



UNIVERSITI SAINS MALAYSIA

# **Laporan Akhir Projek Penyelidikan Jangka Pendek**

## **High Performance Recyclable Poly(butylene terephthalate) / Organo- Montmorillonite Nanocomposites**

**by  
Dr. Chow Wen Shyang**

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**To** : **Malaysia Toray Science Foundation**

**From** : **Dr Chow Wen Shyang**

**Name of University** : **Universiti Sains Malaysia**

**Correspondence Address** : **School of Materials and Mineral Resources Engineering,  
Engineering Campus  
Universiti Sains Malaysia  
Nibong Tebal 14300  
Penang  
Malaysia**

**Tel No.** : **04-5996160**

**Fax No.** : **04-5941011**

**Email Address** : **chowwenshyang@yahoo.com**  
**shyang@eng.usm.my**

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# FINAL REPORT

## HIGH PERFORMANCE RECYCLABLE POLY(BUTYLENE TEREPHTHALATE)/ORGANO-MONTMORILLONITE NANOCOMPOSITES

**Chow Wen Shyang**

School of Materials and Mineral Resources Engineering, Engineering Campus,  
Universiti Sains Malaysia, Nibong Tebal 14300 Penang, Malaysia

### 1. ABSTRACT/SUMMARY OF REPORT

3wt% of organo-montmorillonite (OMMT) was incorporated into poly(butylene terephthalate) (PBT) by using melt intercalation method. The PBT/OMMT nanocomposites were produced by using twin screw extrusion followed by injection molding. The effects of thermal cycles (2 times extrusion followed by injection molding) were studied on both PBT and PBT/OMMT nanocomposites. The samples were characterized by using tensile tests, field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray analysis (EDX), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The intercalation of the OMMT in the PBT was confirmed by using XRD. The tensile modulus and strength of PBT was slightly improved by addition of OMMT. Multiple melting endothermic peaks were observed in both PBT and PBT/OMMT nanocomposites. DSC results revealed that OMMT improved the crystallinity of PBT. The percentage retention in tensile properties of PBT/OMMT(E2) intercalated nanocomposites (i.e. two times extrusion followed by injection molding) is more than 96%. The melting temperature, crystallization temperature and degree of crystallinity of PBT/OMMT(E2) is comparable with PBT/OMMT(E1) (i.e. one time extrusion followed by injection molding). This indicates that PBT/OMMT intercalated nanocomposites exhibit good retention-ability in tensile and thermal properties after subjected to two times twin-screw extrusion followed by injection molding.

## 2. INTRODUCTION

### 2.1 BACKGROUND INFORMATION

In recent years, polymer nanocomposites have attracted great interest. Nanocomposites offer new technological and economical benefits. The incorporation of nanometer scale reinforcement (e.g. layered silicates of clay, nanofibre, nanotubes, metal nanoparticles in polymeric materials) may dramatically improve selected properties of the related polymer. These nanocomposites exhibit superior properties such as enhanced mechanical properties, reduced permeability, and improved flame retardancy.

The present research were focused on the study of thermoplastics nanocomposites based on poly(butylene terephthalate) (PBT). PBT is a thermal engineering plastic. PBT nanocomposites were produced via polymer melt intercalation method (extrusion and injection molding) by incorporation of organophilic modified montmorillonite (organoclay, OMMT). Naturally occurring montmorillonite is the most abundant member of the smectite family of clays. Ion exchange is widely practiced to modify the montmorillonite's surface to increase its compatibility with mostly hydrophobic polymer. Direct polymer melt intercalation is the most attractive because of its low cost, high productivity and compatibility with current processing techniques (i.e. extrusion and injection molding). It is believed that the mechanical properties of a nanocomposites is governed by several factors, these may include (i) interfacial interaction between polymer and clay, (ii) dispersion and distribution of clay, (iii) degree of exfoliation/intercalation of the clay, and (iv) anisotropy of the clay. The exfoliation of the clay in polymer matrix could be induced by shearing (via extrusion and injection molding processes).

From the literature review, most of the nanocomposite produced containing a mixture of exfoliated/intercalated/agglomerated structure. This can be evidenced by Transmission Electron Microcopy (TEM), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). This is may be attributed to the shearing-induced exfoliation is limited by one-step extrusion and injection molding. Thus, in this research work, attempt were made to study the shearing-induced exfoliation on the PBT/OMMT nanocomposites by repeated extrusion processes. It is hypothesizing that higher degree of exfoliation could be achieved by repeated shearing process (e.g. analog to recycling).

Hence, it is expected that the retention-ability of mechanical properties for recycle-PBT/OMMT nanocomposites could be enhanced by intercalation and exfoliation phenomenon.

## **2.1 RESEARCH OBJECTIVES**

- (a) To improve the mechanical and thermal properties of poly(butylene terephthalate) by organo-montmorillonite.
- (b) To develop a high performance recyclable PBT/OMMT nanocomposites by direct melt intercalation method.
- (c) To study the mechanical retention-ability of PBT/OMMT nanocomposites upon subjected to repeated extrusion and injection molding processes.

## **3. METHODOLOGY**

Generally, PBT/OMMT nanocomposites were prepared through extrusion (melt compounding) followed by injection molding. Several techniques and characterization methods were carried out to determine the mechanical, morphological and thermal properties of PBT nanocomposites, these including tensile tests, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Dynamic Mechanical Thermal Analysis (DMTA), and Differential Scanning Calorimetry (DSC). Attempt was made to study the recycle-ability of PBT nanocomposites.

### **3.1 MATERIALS**

Thermoplastic : Poly(butylene terephthalate) (PBT)

Filler : Organophilic modified montmorillonite (OMMT)

In this work, 3wt% of OMMT was incorporated into PBT. The samples were labeled as PBT(E1), PBT/OMMT(E1), PBT(E2) and PBT/OMMT(E2). For PBT(E1) and PBT/OMMT(E1) nanocomposites, the samples were prepared by one time extrusion followed by injection molding. However, for PBT(E2) and PBT/OMMT(E2) nanocomposites, the samples were prepared by two times extrusion processes followed by injection molding.

## **3.2 PBT/OMMT NANOCOMPOSITES PREPARATION**

### **3.2.1 Extrusion**

PBT and OMMT were physically pre-mixed prior to extrusion. Melt compounding of the PBT/OMMT nanocomposites was performed using counter-rotating twin screw extruder (Berstoff). The extrusion zone temperature were ranged from 220-240°C. The screw speed was set at 50 rpm. Prior to extrusion, PBT and OMMT were dehumidified by using a vacuum oven at 80°C for 24 h. The extrudates were pelletized with the Haake pelletizer.

### **3.2.2 Injection Molding**

The pellets were injection molded into standard tensile and flexural bar using a Niigata AN 50 injection molding machine. Injection molding temperature were ranged from 220-240°C. Prior to injection molding, all pellets were dehumidified in vacuum oven (80°C for 24 h). The tensile test specimens were molded in Type I according to ASTM D 638.

## **3.3 MATERIALS PROPERTIES CHARACTERIZATION**

### **3.3.1 Mechanical Properties**

#### **3.3.1.1 Tensile**

Tensile tests were carried out with an Instron-5582 machine at 23°C, according to ASTM D638, at a crosshead speed of 50 mm/min. Tensile modulus, tensile strength and elongation at break were evaluated from the stress-strain data.

### **3.3.2 Thermal Properties**

#### **3.3.2.1 Dynamic Mechanical Thermal Analysis (DMTA)**

Dynamic mechanical thermal analysis (DMTA) test were conducted according ASTM D5023. The storage modulus ( $E'$ ), loss modulus, and mechanical loss factor ( $\tan \delta = E''/E'$ ) as a function of temperature ( $T$ ), were assessed by using an Mettler Toledo DMA 861, Switzerland. DMTA spectra were taken in 3-point bending mode at 1 Hz frequency in a temperature ranged from -30°C to 180°C.

### 3.2.2 Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior of the PBT/OMMT nanocomposites were studied under nitrogen atmosphere by differential scanning calorimetry (Perkin Elmer DSC-6), using 8-10 mg sample sealed into aluminum pans. In order to avoid any effect of moisture, all the test specimens were dried using vacuum oven at 80°C prior to the measurements. Calibration was carried out using indium ( $T_m = 156.5^\circ\text{C}$ ,  $\Delta H_m = 28.45$  J/g). The temperature was raised from 30 to 260°C at a heating rate of 10°C/min, and after a period of 5 min., it was swept back at -10°C/min. Second heating similar to the first was performed in order to erase the thermal history. The melting thermograms were recorded from the second heating.

### 3.3.3 MORPHOLOGICAL STUDIES

#### 3.3.3.1 Scanning Electron Microscopy (SEM)

The morphology of the PBT and PBT/OMMT specimens was inspected in a field-emission scanning electron microscopy (FESEM, Zeiss Supra 35VP). The samples were gold coated to avoid electrostatic charging during examination. Energy Dispersive X-ray Analysis (EDX)(EDAX Falcon System) was used to analyze the occurrence of elements in the specimens that sputtered with gold.

#### 3.3.3.2 X-ray Diffraction (XRD)

Wide-angle X-ray spectra were recorded with a D 500 diffractometer (Siemens) in step scan mode using Ni-filtered Cu  $K\alpha$  radiation (0.1542 nm wavelength). The interlayer spacing of the organoclay was derived from the peak position ( $d_{001}$ -reflection) in the XRD diffractograms according to the Bragg equation (c.f. Equation 3.1).

$$\lambda = 2d\sin\theta \quad (\text{Equation 3.1})$$

where,  $\lambda$  = wave length of the X-ray radiation used in the diffraction experiment

$d$  = the spacing between diffractive lattice planes, and

$\theta$  = the measured diffraction angle

## 4. RESULTS

### 4.1 X-RAY DIFFRACTION (XRD)

XRD is the most commonly used to probe the nanocomposites structure and occasionally to study the kinetic of the polymer melt intercalation owing to its easiness and availability. In XRD patterns the interlayer spacing of clay can be determined by the site of the peak corresponding to the {001} basal reflection of MMT (referred to as  $d_{001}$  peak). Figure 1a shows the XRD patterns in the range of  $2\theta = 1-10^\circ$  for OMMT. The XRD spectrum exhibits a broad intense peak at around  $2\theta = 4.35^\circ$  corresponding to a basal spacing of 2.03nm. Figure 1b shows the XRD patterns for the PBT and PBT/OMMT nanocomposites. The XRD spectra of both PBT/OMMT(E1) and PBT/OMMT(E2) show a new peak at around  $2\theta = 2.85^\circ$  corresponding to a basal spacing of 3.10nm. Note that the  $d_{001}$  peaks in PBT/OMMT nanocomposites are shifted to a lower angle. This indicates that PBT chains diffuse into the gallery of the OMMT and the inter-spacing of silicate layers in OMMT is swollen to a larger distance. This is likely reflects that the OMMT has been successfully intercalated in the PBT matrix. For intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height (interlayer spacing). The increment of the basal spacing indicates that the clay layers are partially intercalated and partially exfoliated in the PBT matrix.



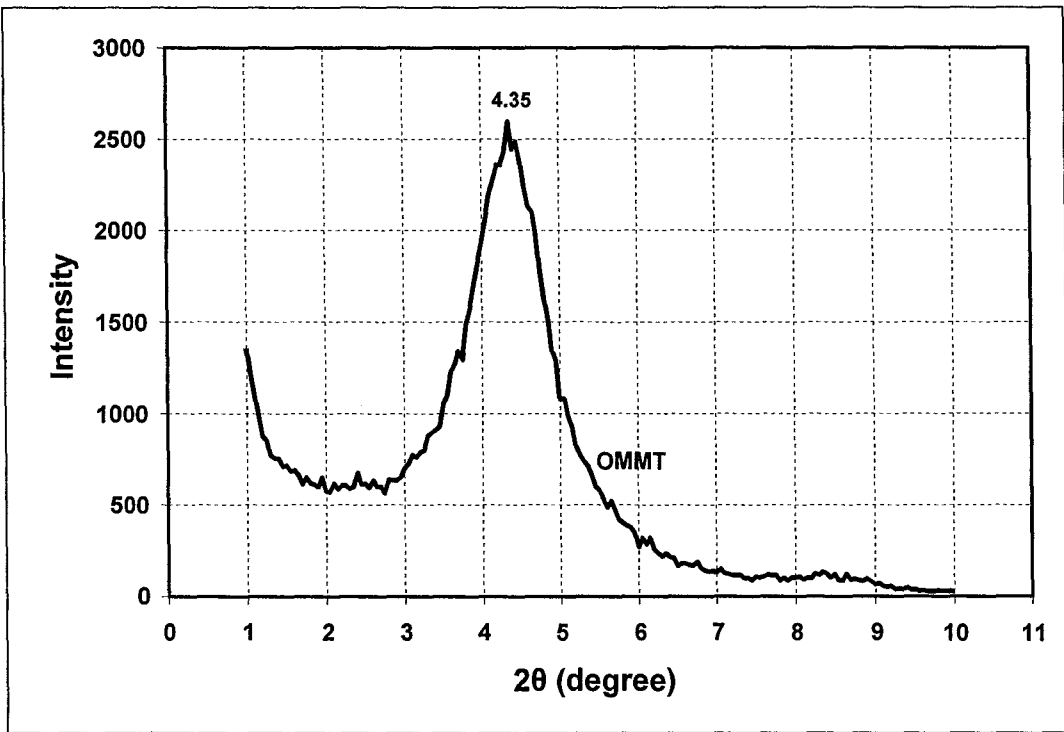


Figure 1a: XRD spectra of OMMT.

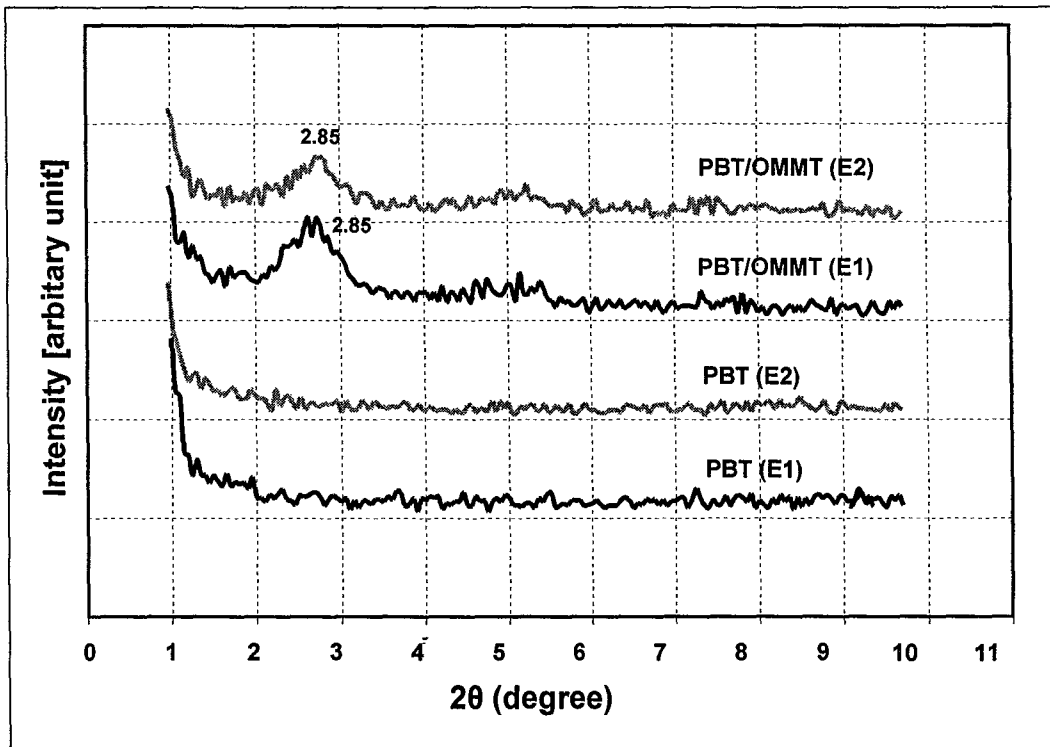


Figure 1b: XRD spectra of PBT and PBT/OMMT nanocomposites.

## 4.2 MECHANICAL PROPERTIES

Table 1 shows the effects of OMMT on the tensile properties of PBT. The tensile modulus of PBT increased with the addition of OMMT. This is attributed to the stiffness and reinforcing effects of OMMT. The OMMT is able to act as reinforcing filler due to its high aspect ratio and platelet structure. The possibility that the modulus improvements are due to the constraint of the polymer chains by the interaction with the clay surface. Note that the tensile strength of PBT/OMMT nanocomposites is higher than that of unfilled PBT. This is believed to be associated to the interfacial interaction between the PBT and OMMT. The elongation at break of PBT decreased in the presence of OMMT. This is likely due to the co-existence of agglomerated layered silicates, and intercalated OMMT silicate layers in the PBT matrix. It is interesting to note that the percentage retention of the tensile properties of PBT/OMMT after subjected to thermal cycle (i.e. 2 times extrusion followed by injection molding) is more than 96% for tensile modulus, strength and elongation at break.

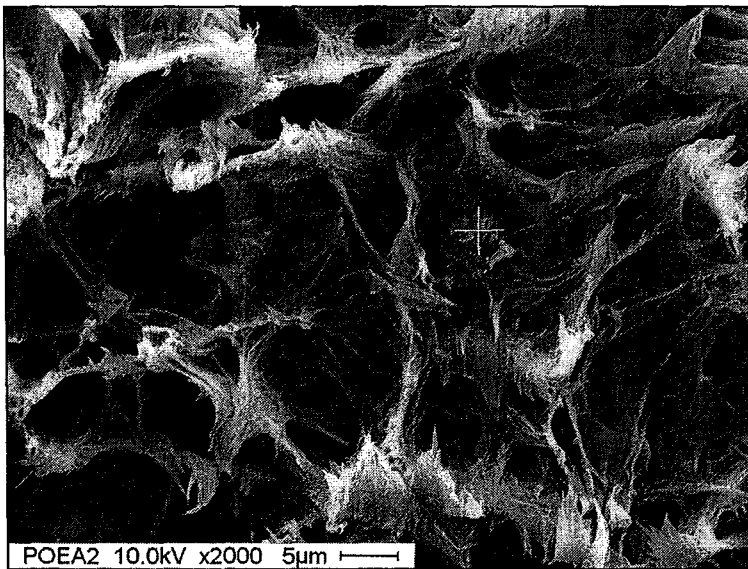
**Table 1: Tensile properties of PBT and PBT/OMMT nanocomposites.**

Tensile Properties	PBT(E1)	PBT(E2)	PBT/OMMT(E1)	PBT/OMMT(E2)
Tensile Modulus (GPa)	1.86	1.75 [94.1%]	1.96	1.94 [99.0%]
Tensile Strength (MPa)	41.2	40.7 [98.8%]	49.5	47.9 [96.8%]
Yield Strength (MPa)	52.6	51.1 [97.1%]	52.4	50.7 [96.8%]
Elongation at break (%)	15.5	14.9 [96.1%]	4.6	4.6 [100%]

\* The values in the parentheses are the percentage retention of the tensile properties after thermal cycles (2 times extrusion followed by injection molding).

### 4.3 MORPHOLOGICAL PROPERTIES

Figure 2a shows the tensile fractured plane taken from the PBT/OMMT(E1) sample, it can be seen that particle adhere with PBT fibrillated structure. The particle size is approximately  $6\mu\text{m}$ . This indicates that some of the OMMT particles did not intercalated/exfoliated. Further information was received by using EDX. Figure 2b shows the EDX spectra of the OMMT particle (shown by arrow). In these EDX spectra, seven elements can be observed, i.e. C, O, Mg, Al, Si, Au, and Pd. The carbon is due to the organic intercalant in the OMMT. The Au and Pd observed in the EDX are associated with the coating materials sputtered on the sample. All remaining elements represent components of the montmorillonite. The chemical structure of montmorillonite is  $M_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$ , where M=monovalent cation and x = degree of isomorphous substitution. The evidence taken from the FESEM and EDX confirmed the co-existence of un-exfoliated layered silicates in the PBT matrix.



**Figure 2a: FESEM micrograph taken from the fractured surface of PBT/OMMT(E1).**

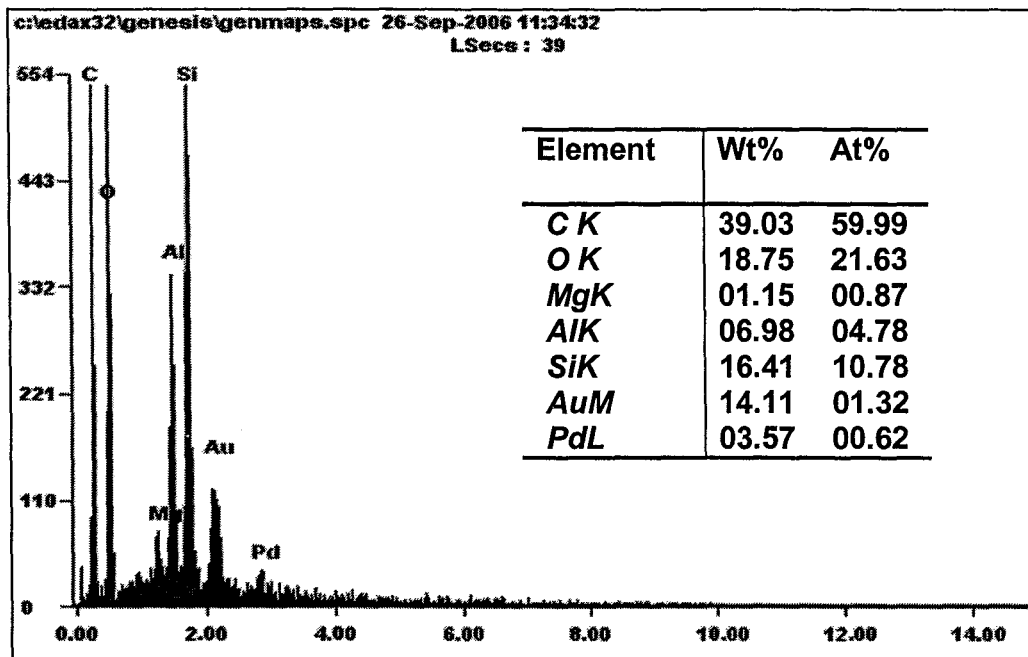


Figure 2b: EDX spectra taken from the PBT/OMMT(E1) sample (c.f. Figure 2a-particle shown by arrow).

#### 4.4 THERMAL PROPERTIES

Table 2 shows the melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of PBT and PBT/OMMT nanocomposites recorded from DSC. The endothermic peak of pure PBT appears at 227°C and corresponding to the melting temperature ( $T_m$ ). Note that only one melting endothermic peak is observed from first heating, however, two melting endothermic peaks are recorded during second heating for both PBT and PBT/OMMT nanocomposites. Multiple melting endothermic peaks are due to the melting-recrystallization process during heating. Double melting was observed in neat PBT and interpreted in terms of reorganization processes occurring during the second heating. The occurrence of the small peaks which appear as shoulders at a slightly lower temperatures may due to the changes of crystal structure of PBT, to changes in the crystallite size or perfection, or to variation of crystal thickness. Addition of OMMT did not alter the  $T_m$

and  $T_c$  of PBT significantly. The degree of crystallinity ( $\chi_c$ ) was calculated from the melting enthalpy  $\Delta H_m$  (J/g) to with  $\Delta H_f = 140$  J/g (the theoretical value of enthalpy for 100% crystalline PBT homo-polymer). It is interesting to note that the degree of crsytallinity of PBT increased in the presence of OMMT. This is attributed to the nucleation effects of OMMT and the improvement in the crystal perfection of PBT. From the thermal properties shown in Table 2, it can be seen that the  $T_m$ ,  $T_c$  and  $\chi_c$  of PBT(E2) and PBT/OMMT(E2) which were subjected to thermal cycle (i.e. 2 times extrusion followed by injection molding) is essentially the same as that of PBT(E1) and PBT/OMMT(E1) (i.e.1 time extrusion followed by injection molding). This suggests that the extra one time extrusion thermal cycles did not produce any apparent effect on the thermal behavior of PBT and PBT/OMMT nanocomposites.

The dynamic storage modulus and loss modulus versus temperature traces for the PBT and PBT/OMMT nanocomposites is shown in Figure 3a & b, respectively. It can be seen that PBT/OMMT nanocomposites exhibits higher storage modulus than PBT (c.f. Figure 3a). The storage modulus of PBT(E2) is relatively higher than that of PBT(E1) in the whole temperature range. This is maybe attributed to the increasing of crystallization and molecular arrangement for PBT after subjected to second time of extrusion. For the OMMT filled PBT, the storage modulus of PBT/OMMT(E1) and PBT/OMMT(E2) was likely influenced by temperature zone. In the glassy zone (below 40°C), the storage modulus of both PBT/OMMT(E1) and PBT/OMMT(E2) is almost the same. In the glass transition zone (40°C-65°C), the storage modulus of PBT/OMMT(E1) was slightly higher than that of PBT/OMMT(E2). At the temperature more than 65°C, it can be seen that the storage modulus of PBT/OMMT(E2) is relatively higher compared to PBT/OMMT(E1).

Figure 3b shows the loss modulus versus temperature traces for the PBT and PBT/OMMT nanocomposites. Dynamic relaxation peak of PBT(E1) and PBT(E2) was recorded at 50.5°C and 53.8°C, respectively. On the other hand, the dynamic relaxation peak for PBT/OMMT(E1) and PBT/OMMT(E2) are 61.5°C and 63.0°C, respectively. Note that the dynamic relaxation peak of PBT/OMMT nanocomposites is higher than that of unfilled PBT. This is maybe attributed to the confinement of the intercalated polymer chains within the silicate clay galleries which could prevent segmental motions of the polymer chains.

**Table 2: Thermal properties of PBT and PBT/OMMT nanocomposites.**

	Thermal properties					
	$T_m^a$ (°C)	$T_{m,1}^b$ (°C)	$T_{m,2}^b$ (°C)	$T_c$ (°C)	$H_m$ (J/g)	$\chi_c$ (%)
PBT(E1)	227.7	216.1	226.8	191.4	21.7	15.5
PBT(E2)	227.4	215.6	226.1	191.4	22.3	15.9
PBT/OMMT(E1)	228.4	215.6	226.4	192.0	29.2	21.7
PBT/OMMT(E2)	227.3	215.7	226.1	192.9	29.9	22.2

Remarks:

$T_m^a$  taken from the first heating thermograms recorded by DSC

$T_{m,1}^b$  taken from the second heating thermograms recorded by DSC

$T_{m,2}^b$  taken from the second heating thermograms recorded by DSC

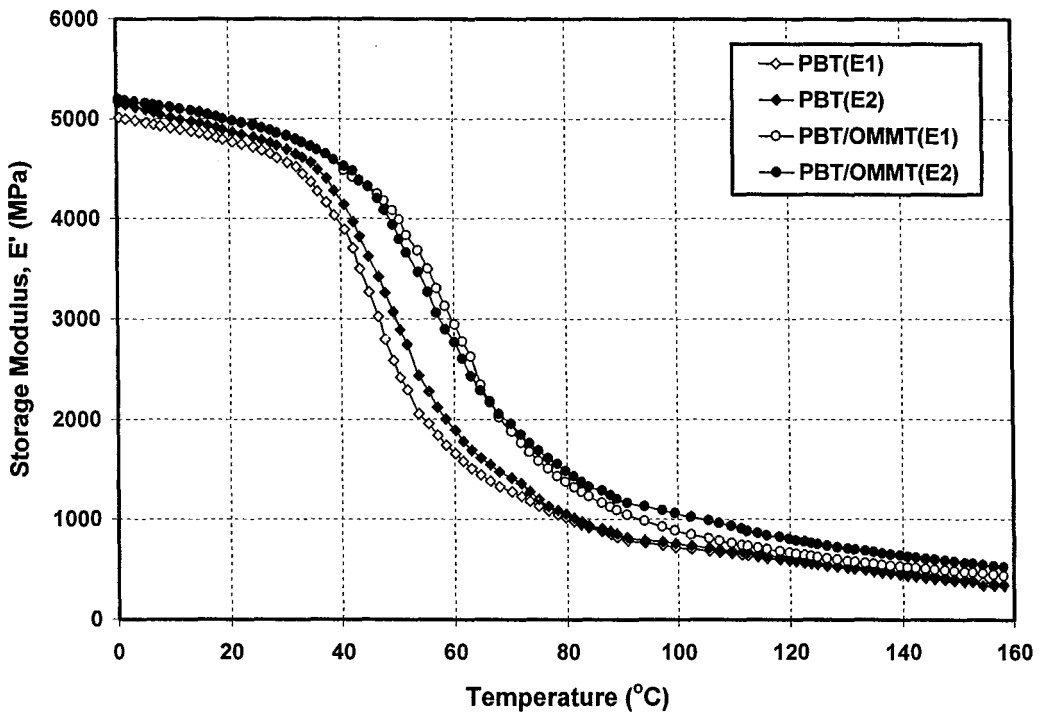


Figure 3a: Storage modulus vs temperature traces for PBT and PBT nanocomposites.

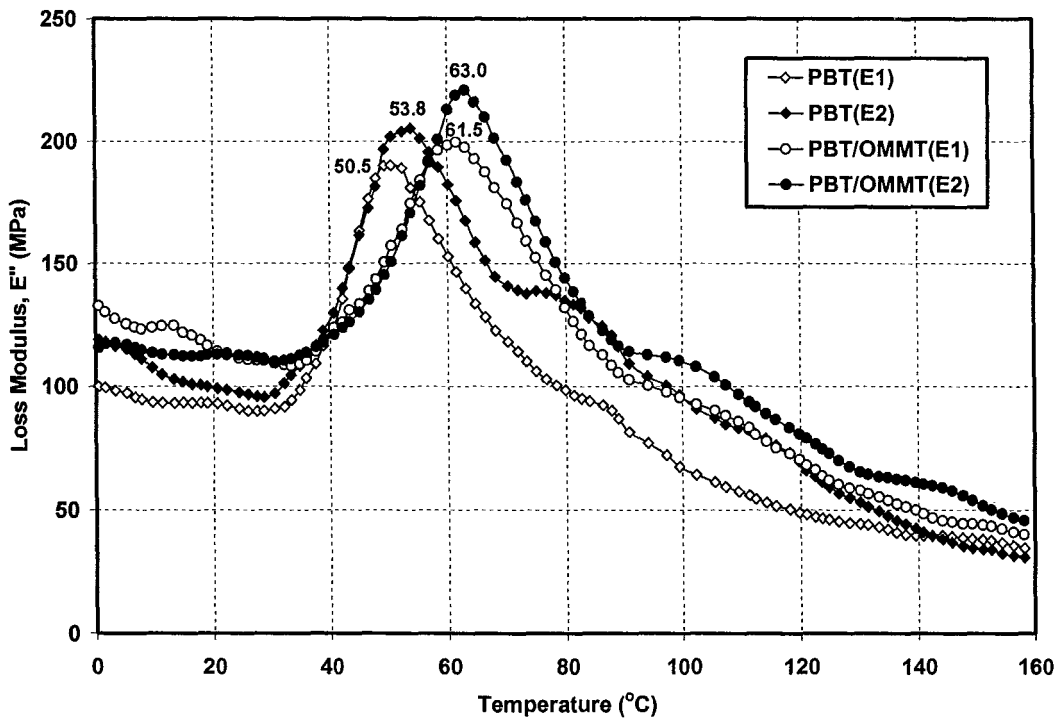


Figure 3b: Loss modulus vs temperature traces for PBT and PBT nanocomposites.

## **5. DISCUSSION**

### **5.1 SIGNIFICANT FINDINGS**

Tensile modulus and strength of PBT/OMMT was slightly improved attributed to the confinement of polymer chains and increment of crystallinity for PBT. Intercalated PBT/OMMT nanocomposites were successfully formed. Two times twin-screw extrusion followed by injection molding did not influence the thermal properties of PBT/OMMT nanocomposites significantly. The percentage retention in tensile properties of PBT/OMMT(E2) intercalated nanocomposites is more than 96%. Thus, repeated extrusion and injection molding processes could enhance the shear-induced melt intercalation of OMMT silicate layers in poly(butylene terephthalate).

### **5.2 INNOVATIVE AND CREATIVE APPROACHES**

Repeated extrusion and injection molding processes could induce and facilitate the intercalation and exfoliation of OMMT silicate layers. This approach could be analog to recycling process, where the PBT materials parts can be re-extruded and re-injection molded. The retention-ability of the PBT/OMMT materials is comparable excellent.

### **5.3 ACHIEVEMENTS OF RESEARCH OBJECTIVES**

The mechanical and thermal properties of poly(butylene terephthalate) was slightly improved by the addition of organo-montmorillonite. The mechanical retention-ability of PBT/OMMT nanocomposites upon subjected to repeated extrusion and injection molding processes is excellent, which is more than 96%. A high performance intercalated PBT/OMMT nanocomposites with high recycle-ability was produced by direct melt intercalation method.

### **5.4 PROBLEMS ENCOUNTERED AND STEPS TAKEN TO OVERCOME THEM**

Problem: To find suitable processing parameter of PBT/OMMT nanocomposites.

Solution: Adjust temperature zone and screw speed in order to obtain good flow-ability of PBT/OMMT nanocomposites.



## **5.5 FUTURE DIRECTION**

### **Future Research Works:**

- (a) Research and Development of recyclable PBT/OMMT nanocomposites using:
  - (i) compatibilizer
  - (ii) blending with other engineering plastics
  - (iii) different types of inorganic fillers

## **6. OUTCOMES/OUTPUT OF RESEARCH**

W.S. Chow (2008). Tensile and Thermal Properties of Poly(butylene terephthalate)/Organo-montmorillonite Nanocomposites. Malaysian Polymer Journal 3(1): 1-13.

## **7. EXECUTIVE SUMMARY**

The research findings achieve the original objectives. Repeated extrusion and injection molding processes could induce and facilitate the intercalation and exfoliation of OMMT silicate layers. This approach could be analog to recycling process, where the PBT materials parts can be re-extruded and re-injection molded. The retention-ability of the PBT/OMMT materials is comparable excellent. The next step is to further study on the fundamental of recycling and intercalation/exfoliation mechanism of OMMT in PBT. In the future, more research work will be carried on the development of high performance recyclable poly(butylene terephthalate) nanocomposites.

## **8. FINANCIAL STATEMENT**

Please kindly refer to the **ATTACHMENT 1** (Financial Statement)

## **9. CERTIFICATION/VERIFICATION OF REPORT**

Please kindly refer to **ATTACHMENT 2** (Letter of Certification/Verification of Report)

***Report prepared by:***

***Dr Chow Wen Shyang***  
***Universiti Sains Malaysia***