



# PMMA/MONTMORILLONITE NANOCOMPOSITES BY BULK POLYMERIZATION: MECHANICAL AND THERMAL PROPERTIES

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## Abstract

This paper researched the mechanical and thermal properties of poly(methyl methacrylate) (PMMA)/montmorillonite (MMT) and PMMA/organic modified montmorillonite (OMMT) nanocomposites. PMMA/MMT and PMMA/OMMT nanocomposites have been synthesized by bulk polymerization. The particles of MMT and OMMT were dispersed using forced agitation and the composites were polymerized using free radical polymerization. The comparison of the addition MMT and OMMT also have been investigated in this experiment. The X-ray analysis showed that exfoliation occurred for the OMMT in the polymer matrix. The effects on the properties of experiment results have been found by static mechanical tests based on flexural strength and modulus, tensile strength and modulus, and impact strength. The dynamic mechanical analysis (DMA) based on dynamic storage modulus ( $E'$ ). The thermal analysis based on differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

## 1 Introduction

In the last few years, great attention has been focused on organic polymer/inorganic nanocomposites, from either a scientific or technological point of view [1-3]. These polymer nanocomposites can exhibit increased modulus [4-5], decreased thermal expansion coefficients [4], reduced gas permeability [4,6], increased solvent resistance [7] and enhanced thermal stability [8] when compared with polymer alone. Polymer/montmorillonite (MMT) nanocomposites

have attracted much significant academic and industrial interest due to their remarkable enhancement dimensional stability and gas barrier performance, in addition to mechanical and thermal properties as compared with the conventional microcomposites [9-10]. Polymer/montmorillonite nanocomposites have become an important area of polymer composite research. The first work of polymer/montmorillonite nanocomposites was reported by the Toyota research group. In their work, nylon 6/montmorillonite nanocomposites were successfully prepared, for which very small amounts of montmorillonite loading results can improve their mechanical and thermal properties. Since then, several types of polymer materials have been conducted globally, such as polypropylene [11], polystyrene [12], polyurethane [13], poly(vinyl chloride) [14], epoxy [15], rubber [16,17], ABS [18], and poly(L-lactide) [9].

Poly(methyl methacrylate) (PMMA) is an important member in the family of polyacrylic and methacrylic esters. The objective of utilizing PMMA for organic/inorganic nanocomposites is to take advantage of the unique properties of PMMA including excellent mechanical properties, exceptional optical clarity, weather resistance, and dimensional stability. PMMA organic/inorganic nanocomposites offer the potential for reduced gas permeability, improved physical performance, and increased heat resistance, without a sacrifice in optical clarity [8]. The PMMA/montmorillonite nanocomposites have been prepared by several methods. A common method is the intercalation of monomer or polymers into swellable-layer montmorillonite hosts. In most cases, the synthesis involves either the intercalation of a suitable monomer and then exfoliation of the layered host

into nanoscale elements by bulk polymerization or direct melt polymer intercalation with a polymer extrusion processes [1,19].

In this study, PMMA/MMT and PMMA/OMMT nanocomposites have been synthesized by bulk polymerization. The particles were dispersed using forced agitation and the composites were polymerized using free radical polymerization. The comparison of the addition MMT and OMMT also have been investigated in this experiment. The paper is focused on the X-ray analysis, static and damping mechanical properties of PMMA/MMT and PMMA/OMMT nanocomposites. Meanwhile, the thermal tests based on differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of nanocomposites have been discussed.

## 2 Experimental

### 2.1 Materials

The MMA monomer was a commercially available materials, was supplied by the Shimakyu Co., Japan; it has a specific gravity of 0.94, a viscosity of 10 mPa.s at 25°C, and a molecular weight of 100. The initiator benzoyl peroxide (BPO) used was a guaranteed reagent supplied by the Kanto Chemical Co., Japan; it has a molecular weight of 242. Sodium montmorillonite were a purified Na<sup>+</sup>-montmorillonite (Na-MMT) with a cation-exchange capacity (CEC) of 76.4 mequiv/100g which was supplied by the University of Missouri, USA.

### 2.2 Modification of Na<sup>+</sup>-montmorillonite

Ten parts by weight of Na-MMT is dispersed in 90 parts of distilled water under stirring conditions to form aqueous suspension. Three parts of intercalative reagent Cetylpyridinium chloride (CPC) was gradually added to the aqueous suspension at 80°C under vigorous stirring for 10 h. The mixture is filtered and repeatedly washed with distilled water. To ensure the complete removal of chloride ions, the precipitate was titrated with 0.1 N AgNO<sub>3</sub> until no further formation of AgCl was observed. The product is then vacuum-dried to a constant weight and ground into powder to get the organic Na<sup>+</sup>-montmorillonite (Na-OMMT).

### 2.3 Preparation of nanocomposites

(1) One phr (parts per hundred resin) initiator (BPO) was added to the MMA monomer and was stirred continuously 10 min to ensure mixing was

complete to get the B-MMA monomer.

- (2) The contents 1 wt%, 3 wt% and 5 wt% of Na-MMT or Na-OMMT and B-MMA monomer were mixed in a three-necked flask reactor under a nitrogen gas atmosphere for 1 h at room temperature.
- (3) The mixture was molded in an ASTM standard stainless steel die, the surfaces of the stainless steel die have been treated by chrome plating.
- (4) The mixture of mold was polymerized in an oven at 40°C for 48 h by bulk polymerization.

## 3 Results and Discussion

### 3.1 Structural Characterization

The X-ray diffraction (XRD) patterns of PMMA/MMT and the PMMA/OMMT nanocomposites are shown in Fig. 1. It is obvious that the PMMA/OMMT nanocomposites have no obvious diffraction peak, and it indicates two possibilities: One is that exfoliated nanocomposites are prepared; the other is that partially exfoliated and partially intercalated nanocomposites were prepared [8]. Such results suggested the exfoliation of the OMMT platelets in the polymeric matrix [13]. But the PMMA/MMT nanocomposites has a diffraction peak at  $2\theta = 7.4^\circ$ , which corresponds to a *d*-spacing of MMT platelets of 1.2 nm. It declares that intercalated nanocomposites form, or partially exfoliated and partially intercalated nanocomposites are formed, but the intercalated state is majority. This specifies that intercalated structures occupy major of the MMT platelets in the polymeric matrix [13].

### 3.2 Static Mechanical Properties

Fig. 2 illustrated the flexural strength versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites. From this figure, it can be seen that the flexural strength increased with increasing of particle content. Figs. 3 and 4 illustrated the flexural modulus and tensile modulus versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites. As expected, the moduli PMMA/MMT and PMMA/OMMT nanocomposites increased with increasing of particle content. This can be explained that the nano-sized inorganic particles have long been used in polymer industry to increase modulus. The enhancement in moduli is directly attributable to the reinforcement provided by the dispersed montmorillonite nano-layers which contribute to

dangling chain formation in the matrix, as well as to conformational effects on the polymer at the montmorillonite-matrix interface. Although the flexural strength, flexural modulus and tensile modulus of nanocomposites also increased, the rate of increase of PMMA/OMMT is more. At the same montmorillonite particle contents, the PMMA/OMMT had a higher flexural strength, flexural modulus and tensile modulus than that of PMMA/MMT, especially at higher montmorillonite particle contents (Figs. 2 and 3).

In general, the modulus increased by inorganic fillers is achieved at the loss of tensile strength and impact strength. Figs. 5 and 6 illustrated the tensile strength and notched Izod impact strength versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites. As shown in Figs. 5 and 6, tensile strength and impact strength of PMMA/MMT and PMMA/OMMT decreased with higher particle content. Although the tensile strength and impact strength of nanocomposites also decreased, the rate of decrease of PMMA/OMMT is less. At the same montmorillonite particle contents, the PMMA/OMMT had higher tensile strength and impact strength than that of PMMA/MMT, especially at higher particle contents (Fig. 5). At low particle contents, the differences were small. The all mechanical properties of PMMA/OMMT are larger than that of PMMA/MMT due to the OMMT particles has been organized. When the montmorillonite particles are dispersed in organic PMMA matrix, OMMT had a larger bonding force with PMMA matrix than that of MMT, so the OMMT had better dispersedness in PMMA matrix than that of MMT.

### 3.3 Dynamic Mechanical Properties

Figs. 7-9 showed the dynamic storage modulus ( $E'$ ) versus temperature of nanocomposites at 1 wt%, 3 wt% and 5 wt% MMT and OMMT particle contents, respectively. From these figures, it is evident that the PMMA/MMT and PMMA/OMMT nanocomposites exhibit enhanced storage modulus ( $E'$ ) compared with virgin PMMA. At the same time, the storage modulus  $E'$  for the PMMA/OMMT is higher than for the PMMA/MMT. Figs. 10 and 11 illustrated the dynamic storage modulus ( $E'$ ) versus temperature of PMMA/MMT and PMMA/OMMT nanocomposites at various particle contents, respectively. From these figures, we can found that the  $E'$  of PMMA/MMT and PMMA/OMMT nanocomposites increased with increasing of nanocomposites particle contents. This can be

explained that the nano-sized inorganic particles have long been used in polymer industry to increase modulus. The enhancement in moduli is directly attributable to the reinforcement provided by the dispersed montmorillonite nano-layers which contribute to dangling chain formation in the matrix, as well as to conformational effects on the polymer at the montmorillonite-matrix interface. The  $E'$  of PMMA/OMMT is larger than that of PMMA/MMT due to the OMMT particles has been organized. When the montmorillonite particles are dispersed in organic PMMA matrix, OMMT had a strong interaction between PMMA and montmorillonite particle surface than that of MMT.

### 3.4 Thermal Properties

#### 3.4.1 DSC analysis

The glass transition temperature ( $T_g$ ) was measured from the peak temperature by differential scanning calorimetry (DSC).  $T_g$  is strongly dependent on the mobility of the polymer chains[20]. It is well known that the addition of a filler particle to a polymer increased the  $T_g$  if a strong interaction between the polymer and the filler particle surface is present [20]. Fig. 12 illustrated the  $T_g$  versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites by DSC test. The  $T_g$  of PMMA/MMT and PMMA/OMMT nanocomposites all increased with increasing of montmorillonite particle content. The  $T_g$  of PMMA/MMT and PMMA/OMMT increased significantly from 102 °C to 122.6 °C and from 102 °C to 138 °C, respectively when the montmorillonite particle content are added from 0 wt% to 5 wt%. The  $T_g$  increase is due to the confinement of PMMA chain motion, which is imposed by the covalent bond between PMMA and montmorillonite particle. The higher the montmorillonite particle content, the larger the restriction of chain motion, and the higher the  $T_g$ . Although the  $T_g$  of nanocomposites also increased, the rate of increase of PMMA/OMMT is more. At the same montmorillonite particle contents, the PMMA/OMMT had higher  $T_g$  than that of PMMA/MMT, especially at higher particle contents (Fig. 12). At low particle contents, the differences were small. The  $T_g$  of PMMA/OMMT is larger than that of PMMA/MMT due to the OMMT particles has been organized. When the montmorillonite particles are dispersed in organic PMMA matrix, OMMT had a strong interaction between PMMA and montmorillonite particle surface than that of MMT.

### 3.4.2 TGA analysis

The thermal stability of PMMA/MMT and PMMA/OMMT nanocomposites is characterized by TGA, as shown in Figs. 13-15 and Table 1. Figs. 13-15 show the weight loss versus temperature when the MMT and OMMT particle contents are set at 1 wt%, 3 wt% and 5 wt%, respectively. They can be seen when the MMT and OMMT particle are added in PMMA, the weight loss of PMMA/MMT and PMMA/OMMT are smaller than that of virgin PMMA. In the meanwhile, the weight loss of PMMA/OMMT is smaller than that of PMMA/MMT. Table 1 shows the thermal degraded temperatures ( $T_d$ ) of PMMA/MMT and PMMA/OMMT nanocomposites at various particle content by TGA test. The thermal degraded temperature is defined as that the weight loss of nanocomposites is 5%. From this table, one can observe that the thermal degraded temperature of nanocomposites increased with increasing of particle contents. In addition, the difference between the PMMA/OMMT and PMMA/MMT nanocomposites are also recorded. The  $T_d$  is clearly higher for the PMMA/OMMT nanocomposites than for the PMMA/MMT nanocomposites. This means that the thermal stability of PMMA/OMMT nanocomposites is excellent than that of PMMA/MMT nanocomposites.

From the TGA curves in Figs. 13-15 and TGA data in Table 1 clearly show that the PMMA-montmorillonite nanocomposites exhibit enhanced thermal stability compared with virgin PMMA. The enhancement of thermal stability can be attributed to the strong interaction between PMMA chains and montmorillonite particles. The montmorillonite particles link to different PMMA chains by conalnt bonds, and reduce the degradation of PMMA. This will efficiently enhance thermal stability of the composites.

## 4 Conclusions

In this article, PMMA/MMT and PMMA/OMMT nanocomposites have been synthesized by bulk polymerization. The particles of MMT and OMMT were dispersed using forced agitation and the composites were polymerized using free radical polymerization.

From the results of XRD pattern that suggested the exfoliation of the OMMT platelets in the polymeric matrix. This specifies that intercalated structures occupy major of the MMT platelets in the polymeric matrix.

The flexural strength, flexural modulus and tensile modulus of PMMA/MMT and PMMA/OMMT nanocomposites increased with increasing of MMT and OMMT particle content. The tensile strength and notched Izod impact strength decreased with increasing of MMT and OMMT particle content. The dynamic storage modulus ( $E'$ ) of nanocomposites increased with increasing of MMT and OMMT content. At the same time, the storage modulus  $E'$  for the PMMA/OMMT nanocomposite is higher than for the PMMA/MMT nanocomposite.

The glass transition temperature ( $T_g$ ) of PMMA/MMT and PMMA/OMMT nanocomposites by DSC test were shifted to a higher temperature with increasing MMT and OMMT particle content. The weight loss of PMMA/MMT and PMMA/OMMT nanocomposites by TGA test decreased with increasing MMT and OMMT particle content. The thermal degraded temperature of PMMA/MMT and PMMA/OMMT nanocomposites increased with increasing of particle contents. This means that the thermal stability of PMMA with montmorillonite is excellent than that of virgin PMMA.

The all mechanical and thermal properties for the PMMA/OMMT nanocomposites were better than for the PMMA/MMT nanocomposites due to the OMMT particles has been organized. When the montmorillonite particles are dispersed in organic PMMA matrix, OMMT had a larger bonding force with PMMA matrix than that of MMT.

## 5 Acknowledgments

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Table 1. The  $T_d$  of nanocomposites at various particle content by TGA test.

Particle content (wt%)	PMMA/MMT	PMMA/OMMT
	$T_d$ (°C)	$T_d$ (°C)
0	251	251
1	253	260
3	259	289
5	261	315

$T_d$ : the degraded temperature is defined as that the weight loss of sample is 5%.

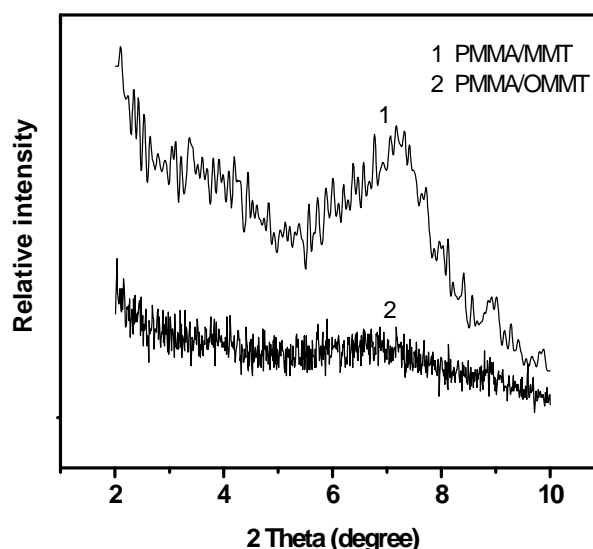


Fig. 1. The X-ray diffraction (XRD) patterns of PMMA/MMT and the PMMA/OMMT nanocomposites.

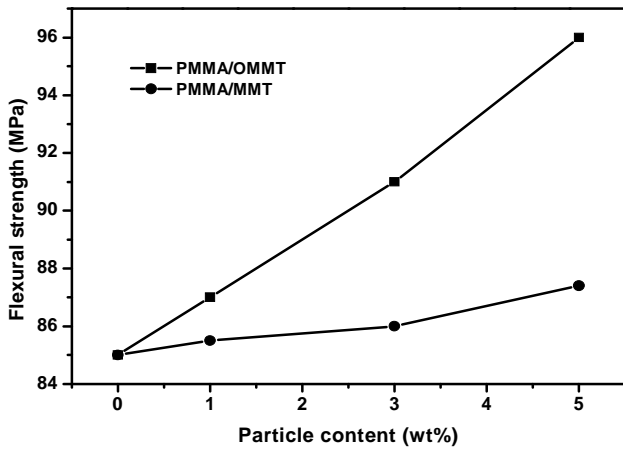


Fig. 2. Flexural strength versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

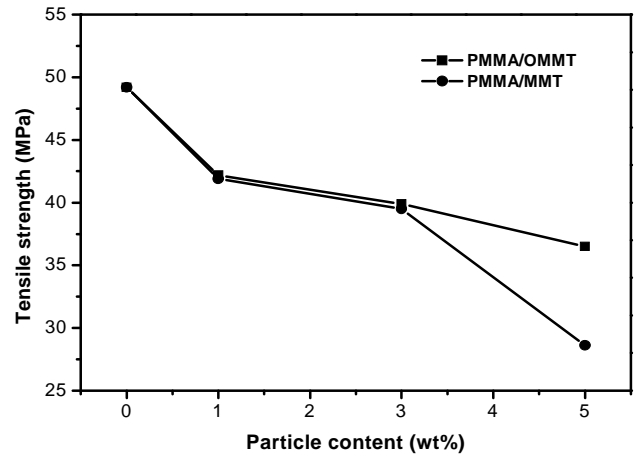


Fig. 5. Tensile strength versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

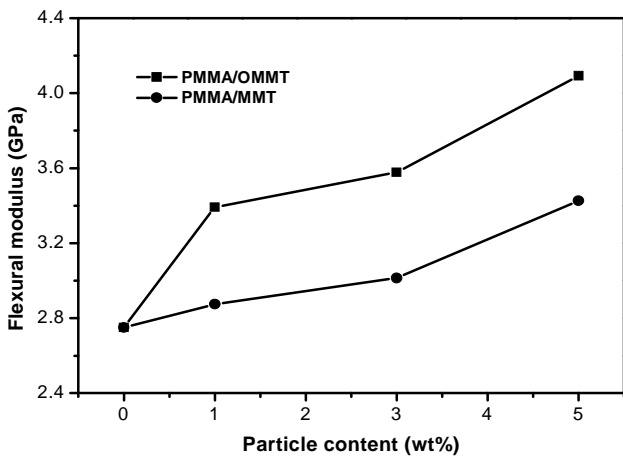


Fig. 3. Flexural modulus versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

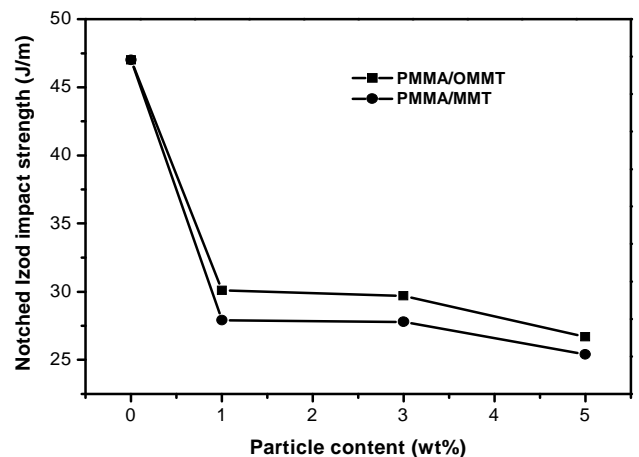


Fig. 6. Izod impact strength versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

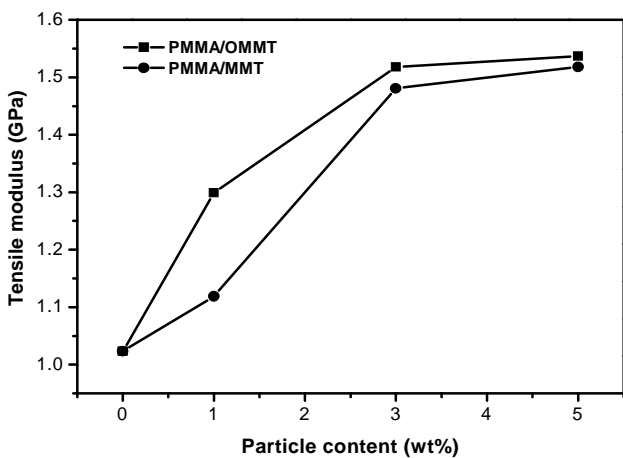


Fig. 4. Tensile modulus versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

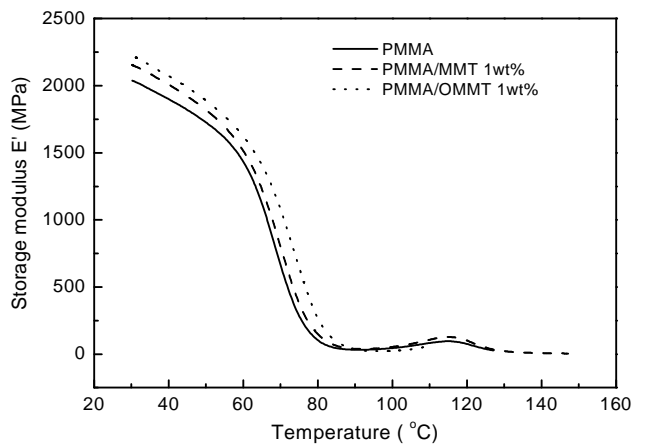


Fig. 7. Dynamic storage modulus ( $E'$ ) versus temperature of nanocomposites at 1 wt% MMT and OMMT particle contents.

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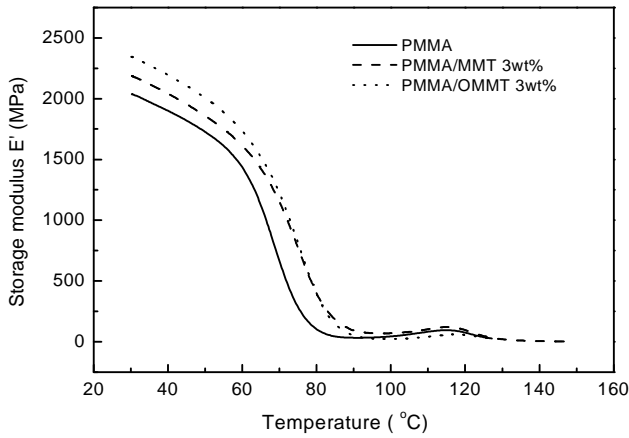


Fig. 8. Dynamic storage modulus ( $E'$ ) versus temperature of nanocomposites at 3 wt% MMT and OMMT particle contents.

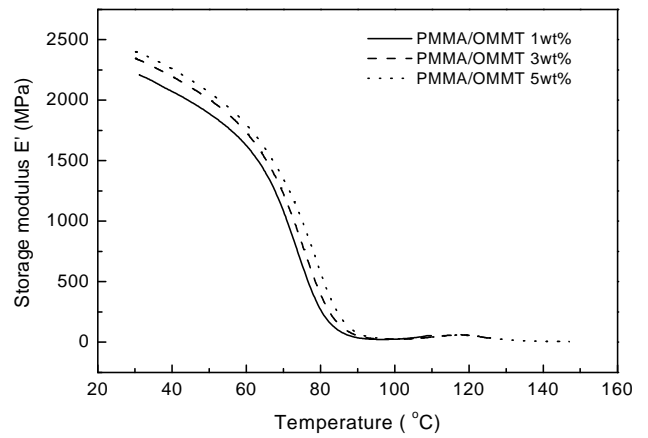


Fig. 11. Storage modulus ( $E'$ ) versus temperature of PMMA/OMMT nanocomposites at various OMMT particle contents.

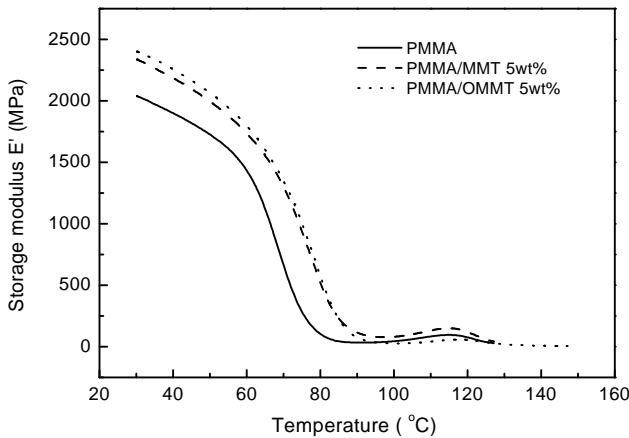


Fig. 9. Dynamic storage modulus ( $E'$ ) versus temperature of nanocomposites at 5 wt% MMT and OMMT particle contents.

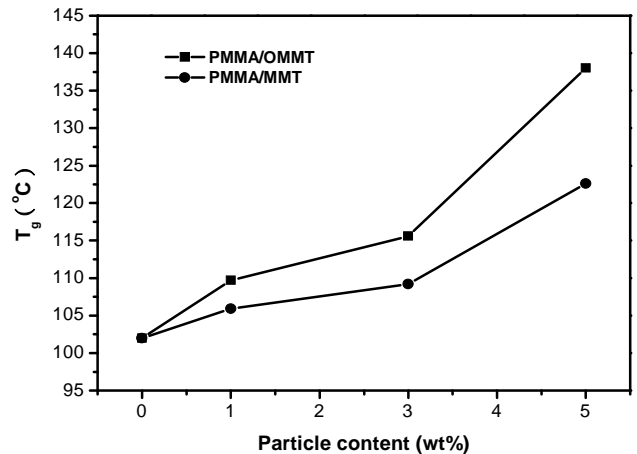


Fig. 12. Glass transition temperature ( $T_g$ ) versus montmorillonite particle content of PMMA/MMT and PMMA/OMMT nanocomposites.

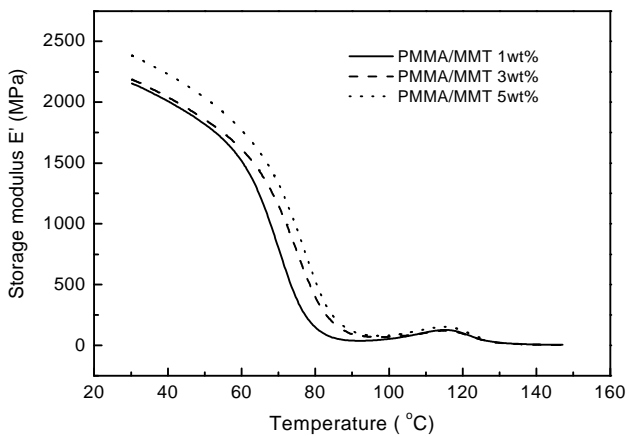


Fig. 10. Storage modulus ( $E'$ ) versus temperature of PMMA/MMT nanocomposites at various MMT particle contents.

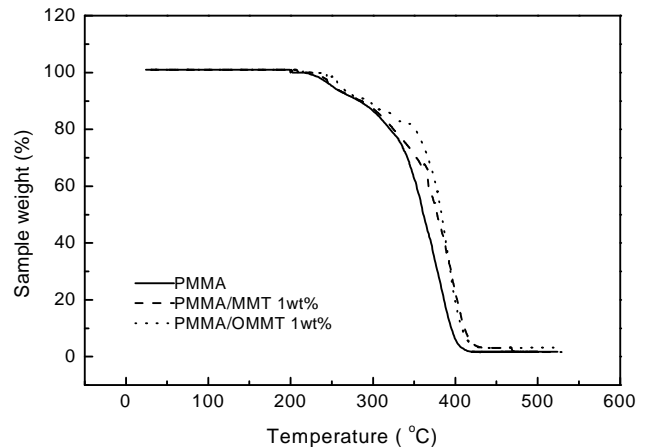


Fig. 13. Weight loss versus temperature of nanocomposites at 1 wt% MMT and OMMT particle contents.

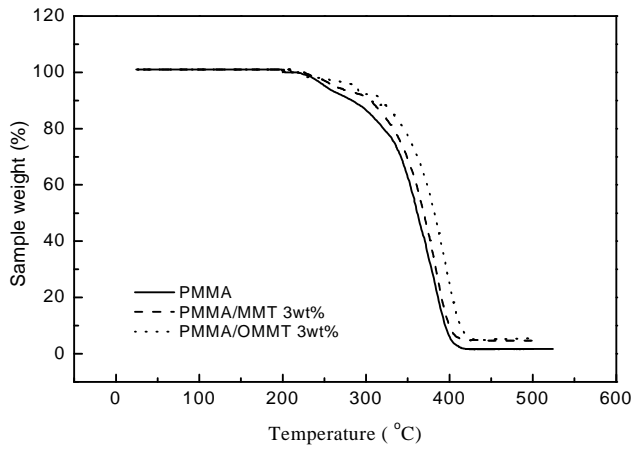


Fig. 14. Weight loss versus temperature of nanocomposites at 3 wt% MMT and OMMT particle contents.

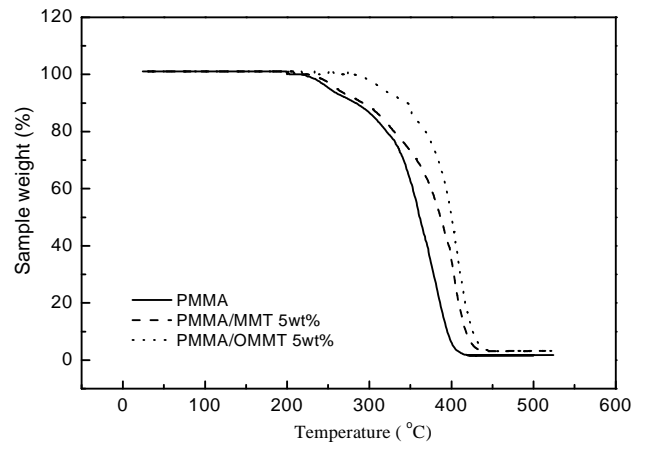


Fig. 15. Weight loss versus temperature of nanocomposites at 5 wt% MMT and OMMT particle contents.