Preparation and characterization of PET/SEBS incorporated with organomontmorillonite

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This study is focused on the characterization of polyethylene terephthalate (PET)/Styrene-Ethylene-Butylene-Styrene (SEBS)/Organomontmorillonite (OMMT) blends. SEBS-g-MA is used as compatibilizer and SEBS is the impact modifier at 30 %wt. The compounds were blended by twin-screw extruder and molded for test specimen by injection molding. The effect of OMMT types (Cloisite15A and Cloisite30B) and contents (1 and 3 %w/w) on properties of PET blends with SEBS and SEBS-g-MA were investigated. The PET composites incorporated with Cloisite15A had higher impact strength and %elongation at break whereas lower tensile strength than the one with Cloisite30B. Comparing with PET/SEBS/SEBS-g-MA blends, adding OMMT into PET/SEBS/SEBS-g-MA would increase thermal property. However, it had no significant changes with higher OMMT. %Crystallinity of PET would be increased with OMMT contents. PET/SEBS/SEBS-g-MA had lower %LOI but higher burning rate compared with PET. However, the addition of OMMT could improve flame retardant properties of PET blends. Addition of Cloisite15A and Cloisite30B into PET/SEBS/SEBS-g-MA increased %LOI. From UL 94 tests, polymer composites could be classified in HB class. The burning rate of polymer composites was decreased with increasing OMMT due to decomposition of OMMT act as a barrier to inhibit combustion.

1. Introduction

Polymers are commonly used in everyday life because the materials have more distinctive properties and could replace the other materials. Polyethylene terephthalate (PET) is one of engineering material which has excellent processability, rigidity, thermal stability, resistance to oil, recyclability, light weight and relatively low cost. Nevertheless, one major disadvantage of PET is the notch sensitive, which decrease the impact properties of PET and limit the engineering applications of this material [1]. Blending PET with thermoplastic elastomer such as Styrene-Ethylene-Butylene-Styrene (SEBS) is an efficient way to increase its toughness. SEBS is saturated elastomer [2], consisting of a hard end-block polystyrene phase and a soft elastomeric phase. Thus SEBS can act as impact modifier [3]. However, due to the immiscibility between PET and SEBS, SEBS-g-MA was used as the compatibilizer in the system.
The pristine clay minerals are not compatible with most polymeric systems due to hydrophilic nature of clay minerals. However, cation exchange modification of clay minerals with long chain ammonium or phosphoniumquaternary ions increases the inter-layer spaces and also the dispersibility of layered-silicates by increasing compatibility with polymers. The clay-polymer compatibility as well as the exfoliation of clay-layers strongly depends on type of modifier and the polarity of polymer matrix [4]. In our study, the two different OMMT i.e., Cloisite15A (montmorillonite modified with dimethyl dehydrogenated tallow quanternary ammonium) and Cloisite30B (montmorillonite modified with methyl tallow bis-2-hydroxethyl quanternary ammonium) are used. The incorporation of this nanoclay will generally improve the Young’s modulus and tensile strength of the thermoplastic elastomer nanocomposite while the elongation at break decreased [3]. Additionally, the incorporation of a relatively low quantity of nanoclay in the polymer matrix creates a protective layer during combustion that effectively shields the underlying polymer and limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material. [5] This article aims to study the effect of OMMT types and content on mechanical, morphology and thermal properties and flame retardant of PET blends.

2. Experimental

2.1 Materials
Polyethylene terephthalate (PET) was obtained from Indorama Ventures Public Co., Ltd. Styrene-Ethylene-Butylene-Styrene (SEBS) was purchased from Toyota Tsusho (Thailand) Co., Ltd. SEBS-g-MA used as a compatibilizer, was obtained from Connell Bros. (Thailand) Co., Ltd. Organically modified montmorillonite is modified with dimethyl dehydrogenated tallow quanternary ammonium called as Cloisite15A and Cloisite 30B is montmorillonite modified with methyl tallow bis-2-hydroxyethyl quanternary ammonium as shown in Table 1.

| Clay type     | Chemical structure | D spacing (nm) |
|---------------|--------------------|----------------|
| Cloisite15A   | CH₃ | N—HT            | 3.15           |
|               | ClI₃ |                |                |
| Cloisite30B   | C₄H₁₀ | N—CH₄OHCH₃ | 1.81           |
|               | HOCH₃ |                |                |

2.2 Preparation of PET blends
The master-batch was prepared by mixing organoclays with SEBS in chloroform where the concentration of organoclays was 30 phr with respect to neat SEBS. Initially, organoclays and SEBS were dried at 70 ºC for 24 h to remove the moisture. The SEBS was dissolved in chloroform until it became homogeneous mixture then added organoclays to the SEBS solution and stirred continuously with a magnetic stirrer for 4 h to disperse the clay-platelets uniformly in SEBS solution. The SEBS/organoclays dispersion was cast on a tray and placed in the oven at 70 ºC for 24 h to remove the solvent. After solvent evaporation, a sheet was formed, which was cut to small pieces.

PET was dried at 100 ºC for 24 h. Then, PET, master-batch of SEBS/OMMT and SEBS-g-MA were mixed and melt blended using twin screw extruder (EN-MACH, SHJ-25). The temperature setting
along the extruder barrel ranged from 155-250 °C at screw speed 30 rpm. Cloisite15A and Cloisite 30B is varied at the content of 1.00 and 3.00 %wt. The pellets were molded for tested specimen by injection molding machine (Sumitomo Heavy industries, SG50M).

2.3 Characterization
The mechanical properties were examined by impact tests which performed by Izod testing method according to ASTM D-256 on the notched samples. The work of the pendulum was 1.0 J and the amount of energy required to break the sample were recorded. The tensile tests according to ASTM D-638 were performed on a universal testing machine (Instron 5956) at 50 kN load with 50 mm/min elongation rate. Thermogravimetric analysis (TGA) was performed by using a Thermogravimetric Analyzer (TGA7, Perkin Elmer Co., Ltd) with the temperature scan mode. The samples were heated from 50 °C to 700 °C at heating rate of 10 °C/min in nitrogen atmosphere. Differential scanning calorimeter (DSC) was performed by Perkin Elmer Pyris 1 to obtain the heating thermogram and the percent of crystallinity under nitrogen flow at heating rate of 10 °C/min and temperature range was 50-300 °C. The morphology and fracture surfaces of selected samples after impact and tensile tests were examined via scanning electron microscopy (SEM). The fracture surfaces of the samples were coated with Cu-Pt prior to SEM observation. Flammability of samples was determined according to ASTM D3801 and ASTM D635 for UL-94 vertical and horizontal burning test respectively. The Limiting Oxygen Index (LOI) according to ASTM D2863.

3. Results and discussion

3.1 Mechanical Properties
Impact strength of PET/SEBS/SEBS-g-MA with different types and content of OMMT (Cloisite15A and Cloisite30B) are shown in Figure 1. The incorporation of OMMT into PET/SEBS/SEBS-g-MA leads to considerably reduce the impact strength because OMMT particles are relatively stiff that could obstruct the mobility of polymer chains.

Considering two types of OMMT, Cloisite 15A is less polarity than Cloisite 30B. In this research, OMMT is dispersed in SEBS phase (Master-batch) before it melt-blended with PET. Cloisite15A is well dispersed in SEBS than Cloisite30B due to polarity, this affect to PET/(SEBS/SEBS-g-MA)/Cloisite15A has higher impact strength than PET/(SEBS/SEBS-g-MA)/Cloisite 30B because Cloisite15A has good compatibility with SEBS so it increases shear force during mixing process that reduce size of SEBS particles. Furthermore, SEBS could well disperse on PET matrix as confirmed by SEM image in Figure 2.
Figure 2. SEM of PET/SEBS/SEBS-g-MA) and PET/(SEBS/SEBS-g-MA) composite with different types of OMMT (Cloisite15A and Cloisite30B) (a-c) before (d-e) after immerse in chloroform

Tensile properties of PET/SEBS/SEBS-g-MA and its composites are presented in Fig. 3. The tensile strength of polymer composites was evidently decreased with the presence of OMMT. However, Young’s modulus of PET/SEBS/SEBS-g-MA/OMMT has no significant change compare with the one without OMMT. PET/SEBS/SEBS-g-MA/Cloisite15A possesses lower tensile strength than PET/SEBS/SEBS-g-MA/Cloisite 30B. And tensile strength of PET composites was decreased with increasing the amount of OMMT. Therefore, Cloisite15A has less polarity somewhat similar to SEBS which makes them to be compatible. Therefore, it would increase shear force during melt blending process and enables SEBS to well-disperse in PET. This effect would then reduce tensile strength of polymer composites. Cloisite30B is less compatible with SEBS and cause less shear force during the process. Along with the different viscosity of SEBS and PET, relatively larger size of SEBS would disperse in PET as seen in Fig. 2d-e. This could make it has higher tensile strength and Young’s modulus than composites with Cloisite15A especially at 3 %wt of Cloisite. In case of percentage of elongation at break, it decreased for OMMT loading up to 3.00 %wt and increased for higher Cloisite15A loading (3.00 %wt).
Figure 3. Tensile properties of PET/SEBS/SEBS-g-MA composites with different types of OMMT (Cloisite 15A and 30B).

### 3.2 Thermal Properties

Table 2 shows thermal properties of PET composites compared with neat PET. Both of onset and degradation temperatures of PET/SEBS/SEBS-g-MA increased with incorporation of both types of OMMT. Nonetheless, it has no significant change with increasing concentration of OMMT.

**Table 2.** TGA data of PET, PET/SEBS(SEBS-g-MA) and PET/SEBS(SEBS-g-MA)/OMMT (Cloisite 15A and Cloisite 30B)

| Samples                  | T$_{onset}$ (°C) | T$_{d}$ (°C) |
|--------------------------|------------------|--------------|
| PET                      | 408.63           | 429.35       |
| PET/SEBS/SEBS-g-MA       | 411.02           | 432.95       |
| PET/SEBS/SEBS-g-MA-1.00-15A | 412.07         | 434.76       |
| PET/SEBS/SEBS-g-MA-3.00-15A | 411.46         | 438.05       |
| PET/SEBS/SEBS-g-MA-1.00-30B | 408.26         | 434.10       |
| PET/SEBS/SEBS-g-MA-3.00-30B | 410.73         | 436.22       |

The addition of SEBS and OMMT (Cloisite15A and Cloisite30B) had nearly no effect on melting temperature of PET. However, it had impact on percentage of crystallinity of composites. SEBS reduces the percentage of crystallinity of composites whereas both of Cloisite15A and Cloisite30B increases percentage of crystallinity compared with PET/SEBS/SEBS-g-MA because OMMT acts as a nucleating agent [6] as shown in Table 3.
3.3 Flame Retardant

The effect of OMMT on flammability resistance properties is shown in Table 4. PET has the highest limit oxygen index. When adding SEBS, %LOI of composite was dramatically decreased since SEBS itself has lower %LOI and could be burnt quickly. The addition of OMMT increased %LOI of PET/SEBS/SEBS-g-MA/OMMT compared with PET/SEBS/SEBS-g-MA. For UL94 test, all samples were classified as horizontal burning (HB). The OMMT addition reduces the burning rate of the composites when compared with PET/SEBS/SEBS-g-MA. Supposedly, there was organo-modified thermal degradation and strong proton-catalytic sites built-up onto the surface, which can catalyze the formation of a stable char residue. Therefore, the clay accumulation on the surface of the composites acts as a protective barrier that limits heat transfer into the material and diffusion of oxygen into the material. [5]

Table 3. The melting temperature and %crystallinity ($X_c$) of PET, PET/SEBS/SEBS-g-MA and PET/SEBS/SEBS-g-MA/OMMT (Cloisite 15A and Cloisite 30B)

| Samples                      | $T_m$ (°C) | $X_c$ (%) |
|------------------------------|-----------|-----------|
| PET                          | 250.01    | 26.36     |
| PET/SEBS/SEBS-g-MA           | 248.70    | 18.58     |
| PET/SEBS/SEBS-g-MA-1.00-15A  | 249.83    | 20.17     |
| PET/SEBS/SEBS-g-MA-3.00-15A  | 250.34    | 28.76     |
| PET/SEBS/SEBS-g-MA-1.00-30B  | 250.02    | 24.87     |
| PET/SEBS/SEBS-g-MA-3.00-30B  | 250.36    | 26.27     |

| Samples              | %LOI | BR (cm/min) |
|----------------------|------|-------------|
| PET                  | 25   | 0.50        |
| PET/SEBS/SEBS-g-MA   | 13   | 1.80        |
| PET/SEBS/SEBS-g-MA-1.00-15A | 15 | 1.10        |
| PET/SEBS/SEBS-g-MA-3.00-15A | 16 | 0.70        |
| PET/SEBS/SEBS-g-MA-1.00-30B | 17 | 1.80        |
| PET/SEBS/SEBS-g-MA-3.00-30B | 18 | 1.70        |

4. Conclusions

In this study, PET/(SEBS/SEBS-g-MA) and PET/(SEBS/SEBS-g-MA)/OMMT (Cloisite 15A and Cloisite 30B) blends were prepared via melt-blending process. The effect of OMMT types and contents on properties of PET blends with impact modifier at weight ratio between PET and SEBS/SEBS-g-MA of 70:30 was investigated. The types and contents of OMMT influenced the mechanical properties. The addition of Cloisite15A into PET/SEBS has raised the impact strength and %elongation at break whereas lower tensile strength. Moreover, Young’s modulus had no significant change. For thermal properties, comparing with PET/(SEBS/SEBS-g-MA) blends, adding either Cloisite15A or Cloisite30B into PET/(SEBS/SEBS-g-MA) increased the onset and degradation temperature. PET/SEBS/SEBS-g-MA had lower %LOI but higher burning rate compared with PET. However, the addition of OMMT could improve flame retardant properties of PET blends. Addition of Cloisite15A and Cloisite30B into PET/SEBS/SEBS-g-MA increased %LOI up to 16% and 18%,
respectively. From UL 94 testing, polymer composites could be classified in HB class. The burning rate of polymer composites was reduced once increasing OMMT.

Acknowledgement
The authors gratefully acknowledge the financial support and materials of following: Department of Materials Science and Engineering, Faculty of Engineering and Industrials Technology, Sipakorn University and Indorama Ventures Public Co., Ltd.

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