposites, or combinations of the two. Enhanced physical, mechanical, thermal and optical properties have been attributed primarily to the exfoliated clay state [15,16].
Polymer–clay nanocomposites continue to attract significant research interest due to the potential of enhanced modulus, barrier resistance [17], gas permeability [18], thermal stability [19], flame retardancy [20], scratch/wear resistance [21] as well as optical [22], magnetic [23] and electrical properties [24] with incorporation of low clay concentrations. The improved material properties have been attributed to polymer–clay interactions based on inherent nanoscale dimensions of the clay platelets.

In this study, the structure and properties of terpolymer / clay nanocomposites prepared by in situ emulsion polymerization of glycidyl methacrylate (GMA), methyl methacrylate (MMA) and butyl acrylate (BuA) with different monomer composition ratios were investigated via FTIR, thermal analysis, XRD and SEM.

2. Experimental:

Materials:

Potassium persulphate (PPS), sodium bisulphite (SBS), sodium dodecyl sulphate (SDS), cetyl ammonium bromide (CAB), the monomers gLycidyl methacrylates (GMA), methyl methacrylate (MMA) and butyl acrylate (BuA) were provided by Merck, armstadt, Germany. The monomers were redistilled and stored at -20 ^{o}C. Polyoxyethelene monomethyl ether (MPOE) Union Carbide Company (USA) (M.wt. 5000 g/mol.), was dried in a vacuum oven at 70 ^{o}C for 24 hours prior to use.

Methods:

Intercalated Modification of Montmorillonite (MMT) Clay [25]

MMT (2.5g) was dispersed into 250 ml deionised water; the mixture was stirred for 1h and then heated to 70 °C to obtain an aqueous suspension of clay. 5 grams of cetyl ammonium bromide (2x concentrations of the clay based on cation exchange capacity (CEC)) in 50 ml deionised water was added into the mixture, The pH value of the solution was adjusted to 6.8 ± 0.1 using sodium carbonate/ acetic acid buffers and stirring was continued for 4h. A white liberated precipitate was filtered off and washed with deionised water. The obtained wet precipitate was dried under vacuum at 80 °C for 24h.

Synthesis of terpolymer / clay nanocomposites[26]

Terpolymer emulsion latices having different composition ratios of GMA, MMA and BuA was prepared by semicontinuous technique with a solid content of ca 30 ± 1% in absence or in presence of modified MMT clay (3% ,wt%). The polymerization was carried out according to the following procedure: in a 250 ml three nicked flask, mixture of SDS (1gm) and MPOE (1gm) were dissolved in distilled water (30 ml). The desired amount of the monomers, according to the selected composition ratios (20/20/60, 20/40/40 &20/60/20 GMA/MMA/BuA), were added and well emulsified in period of one hour using mechanical stirring (500rpm). A redox initiation system composed of PPS (0.27gm) and SBS (0.416 gm) dissolved in 40 ml distilled water was added drop wise to the reaction mixture during 30 minutes. The polymerization reaction was carried out at 70°C under stirring at 500 rpm. For nanocomposites terpolymer latices prepared in presence of MMT. The previous procedure was carried out in the presence of the modified clay in the flask.

Characterization:

X-ray diffraction (XRD) measurements were performed using a Philips powder-Diffractogram PW 1050 with ADM software and with Ni-filtered Cu K radiation. The accelerating voltage was 40 KV, and the current was 30 mA. IR Spectroscopy was carried out using Bruker FTIR Spectrometer. The morphology and fracture surface of the composites were examined by Scanning electron microscope (SEM) analysis using Zeiss,DSM 962 microscope. Thermogravimetric analysis (TGA) was determined on TGA 7 thermogravimetric analyzer (Perkin–Elmer instrument) under a nitrogen flow at heating rate 10°C min-1.

3. Results and Discussion:
A-Modification of MMT Clay
I-SEM

Pristine MMT clay was modified with CAB and then incorporated in terpolymerization of GMA, MMA and BuA with different monomer composition ratios to prepare terpolymer / MMT nanocomposites via in situ emulsion technique. When the modification of the clay is completed, the appearance of a colloid like suspension without any visible solid particles is obtained, a small portion of the stable suspension was dried to evaporate the water solvent and the residue was examined by scanning electron microscope. In order to investigate the effect of the modification, pristine Na-MMT was also deposited from water suspension free of any modifier and examined by scanning electron microscope. Figure 1A &1B shows the SEM for each of pristine Na-MMT and modified MMT. Pristine Na-MMT (Figure 1A) exhibits agglomeration morphology due to its poor dispersion in the solvent, where modified MMT (Figure 1B) displays a uniform distribution implying a good dispersion in the solvent which can be attributed to an effective organophilic transformation of the MMT surface after modification [27].
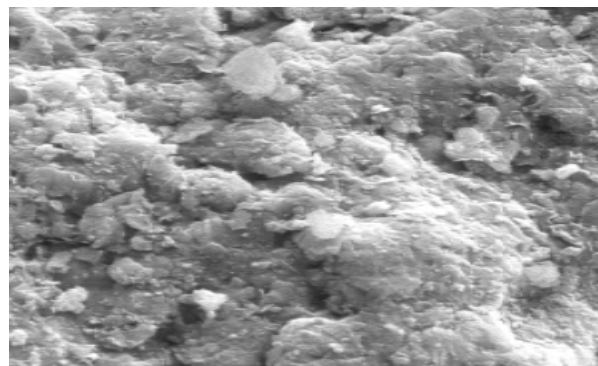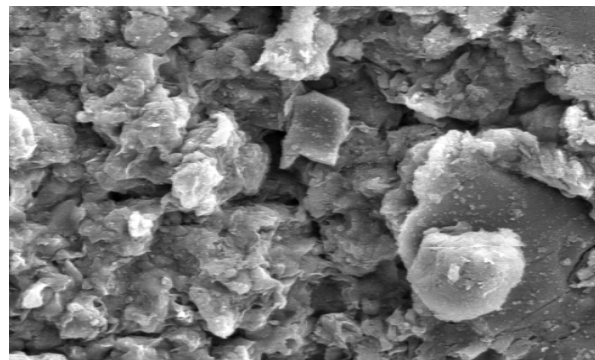
A   **B**
Figure 1: SEM of (A) Pristine MMT and (B) Modified MMT

II-XRD

Figure 2 shows XRD curves of pure MMT and modified MMT clays. These peaks are assigned to the d-spacing of MMT. It could be seen (Figure 2) that the d-spacing of the modified MMT clay were found to be 10.26 nm which is larger than the d-spacing of pristine MMT (7.92nm). This indicates that MMT clay was successfully intercalated with cetyl ammonium bromide modifier.
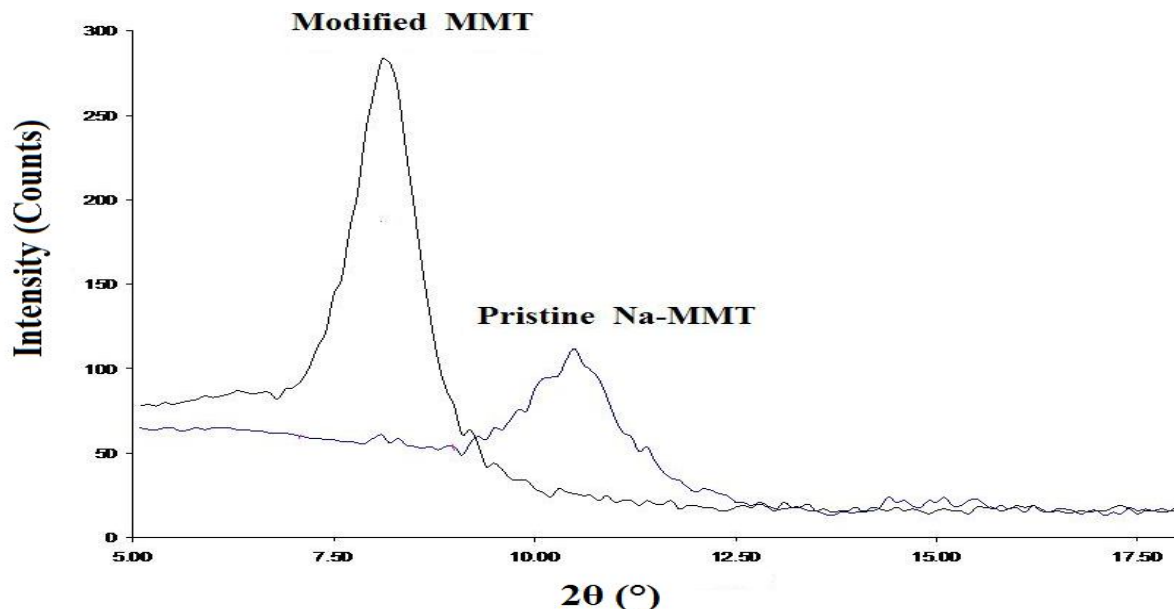

Figure 2: XRD patterns of pristine Na-MMT and modified MMT clays.

III-FTIR

Figure 3 displays the FTIR of pristine MMT clay and MMT clay modified by cetyl ammonium bromide. From the figure it can be concluded that, the appearance of the absorption bands 2950 cm^{-1} and 2850 cm-1 which are the characteristic bands of aliphatic groups [28] in the CAB modifier. This indicates the successful modification of MMT clay by using CAB.
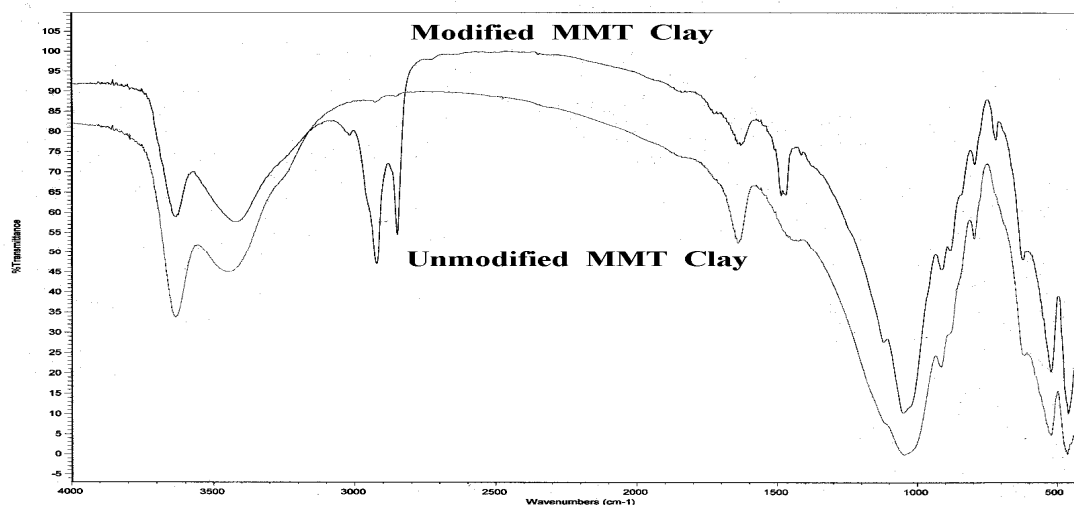

Figure 3: FTIR spectra of unmodified MMT and modified MMT.

B-Structure and properties of terpolymer latices and its nanocomposites

I- SEM

The examination of the surface of the prepared samples was investigated by SEM. The SEM images indicated that the terpolymers with different composition ratios are intercalated in the interlayer of MMT clay to produce clay / polymer nanocomposites.

Figure 4 shows SEM of pure terpolymer and its nanocomposites at monomer composition ratio (GMA/MMA/BuA = 20/60/20) where small aggregates of around 5 um in size together with few large aggregates are observed in the nanocomposite image, the presence of these aggregates indicate the poorly dispersed MMT clay particles in the polymer matrix. On the other hand, Figure 5 shows SEM of the pure terpolymer and its nanocomposites at monomer composition ratio (GMA/MMA/BuA = 20/20/60) where MMT particles did not appear at micro level where the absence of large MMT particles indicates, that the agglomerate did not reveal the inorganic domain. Most of the MMT is well adherent to the polymer. This indicates that the mineral domains are sub microns and homogenous dispersion of MMT clay particles in the polymer matrix and also indicates that the terpolymer was intercalated in the interlayer of MMT clay in a homogenous matter [29].

From Figures 4 &5, It can be concluded that, increasing of the butyl acrylate ratio led to increasing the homogenous dispersion of MMT particles in the polymer matrix.

A

B
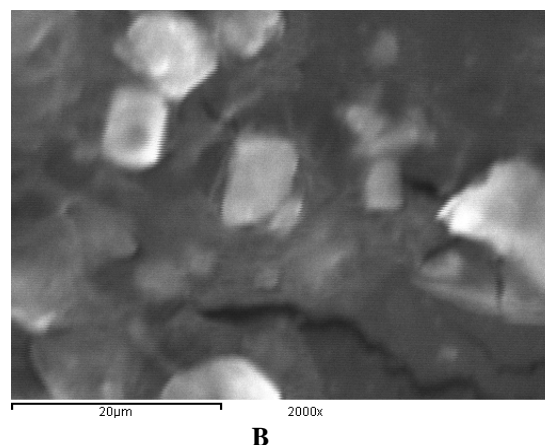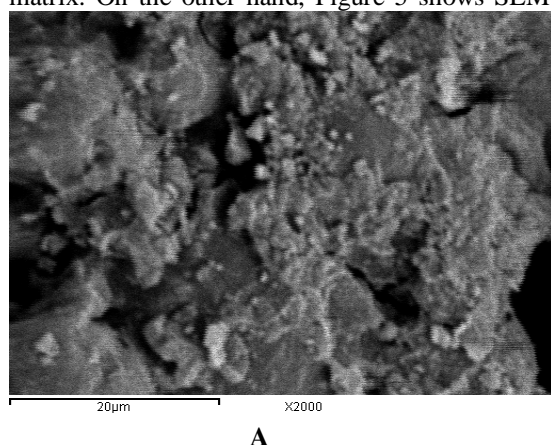
Figure 4: SEM image of A) pure terpolymer and B) nanocomposite at composition ratio (GMA/MMA/BuA = 20/60/20

A

B
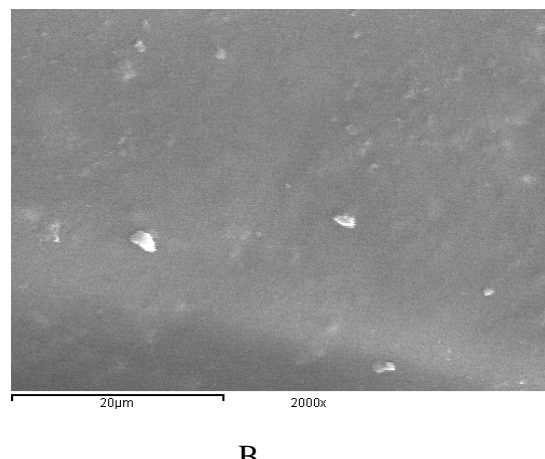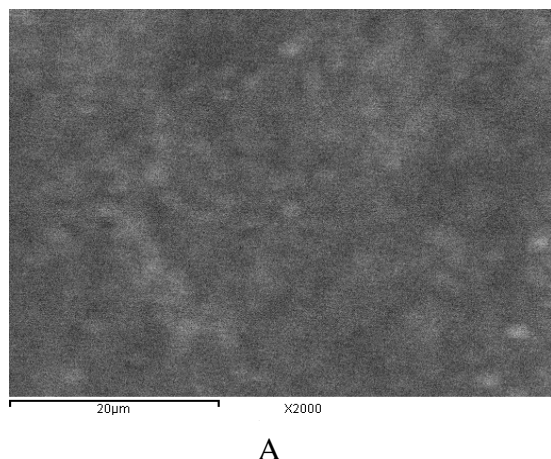
Figure 5: SEM image of A) pure terpolymer and B) nanocomposite at composition ratio (GMA/MMA/BuA = 20/20/60).

X-Ray diffraction (XRD):

X-ray diffractograms of the prepared nanocomposites with different monomer composition ratios with CAB modified clay is used are illustrated in Figure 6. Fig. 6 shows that there is no noticeable organoclay peak reflection appearing in the

diffraction pattern for both composition ratio (GMA/MMA/BuA = 20/20/60) and composition ratio (GMA/MMA/BuA = 20/40/40) nanocomposites. This means that the silica layers were completely delaminated and led to production

of exfoliated nanocomposites [30] with both ratios. On the other hand, intercalated nanocomposites were formed in case of the composition ratio (GMA/MMA/BuA = 20/60/20) and the diffraction peak was present at 2θ value 6.5°.
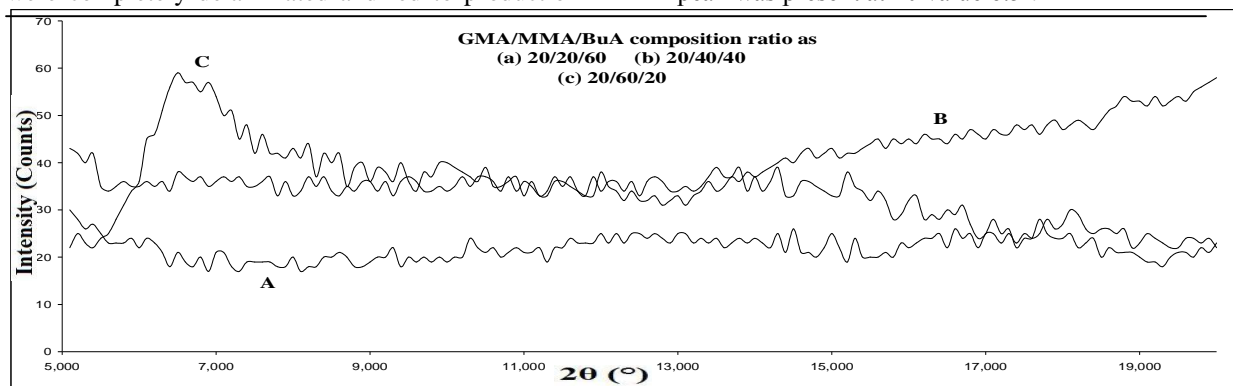

Figure 6: XRD of the nanocomposites with different composition ratios of (GMA/MMA/BuA).

Thermal Gravimetric Analysis (TGA):

Thermal stability of pure terpolymer and the prepared nanocomposites with different composition ratios and costant clay content was determined by measuring the thermogravimetric analysis (TGA) within the temperature range 50-600 ^{o}C, as shown in Figures 7 and 8. It is obvious, that increasing the MMA monomer content plays an effective role in increasing the thermal stability of both terpolymer and nanocomposites which can be explained by the increase in the homogenous dispersion between the individual layers which leads to increase the thermal stability. It is also clear that, at the same composition ratio, all weight lose temperatures for the nanocomposites samples are higher than that of pure terpolymer which can be attributed to the restriction of the motion of organic chains attached to MMT clay [27]. The TGA results of pure terpolymer with different compositions and its nanocomposites are listed in Tables I which shows that the weight lose

temperatures of nanocomposites are higher than that of pure terpolymer in all studied composition ratios. For example, in the composition ratio (MMA = 20%), T_{10} (10% weight lose) of nanocomposite was higher than that of pure terpolymer by 40 ^{o}C, 29 ^{o}C and 26 ^{o}C when 20% , 40% and 60 % of MMA composition ratio was used respectively. Moreover, Tdc (central weight lose) of nanocomposite is higher than that of pure terpolymer by 15 ^{o}C, and 10 ^{o}C when 40% and 60 % of MMA monomer is used respectively. From the results listed in the table, it can also be concluded that, nanocomposites have more thermal resistance compared with pure terpolymer when using the same monomer composition ratio. Pure terpolymer loses the weight more rapidly and at lower temperature than its nanocomposites.
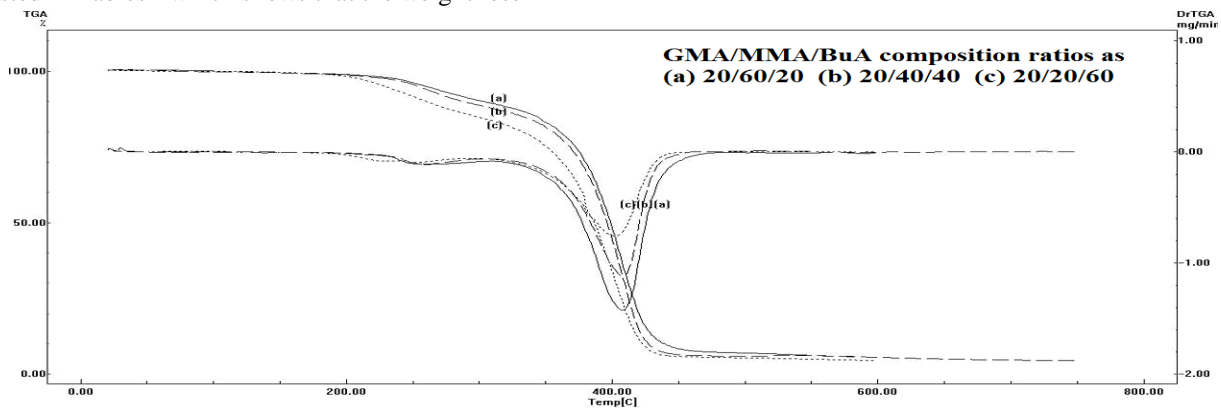
Figure 7 :TGA thermograms of the prepared pure terpolymers of different monomer composition ratios (GMA/MMA/BuA).
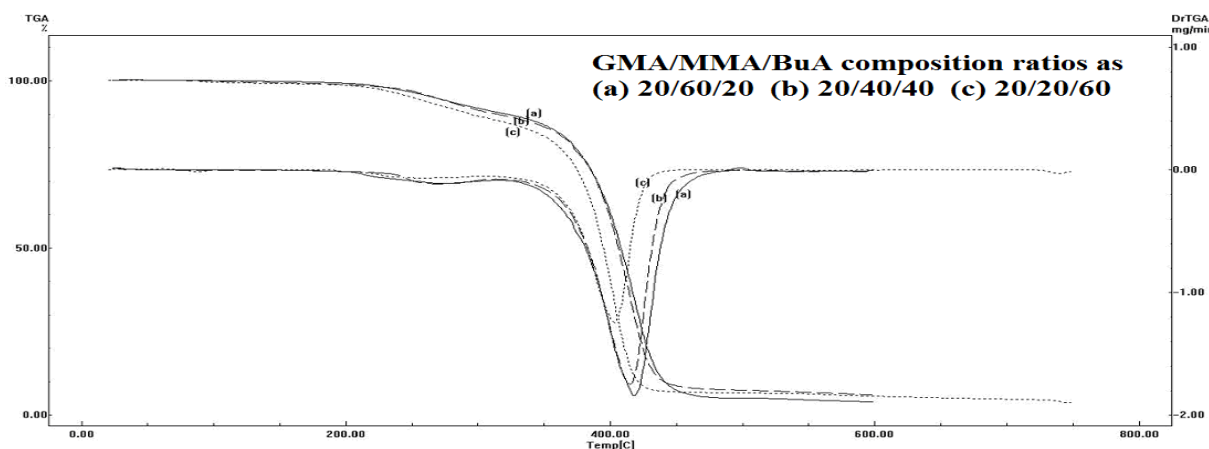
Figure 8 :TGA thermograms of the prepared nanocomposites of different monomer composition ratios (GMA/MMA/BuA) and 3wt% of modified MMT clay.

Table I: TGA data obtained for pure terpolymer and its nanocomposite at different monomer composition ratios

Degradation Temperature	Monomer composition ratio (GMA/MMA/BuA)					
	20/20/60		20/40/40		20/60/20	
	Terpolymer	Nano-composite	Terpolymer	Nano-composite	Terpolymer	Nano-composite
T10	255	295	285	314	299	325
T25	349	371	367	382	371	382
Tdc	380	395	395	405	398	408
T75	406	406	410	419	415	423
Remain	434	436	436	458	433	452

4. Conclusion:

1- Montmorillonite clay (MMT) with interlayer spacing 7.92 nm and cation exchange capacity (CEC) 100 meq per 100g was successfully modified with cetyl ammonium bromide modifier.

2- Pristine MMT exhibits agglomeration morphology due to its poor dispersion in the solvent, where modified MMT displays a uniform distribution implying a good dispersion in the solvent which can be attributed to an effective organophilic transformation of the MMT surface after modification.

3- Terpolymer nanocomposites were successfully prepared by in situ emulsion polymerization of glycidyl methacrylate (GMA) methyl methacrylate (MMA) and Butyl acrylate (BuA) monomers using redox initiation systems.

4- X-ray diffraction (XRD) investigation showed that exfoliated structures were obtained during the preparation of terpolymer nanocomposites with monomer ratios (GMA/MMA/BuA = 20/20/60) and (GMA/MMA/BuA = 20/40/40) where intercalated terpolymer nanocomposite was obtained during the preparation of terpolymer nanocomposites with monomer ratio (GMA/MMA/BuA = 20/60/20).

5- Thermal gravimetric analysis (TGA) results show that all weight loses temperatures for the nanocomposite samples are higher than that of its pure terpolymers in all monomer ratio studied which can be attributed to the restriction of the motion of organic chains attached to MMT clay. It is also obvious that, increasing the MMA monomer content plays an effective role in the increase of thermal stability of the prepared terpolymer and nanocomposite which can be explained by the increasing in homogenous dispersion between the individual layers which lead to increasing in the thermal stability.

6- Scanning electron microscope SEM shows that MMT clay is poorly dispersed in the polymer matrix in case of monomer composition ratio (GMA/MMA/BuA = 20/60/20) where small aggregates of around 5 um in size together with few large aggregates are observed in the nanocomposite image. Where, terpolymer was intercalated in the interlayer of MMT clay in a homogenous matter in case of monomer composition ratio (GMA/MMA/BuA = 20/20/60).

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