Nanocomposites have a dramatic improvement in mechanical and physical properties that can be formed by adding very small amount of clay to neat polymer. In these nanocomposites, the movement of the polymer chains is confined, and then the interactions between the polymer chains are greatly affected by the confinement of the nanometer space. Therefore, as advanced structural materials, these layered silicate/polymer nanocomposites can exhibit improvement in its thermal stability, enhancement in the mechanical properties, reduction of gas permeability, and increase the solvent resistance as well as enhancement in the ionic conductivity when compared with the polymers alone. There are two possible idealized layered silicate/polymer structures: exfoliated and intercalated. In the exfoliated clay-polymer nanocomposites, the montmorillonite (MMT) clay is completely exfoliated into individual layers (≈1 nm) and homogeneously dispersed in the polymer matrix. In the intercalated clay-polymer, a single extended polymer chain (sometimes more than one) is intercalated between the silicate layers, resulting in a well-ordered multiplayer morphology built up with alternating polymeric and silicate layers.

It is difficult to achieve true nano-dispersion of clay in the polymer matrix because the majority of polymers are hydrophobic while the clays are hydrophilic. Many methods have been used to improve the compatibility between the clay and the polymer. The commonly used method is the ion exchange of onium ions of organic molecules with the inorganic cations in the interlayer space of the clay. The addition of monomeric modified clays can improve the interfacial adhesion.

Nanocomposites were prepared starting with organoclay pre-intercalated with a vinyl-terminated reactive moieties such as vinyl benzyl dimethyl dodecyl ammonium chloride, vinyl tri-ethoxy silane (used with cetylpyridinium chloride), vinyl benzyl dimethyl ethanol ammonium chloride, the quaternized product of azo-bis[methyl-N-(2-ethoxy) propionamide] with bromo acetyl bromide, [2-(acyrloyloxy)
ethyl](4-benzoylbenzyl)dimethyl ammonium bromide, or tri-methyl-N-methyl-styrene.

A great deal of attention has been focused on clay-PS nanocomposites. The improvements in the physical properties are obtained at very low clay loadings or modified clay with oligomeric units. The number of alkyl chains attached to the organic cation has been varied, and it is evident that the many alkyl chains result in overcrowding in the interlayer space which leads to the formation of high immiscible systems.

Poly(methyl methacrylate) (PMMA) is an important member of the family of poly (acrylic esters). PMMA has some desirable properties, including exceptional optical clarity, high strength, and excellent dimensional stability. However, its biggest disadvantage is its poor heat resistance. MMT/PMMA nanocomposites offer the potential for excellent thermal properties and improved physical performance. Many studies have been reported on the MMT/PMMA nanocomposites focused on the structure, preparation methods and properties of the final hybrids.

A developed method for the preparation of polymer-clay nanocomposites that includes a variety of polymers has been reported. This method involves copolymerization of vinylbenzyl chloride, styrene and maleic anhydride followed by the formation of onium salts and then ion exchange onto montmorillonite. This method leads to the production of macromolecules into the MMT layers having many onium ions, hence linking with more than one clay layers and acting as crosslinkers which restrict penetration of large amounts of monomers inside the clay interlayer space.

Recently, the vinyl-modifier was used to prepare polymer nanocomposite, however the exfoliated morphology was not achieved above 3% filler content. This may be due to the high steric hindrance caused by the long chain hydrocarbox of the surfactant. Based on the above study, we suggested that alkyl tail is expected to reduce the platelet-platelet cohesion while adding more hydrocarbon units may facilitate the access of the monomer moieties between the clay layers, and decreasing the unfavorable alkyl/PMMA interaction. On the other hand, non-polar polystyrene segments have no attraction to the polar silicate layers, and in this case, increasing the number of hydrocarbon moieties from the surfactant. Based on the above study, we suggested that alkyl tail is expected to reduce the platelet-platelet cohesion while adding more hydrocarbon units may facilitate the access of the monomer moieties between the clay layers, and decreasing the unfavorable alkyl/PMMA interaction.

The goal of this work is directed toward the production of exfoliated organoclay-PS and organoclay-PMMA nanocomposites by bulk polymerization technique and solution mixing (solution blending) using a new organically modified clay. The investigation of the morphology and thermal properties of the produced nanocomposites has been determined.

**Experimental**

**Materials**

Chloromethylstyrene (CMS) was purchased from Polyscience, Inc., as a mixture of m-/p-isomers (=30:60%) and used as received. Methyl methacrylate (MMA) and styrene (St) were used as obtained from Aldrich. Styrene was used after washing with 1 M NaOH solution then dried over Na2SO4. Sodium Montmorillonite clay (Na+-MMT) was supplied by Kunimine Industry Co (Japan) under trade name Kunipia-F with cation exchange capacity (CEC) of ca. 119 mEq per 100 g. N, N-dimethyl-n-octadecylamine was obtained from Kunimine Industry Co (Japan) and used as received. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Fluka (Switzerland). Commercial polystyrene (PS100) was obtained from El-Nasr Chemical Co., Egypt. Toluene and Dimethylformamide (DMF) were purchased from Advic, Egypt and used after distillation and drying over A4 molecular sieve directly before use. THF, methanol, ethanol, and diethyl ether were used as purchased from Advic (Egypt).

**Measurements and procedures**

1H NMR spectroscopic measurements were measured in CDCl3, with a Lambda, Jeol NM300 spectrometer. Infrared spectra (IR) were obtained using a Perkin-Elmer 1430 Ratio-recording infrared spectrometer, by casting a very thin film of the sample on KBr disk with a resolution of 4 cm⁻¹ and 32 scans per sample in the wavenumber range of 4000–400 cm⁻¹.

X-ray diffraction (XRD) measurements were performed using a Phillips Powder-Diffractionmeter equipped with an Ni-filtered Cu-Kα radiation (30 kV, 20 mA, λ = 1.5418 Å). The characterization was carried out in a range of 20–10° with scan rate 0.005°/s and scan step of 0.01°. Measurements were made for the dried product to examine the interlayer space activity in the composite as prepared.

Morphology of the nanocomposite was observed through a Joel JXA-840 SEM at an accelerating voltage of 20 kV to examine the morphology and particle size of MMT in the MMT-polymer composites. The sample was placed on double-sided scotch tape and examined at their surface.

Thermogravimetric analyses (TGA) were observed with Rigaku Thermo Plus 2 TG-DTA TGB120 under air or nitrogen atmosphere. The heating rate was 10 °C/min in the temperature range ~30–850 °C.

Calcination measurements: A definite weight of the sample was placed into a porcelain crucible and dried in an electric oven at 120 °C overnight, then placed into an ignition oven and the temperature was increased to 1000 °C and adjusted at this temperature for 5 h. The loading of each sample is expressed as the weight loss by ignition per 100 g of the dry sample.

**Synthesis of vinylbenzyl derivative ammonium salt**

The ammonium salt (I) was prepared by mixing 11.64 g (40 mmol) of N, N-dimethyl-N-octadecylamine dissolved 10 ml freshly distilled THF and 6.10 g (40 mmol) of CMS in the presence of 0.03 g of hydroquinone. The mixture was stirred for 2 h at room temperature and recrystallized from ethyl acetate at 45 °C, to give 16.42 g (yield = 93%) of (I). The 1H NMR and IR spectra were similar to the results obtained by the Ref. 3

1H NMR (CDCl3): δ (ppm) 3.73–7.2 ppm (m, 4 H, ring H); 6.7 (dd, 1H, vinyl H), 5.85 (d, 1H, vinyl H), 5.4 (d, 1H, vinyl H), 5.1 (s, 2H, Ph-CH2), 3.5 (2H, N+-CH2, aliphatic H), 3.3 (s, 6H, 2CH3-N+), 1.3 (m, 30 H, aliphatic), and 0.9 (m, 3H, CH3).

IR (KBr disc): 3433 cm⁻¹ for (–N+Me2) stretching, 1500 cm⁻¹ for (–C=C–), 1430 cm⁻¹ for (C–H stretching vibration of methyl group and –N+ vibration) and at 1634 cm⁻¹ for (C–H stretching vibration of methyl group and –N+ vibration).
Preparation of the ammonium salt-modified clay

10 g (11.9 mEq) of Na+-MMT was dispersed in 300 ml of distilled water with stirring overnight to obtain a homogeneous dispersion. Then, ≈30 ml of methanol was added portion wise with stirring and the stirring was continued for 2 h. A solution of N,N-dimethyl-n-octadecyl-(4-vinylbenzyl)ammonium chloride (7.0 g, 15.5 mmol) in 100 ml of water/methanol (70:30 v/v) was added dropwise to the dispersed clay at room temperature with vigorous stirring. The mixture was kept under stirring overnight at room temperature. After settling for a few hours, the product was filtered off and washed with distilled water until free from chloride ions, followed by washing twice with 80/20 (v/v) ethanol/water. The white product was dried overnight under vacuum at room temperature followed by grinding to obtain particles with size ≤63 μm to give 13.9 g of (II). The characteristic data were corresponding to Ref. 25.

Preparation of clay/PS modifier

The synthesis of clay-PS modifier (III) was carried by mixing 9 g of styrene monomer, AIBN dissolved in 30 ml dry toluene and 6.0 g of organically modified clay (II). After stirring under nitrogen atmosphere overnight at room temperature, the homogenous mixture was heated at 80 °C for 24 h, and finally, the mixture was heated under reflux for 6 h. The resulted product was swelled in toluene and then precipitated in an excess of methanol to give 11.8 g of the product (III). The characteristic data were corresponding to Ref. 25.

Preparation of clay/PMMA modifier (IIIb)

It was prepared as described in Ref. 25 by mixing 9 g of MMA monomer and AIBN dissolved in 30 ml dry toluene, and 6.0 g of organically modified clay (II) then completed as in (III) to give 13.5 g of (IIIb). The characteristic data were corresponding to Ref. 5.

Preparation of PS and PMMA nanocomposites

The preparation of highly dispersed and exfoliated polymer-clay nanocomposites were obtained by dispersion of both organo clay (OC) (III), and (IIIb) in the polymer matrix. Two methods have been used, solution blending and in situ polymerization. The procedures are described below, and the data are summarized in Table 1.

| Sample | Type | Monomer | Wt (g) | Type | Wt (g) | Wt (g) | Calcination (%) | Wt loss | Wt residue |
|--------|------|---------|--------|------|--------|--------|----------------|---------|------------|
| IVa    | IIIa | St      | 0.84   | St   | 9.5    | 8.9    | 97.9           | 2.1     |            |
| IVb    | IIIa | St      | 1.70   | St   | 9.0    | 8.5    | 95.6           | 4.4     |            |
| IVc    | IIIa | St      | 1.00   | St   | 9.5    | 9.1    | 97.8           | 2.2     |            |
| IVd    | IIIa | St      | 2.00   | St   | 9.0    | 8.7    | 94.9           | 5.1     |            |
| Vb     | IIIa | MMA     | 0.84   | MMA  | 9.5    | 9.2    | 94.4           | 5.6     |            |
| Vc     | IIIa | MMA     | 1.70   | MMA  | 9.0    | 8.7    | 93.8           | 6.2     |            |
| Vd     | IIIa | MMA     | 1.00   | MMA  | 9.5    | 9.5    | 95.4           | 0.5     |            |
| VIa    | IIIb | St      | 0.84   | St   | 9.9    | 10.5   | 97.2           | 2.8     |            |
| VIb    | IIIb | St      | 1.70   | St   | 9.5    | 10.9   | 94.7           | 5.3     |            |
| VIc    | IIIb | St      | 1.00   | St   | 9.0    | 9.7    | 89.4           | 11      |            |

Preparation of modified clay-PS and modified clay-PMMA

The nanocomposite samples were prepared through bulk polymerization, by stirring for 24 h at room temperature, a mixture of 0.84 g of modified clay (III) with 9.5 g of styrene, and 0.02 g of AIBN then the temperature was raised to 80 °C for 24 h. Finally, the product was dried under vacuum at 100 °C for 6 h to give 8.9 g of PS-Clay (IVa).

The data relevant to the preparation of different Clay-PS nanocomposites (IVa–d) and Clay-PMMA nanocomposites (VIa–d) using different modified-clays (IIIa–b) and different monomers (St or MMA) are illustrated in Table 1.

Preparation of PS-modified clay nanocomposites (VIa–d)

The samples (VIa–d) were prepared by mixing a solution (blending) of 9.9 g polystyrene (Mw = 1,00,000) (PS100) dissolved in 30 ml dry toluene and 0.16 g modified clay-PS (III) swelled in 10 ml dry toluene. The highly viscous mixture was stirred for 2 h then free cast in a film form on a pre-treated glass plate. The solvent was removed by heating at 80 °C under reduced pressure for overnight to give 8.9 g of sample (VI).

The preparations conditions of the other samples (VIa–d) with different ratios of polystyrene (PS100) and modified clay-PS (III) are summarized in Table 1.

Results and discussions

Preparation of nanocomposites

The highly exfoliated chemically grafted organoclay-PS nanocomposites can be obtained by either solution blending or in situ polymerization techniques. The synthesis can be accomplished through four steps as outlined in Scheme 1. The first step is the preparation of ammonium chloride salt (I) as a monomeric surfactant. The second step includes the formation of clay-vinyl monomer intercalate (II) through cation exchange between onium groups of the vinyl monomer forming an ionic bond with the negative charges of montmorillonite clay interlayer space. The third step consists of a complete dispersion of clay-vinyl monomer with ratio 40 mass-% in St or MMA monomers followed by polymerization to produce the clay-PS (III) and clay-PMMA (IIIb) composites. The fourth step involves re-polymerization of the prepared samples (IIIa–b) with St and MMA monomers or solution mixing with commercial polystyrene. The relevant preparation data for the different series are recorded in Table 1.
the organo-MMT interlayer space and the free monomer molecules could facilitate the penetration of monomers into the lamellae. The increasing of the basal spacing can be associated with the formation of nanocomposite, due to the expansion of the interlayer space (swelling) which leads to accommodate the intercalating polymer. The interaction of the organo-MMT with monomer depends not only on the nature of the organic group intercalated in the organo-MMT but on the chemical structure of the monomer used.

$^1$H NMR data for vinyl monomer (I), illustrate that the $^1$H of chloromethyl group (CH$_2$Cl) was shifted from 4.6 ppm for CMS to 5.1 ppm which corresponds to the quaternary salt. Also, the peak at 6.7 ppm showed the existence of the vinyl group.

The structural composition of the materials was confirmed by using IR spectra. The spectra show a characteristic band at 1605 cm$^{-1}$ for the vinyl group (C=C), and band at 838 cm$^{-1}$ for C−Cl of chloromethyl group in the monomer (I) as shown in Figure 1. The IR spectrum of (II) showed that the band at 838 cm$^{-1}$ for C−Cl of chloromethyl groups disappeared and a characteristic band corresponding to the ammonium salt, N⊕(R)$_3$, at 3433 cm$^{-1}$ appeared. Moreover, the IR spectra for OC (IIIa,b) shows characteristic bands at 3061 and 3025 cm$^{-1}$ corresponding to aromatic CH stretching, 2925 or 2923 cm$^{-1}$ corresponding to CH$_3$ asymmetric stretching, and 2850 or 2854 cm$^{-1}$ corresponding to CH$_2$ symmetric stretching (Figure 1). The absorption bands at 1602, 1493, and 1453 cm$^{-1}$ correspond to C=C in-plane vibration, CH$_2$ plane scissoring at 1474 cm$^{-1}$, CH out-of-plane bending of phenyl ring at 757 or 756, 698 or 690 cm$^{-1}$, and out-of-plane deformation of phenyl ring at 540 cm$^{-1}$ for PS.$^{26}$ The absorption at
(III a,b). This can be explained by attaching a more monomer to crowd vinyl-onium cation at one edge leading to high d-value than another that has a low volume of vinyl-cations.

Furthermore, Figure 2 illustrates a typical XRD for the OC-PS, OC-PMMA, and OC-PS100 nanocomposites. No reflection can be seen for all samples, which indicate the formation of a delaminated system or disordered system, due to an increasing in the d-value of these nanocomposites compared with (III a) or (III b), which could result from insertion of more polymers due to the good swelling character. The disappearance of the reflection in the XRD can be explained by entering the monomers or polymer solution into the clay interlayer space pushing the layers apart (i.e. intercalation). As more monomers or polymer chains enter the interlayer space, two possible changes can occur. The first change is the loss of the ordering and crystalline structure of the layers which become disordered with no longer a parallel arrangement of nanosheets, without pushing the layers apart. This leads to broadening of the reflection. The second change is the entering of the polymer into the interlayer space which pushes the layers far enough apart leading to the separation of the layers (i.e. exfoliation occurred).

**XRD results**

XRD is a powerful technique to observe the extent of montmorillonite dispersion ordered or disordered structure in the clay-polymer nanocomposites. The XRD for MMT-monomer reveals that the d-value of Na+/MMT clay was increased from 12 Å (2θ = 7.2°) to 33.6, 18.48 Å (2θ = 2.63°, 4.78°) for neat PMMA to 1715 cm−1 for PMMA nanocomposites in the sample (V a) and to 1690 cm−1 for (V b). It could be concluded that relatively stronger intermolecular and intramolecular hydrogen bonding tethered the MMT and PMMA chains.

**SEM results**

The SEM images of the surface of the deposition-molded samples are shown in Figure 3. The micrograph shows that the polymers were intercalated/exfoliated in the interlayer space of MMT in a homogenous manner to produce new composite materials. The micrograph does not show the MMT particles on the micron level. Figure 3 shows a micrograph of the surface for the samples (III a,b), (IV c) and (V b) as examples. The absence of MMT particles reveals that the agglomerates did not display the inorganic domains at the possible magnification. This means

![Figure 2 XRD pattern for MMT, the modified clay II, IIIa,b, the PS nanocomposites IVa–d, and the PMMA nanocomposites Va–d](image-url)
that the particle size of MMT (0.1–10 μm) is not visible due to well adherent to the polymer matrix and the size of the particle is below the resolution of SEM. This result indicated that the mineral domains are submicron and homogeneously dispersed in the matrix. Therefore, we can conclude that the polymer was intercalated in the interlayer space of MMT in a homogenous manner to produce new MMT-polymer nano-composite materials.

**Thermal properties**

The thermal degradation of the neat polymers and the intercalated materials were performed by TGA in the temperature range 30–850 °C as shown in Figures 4–7 and Table 2. There are some interesting parameters which can be calculated from the TGA thermograms such as (a) temperature at which 5% degradation occurs $T_{0.05}$, (b) The onset of the degradation,
temperature due to the instability of char formed by aliphatic
chain polymer.
In another way, it was found that the clay-vinyl monomer
(II) started the degradation process at ≈220 °C, due to the deg-
radation of the octadecylammonium chain obeying Hoffmann
elimination. The rate of weight loss was shown at ≈277 °C
with residue 11 mass-%. Another stage of the decomposi-
tion occurred in the temperature range 278−625 °C with 39
mass-% of the residue, which can be attributed to the decom-
position of adsorbed polyvinyl benzyl chloride and attached
benzyl amine from 287 to 550 °C. With increasing tempera-
ture, the rate of mass loss increased in the temperature range
551–768 °C, due to the decomposition of remaining polyvinyl
benzyl chloride protected by clay-layer and removal of the
structural H2O molecular within the layers of MMT.27 Moreover,
compound IIIa curve displayed two stages: the first stage is
found in the temperature range 225−434 °C with a weight
loss of about 60 mass-%, as shown in Figure 5 and Table 2.

which is usually taken as the temperature at which 10% deg-
radation occurs, \( T_{0.1} \). (c) Mid-point temperature of the deg-
radation, \( T_{0.5} \). (d) Another measure of thermal stability is the
non-volatile residue which remains at ≈850 °C, denoted as char.

These data indicate that the thermal stability of interca-
lated samples is higher than that of the neat polymers. This
is due to the restriction of the motion of polymer chains
attached to the MMT clay.

Figure 4 and Table 2 illustrate that the weight loss of (II),
(III), and (III) at T0.05 the corresponding temperatures are
241, 274 and 246 °C, respectively, while at T0.01 the corre-
sponding temperatures are 269, 318 and 261 °C, respectively.
The data illustrate that the final weight losses were found to be
45, 80, and 83 mass-%, corresponding to the clay contents 55,
20, and 17 mass-%. At 50% mass loss, the thermal degradation
temperature of neat PS and MMT-PS (III) is higher than neat
PS by 36 °C. In contrast, (III) had the same decomposition
temperature due to the instability of char formed by aliphatic
chain polymer.

In another way, it was found that the clay-vinyl monomer
(II) started the degradation process at ≈220 °C, due to the deg-
radation of the octadecylammonium chain obeying Hoffmann
elimination. The rate of weight loss was shown at ≈277 °C
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tion occurred in the temperature range 278–625 °C with 39
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benzyl chloride protected by clay-layer and removal of the
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Scheme 1 Preparation of OC-PS and OC-PMMA and its nanocomposites with St and MMA through different ways

Table 2 Thermal properties data of Mt-PS and Mt-PMMA nanocomposites

| Sample | Atm   | $T_{0.05}$ | $T_{0.1}$ | $T_{0.5}$ | Start | End  | Mass loss% | Char (%) | (%) | (%)  |
|--------|-------|------------|-----------|-----------|-------|------|------------|----------|-----|-------|
| II     | Air   | 241        | 269       | –         | 220   | 277  | 11         | 55       | 49  | 51   |
| IIIa   | Air   | 246        | 261       | 350       | 220   | 307  | 34         | 18       | 80  | 20   |
| IIIb   | Air   | 274        | 318       | 402       | 225   | 434  | 78         | 19       | 77  | 23   |
| IVa    | Air   | 284        | 315       | 420       | 246   | 444  | 85         | 3        | 97.5| 2.2  |
| IVb    | Air   | 270        | 317       | 403       | 209   | 439  | 93         | 6.47     | 94.9| 5.1  |
| IVc    | Air   | 288        | 342       | 418       | 223   | 355  | 11         | 6.3      | 95.6| 4.4  |
| PMMA   | Argon | 225        | 247       | 347       | 160   | 411  | 100        | 0.00     | –   | –    |
| Vc     | Argon | 258        | 328       | 426       | 250   | 467  | 74         | 21       | 97.2| 2.8  |
| Vd     | Argon | 259        | 291       | 399       | 245   | 365  | 24         | 15       | 94.8| 5.2  |
| Ve     | Argon | 226        | 267       | 385       | 160   | 305  | 18         | 15.36    | 97.4| 2.6  |
| Vd     | Argon | 220        | 258       | 378       | 165   | 314  | 31         | 16       | 94.4| 5.6  |
| PS100  | Air   | 268        | 283       | 327       | 260   | 544  | 100        | 0.00     | –   | –    |
| V100c  | Air   | 297        | 321       | 400       | 275   | 443  | 93.5       | 3.2      | 97.2| 2.8  |
| V100d  | Air   | 293        | 312       | 381       | 265   | 559  | 94.5       | 5.2      | 94.7| 5.3  |

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This stage is due to the thermal decomposition of ammonium modifier and the PS on the surface and ungrafted PS in the interlayer space of MMT. The second step of weight loss of about 18 mass-% takes place at the temperature range from 435 to 617 °C and is slower than the first step due to the thermal decomposition of PS chains grafted to MMT and formation of black charred residues. The thermal decomposition of \( \text{III}_b \) is in three steps; the first step is due to decomposition of an ammonium salt. The second step is due to decomposition of organic modifier. The final step is due to decomposition of styrenic or methacrylate units attached to benzyl and takes place in the temperature range of 434–617 °C. This beneficial effect can illustrate the hindrance effect of grafted polymers on MMT layer that increases the interface between MMT and polymers.

This mainly results from the unique ability of nanometer montmorillonite layers to obstruct both penetrated oxygen and volatile gas produced by thermal decomposition and nanolayer inserted between the lamellae of MMT seemed to be shielded from external influences. The organoclay-PS nanocomposites show high thermal stability than neat polymers as described in Table 2 and Figure 5 for the samples \( \text{IV}_{a–d} \). The temperature at which 5% degradation increases by 7–21 °C and at which 10% degradation increases by 13–15 °C and at which \( T_{25} \) degradation increases by 39–56 °C. For the \( \text{IV}_b \), temperature at which 5% degradation increased by 25 °C, 10% degradation increases by 40 °C and \( T_{25} \) degradation increases by 54 °C. The sample \( \text{IV}_d \) shows three degradation steps, the first step is due to degradation of ammonium modifier, which occurred in the temperature range 223–355 °C. The second step is due to degradation of PMMA, which occurred in the temperature range 355–417 °C. The last one is due to the degradation of polystyrene, which occurred in the temperature range of 417–475 °C. These results agree with the behavior of other oligomers modified clays. For clay-PS nanocomposites, the temperature at which 10% degradation occurred increased by 25 °C for the modified/clay-styryl,\(^{26} \) the modified/clay-caprolactone,\(^{27} \) and the modified/clay-butadiene.\(^{27} \)

Additionally, Figure 5 and Table 2 displayed that the thermal behavior of PS100 at 5% degradation increased by 25–29 °C, 10% degradation increased by 29–38 °C, and 50% degradation increased by 54–73 °C. The thermal stability of PMMA, PS, and PS100 nanocomposites depends only on the compatibility between organo-modifier and matrix that leads to more shielding of matrix by clay layer. The thermal behavior of PS-III, nanocomposites indicates that it is more stable than PS-III, nanocomposites, due to improved compatibility between III, nanocomposites, and styrene.

Thermal decompositions of PMMA nanocomposites show higher thermal stability than PMMA as illustrated in Figure 6 and Table 2. For the samples \( \text{V}_{a–d} \), the temperature at which 5% degradation occurs increased by 33–34 °C, the temperature at which 10% degradation occurs increased by 81–44 °C and \( T_{25} \) increased by 52–79 °C. For the samples \( \text{V}_{a–d} \), the temperature at which 5% degradation was increased by 1–4 °C, the temperature at which 10% degradation occurs increased by 11–20 °C, and \( T_{25} \) was increased by 31–38 °C.

Moreover, the thermal stability increases with decreasing organoclay because the system contains nanometer size particles which have a large total interfacial area (the specific surface area of MMT is \( \approx 750 \text{ m}^2/\text{g} \)). Since MMT layers have large aspect ratios (e.g. \( p = \text{diameter/thickness} \approx 100–300 \)), at loadings \(<1.2 \text{ mass-%} \), their encompassed organoclay volumes start to overlap, hindering the free ordering, and random distribution; hence exfoliation. Thus, at higher clay concentrations, a local ordering of layers is expected and the motion of polymer molecules restricted to flow in clay-interlayer space.

**Conclusion**

New exfoliated OC-PMMA and OC-PS nanocomposites were prepared by both bulk polymerization and solution blending techniques. The synthesis was achieved by formation of clay-vinyl monomer followed by solution free radical polymerization to produce clay-PS and clay-PMMA nanocomposites. The prepared samples were used as highly compatible organo-modified/clay to produce highly exfoliated nanocomposites.

The characteristic properties of the prepared compounds were investigated by different analytical methods. The results noted that the formation of clay-polymer nanocomposites in the absence of the solvents has the properties of the individual organic-inorganic molecule, which form a semi-clear solution in many solvents such as toluene, chloroform and DMF. PM modified clay shows high compatibility with linear PMMA, while modified/clay-PMMA shows high compatibility with commercial polystyrene.

The XRD results confirmed that the clay was homogeneously dispersed and exfoliated in the polymer matrixes with an interlayer spacing of d001 value \( \approx 4 \) nm. Furthermore, the micrograph was examined by scanning electron microscopy (SEM) which showed a good dispersion of nanoclays in PS and PMMA into clay interlayer space.

Thermogravimetric analysis (TGA) and calculation showed that the incorporation of nanoclay into the polymer gives a higher thermal stability of organoclay-polymer than the neat polymers. The TGA of the nanocomposites noted increase in the decomposition temperature about 25–50 °C higher than neat PS and about 25–80 °C than neat PMMA.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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