

# Thermal Properties of Maleated Polyethylene/Layered Silicate Nanocomposites<sup>1</sup>

S. H. Lee,<sup>2,3</sup> J. E. Kim,<sup>4</sup> H. H. Song,<sup>4</sup> and S. W. Kim<sup>5</sup>

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Nanocomposites are a new class of composites in which the reinforcing phase dimensions are on the order of nanometer scale. In particular, the layered silicates are considered to be good candidates for the preparation of polymer-inorganic nanocomposites. The mechanical and thermal properties of polymer can be altered by adding a few vol% of the nano-particles. The effect of the nano-sized particles on thermophysical properties such as melting and crystallization, coefficient of thermal expansion, and thermal conductivity was studied. After preparing the PEMA/layered silicate nanocomposites, the thermophysical properties were investigated by the differential scanning calorimetry and  $3\omega$  methods. The content of layered silicate was varied from 0.5 to 5 vol%.

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**KEY WORDS:** melting and crystallization; PEMA/silicate nanocomposite; thermal conductivity; thermal expansion; three omega method.

## 1. INTRODUCTION

One of the most promising composites is a hybrid system consist in organic polymers and inorganic materials [1–9]. In particular, the layered silicates are considered to be good candidates for the preparation of organic-inorganic nanocomposites. The nanocomposites are a new class of composites in which the reinforcing phase dimensions are on the order of nanometers. The silicate layer content in the nanocomposite is only a

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<sup>2</sup>Division of Physical Metrology, Korea Research Institute of Standards and Science, Taejon 305–600, Korea.

<sup>3</sup>To whom correspondence should be addressed. E-mail: leesh@kriss.re.kr

<sup>4</sup>Department of Polymer Science and Engineering, Hannam University, Taejon 306–700, Korea.

<sup>5</sup>Department of Physics, University of Ulsan, Ulsan 680–749, Korea.

small volume fraction, which is about one-tenth of the reinforcing filler content in conventional polymer-based composites. But, yet the mechanical and thermal properties of polymer/silicate nanocomposites are far superior to those of conventional composites [10]. In recent years, the investigation of polymer/clay nanocomposites has become a very important research field [11]. Melt intercalation of polymer matrix into the layered silicate is the most typical method to prepare the polymer/silicate nanocomposites and many kinds of polymer matrices were examined such as polystyrene (PS) [12, 13], polypropylene (PP) [14, 15], polyethylene (PE) [16, 17], polyimide [4], etc.

Among many physical and chemical properties of the nanocomposites, thermal properties, especially, thermal stability, thermal conductivity, and thermal expansion are of great interest. The thermal expansion behavior of nylon 6/silicate nanocomposites was previously investigated [18]. The thermal expansion was highly affected by the alignment of exfoliated platelets. Small changes from the perfect planar orientation result in significant changes in thermal expansion behavior. In polyurethane/layered silicate nanocomposites, the thermal conductivity showed a slight decrease with an increase of silica content [3]. However, by adding a small amount of silicate, the coefficient of thermal expansion was decreased by about 45%, which was ascribed to the high aspect ratio of the exfoliated silicate layers [19]. The maleated polyethylene (PEMA)/silicate nanocomposite was also studied with regard to the behavior of melting and crystallization, morphology, and mechanical properties [20]. The crystallization and melting temperatures of the nanocomposites were strongly related to the filler content and dispersion state.

In this work, the thermophysical properties such as melting and crystallization, thermal expansion coefficient, and thermal conductivity of PEMA/layered silicate nanocomposites were examined by differential scanning calorimetry (DSC), thermomechanical analyzer (TMA), and  $3\omega$  methods, respectively. The silicate content was varied from 0.5 to 5 vol%.

## 2. SAMPLE PREPARATION

Maleic anhydride modified polyethylene (PEMA) (0.85 mass% maleic anhydride grafted) was used for matrix materials and was purchased from Aldrich. The organic-modified laponite (SCPX2231) was used for the nano-sized fillers and was obtained from Southern Clay Products. The laponite (Lapo) has an aspect ratio of 20 to 30. The polyethylene/silicate nanocomposite was prepared by melt intercalation at 140°C using a Brabender mixer with a screw speed of 60 rpm, and the mixing time was 15 min. The silica filler content in the nanocomposite was varied from 0.5 to 5 vol%.

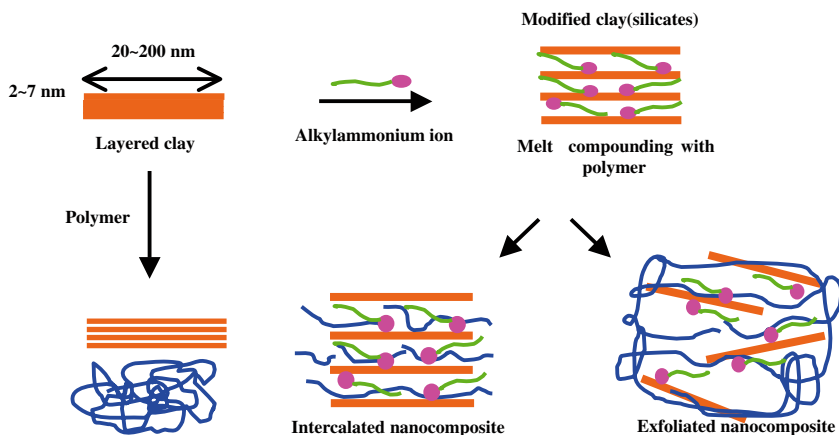


Fig. 1. Schematic representation of polymer/silicate nanocomposite preparation.

Figure 1 shows the conceptual approach to the monomer intercalation. The intercalated structure in which a single, and sometimes more than one, extended polymer chain is intercalated between the silicate layers results in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [1].

### 3. EXPERIMENTAL

The thermal behavior of PEMA/silicate nanocomposites was investigated by means of DSC (Perkin-Elmer Pyris-1) with samples masses of 5 to 10 mg. All operations were carried out under a nitrogen environment with a flow rate of 30 to 50 ml·min<sup>-1</sup> and a heating rate of 10 K·min<sup>-1</sup>. Before the thermal analysis, the samples were heated to 160°C to minimize any remaining thermal history. The polymer crystallinity was determined with DSC by quantifying the heat of fusion of the polymer [21]. In the case of PE, DSC can be used to measure the degree of crystallinity by comparing the heat of fusion for a specific sample with that for a 100% crystalline standard. The DSC was calibrated with indium and zinc pure materials for temperature and heat of fusion, respectively.

The thermal expansion coefficient was measured by TMA (Setaram TMA92) under an argon gas atmosphere. Rectangular samples (5 mm × 5 mm) were prepared and dried in an oven at 105°C for 2 h to remove moisture. The thermal expansion tests were performed in the temperature

range from 20 to 80°C at a heating rate of 5 K·min<sup>-1</sup>. The data for the thermal expansion were averaged for four measurement runs for two samples.

The thermal conductivity was measured by the  $3\omega$  method. The  $3\omega$  method has been widely utilized for thermal conductivity measurements of bulk and film-type samples. An ac current at a frequency  $\omega$  heats the sample, and this signal includes thermal information [22, 23]. A schematic diagram of our apparatus is shown in Fig. 2. The metal strip-line heater made of gold is about 20  $\mu\text{m}$  wide and 3 mm long. Thin gold films were evaporated on the sample using a thermal evaporator. The electrical resistance of the gold layer was controlled to about 10 to 30  $\Omega$  by controlling the evaporation time. The metal strip line is functioning as both the heater and the thermometer for detecting the  $3\omega$  signal.

The thermal conductivity determined from the  $3\omega$  apparatus was calculated from [23]

$$\lambda = -\frac{V^3}{4\pi l R^2} \frac{dR}{dT} \frac{d \ln \omega}{dV'_{3\omega}} \quad (1)$$

where  $V_{3\omega}$  is the in-phase  $3\omega$  voltage at frequency  $\omega$ . The TCR (temperature coefficient of resistance) is defined as  $\frac{1}{R} \frac{dR}{dT}$ .  $R$  is the average resistance of the heater/thermometer line,  $V$  is the voltage across the metal line at  $\omega$ , and  $V_{3\omega}$  is the measured voltage at  $3\omega$ . The TCR was measured by a four-probe method prior to  $3\omega$  measurements. As illustrated in Fig. 2, the

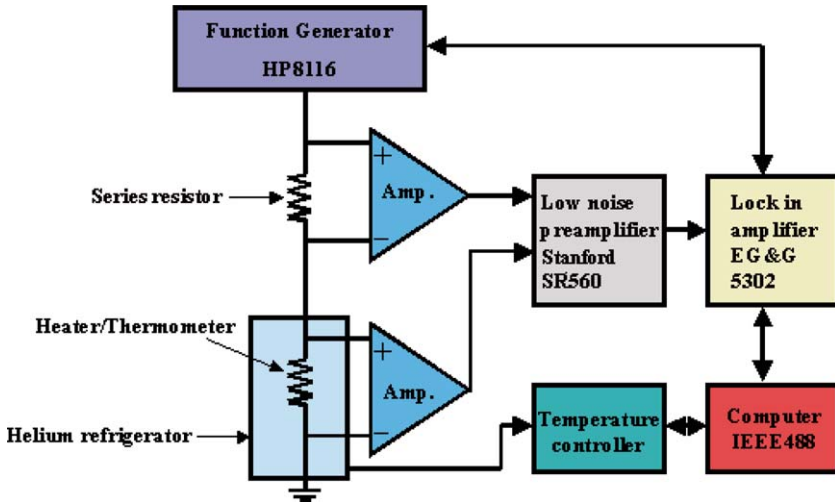


Fig. 2. The schematic diagram of the  $3\omega$  thermal conductivity apparatus.

**Table I.** Thermal Properties of PEMA/Lapo Nanocomposites

Lapo volume fraction (vol%)	Onset of melting temperature <sup>a</sup> (°C)	Melting peak center <sup>a</sup> (°C)	Heat of fusion (J·g <sup>-1</sup> ) <sup>b</sup>	Crystallinity (%) <sup>c</sup>
PEMA	118.5	124.0	119.2	41.1
0.5	111.2	118.3	72.7	25.1
1.0	110.7	118.5	75.9	26.2
3.0	110.6	118.3	72.0	24.8
5.0	109.4	119.0	71.3	24.6

<sup>a</sup>Uncertainty:  $\pm 0.5^\circ$  C.

<sup>b</sup>Uncertainty:  $\pm 2.0$  J·g<sup>-1</sup>.

<sup>c</sup>Uncertainty:  $\pm 1.7\%$ .

experimental apparatus for the  $3\omega$  system consists of a function generator for the  $\omega$  signal, a differential amplifier for signal detection, and a lock-in amplifier for the  $3\omega$  signal.

#### 4. RESULTS AND DISCUSSION

In Figs. 3 and 4, DSC melting and crystallization curve of the PEMA and PEMA/silicate nanocomposites are plotted and related thermal properties derived from the DSC thermograms are summarized in Table I. The PEMA shows an onset temperature of a melting endotherm at  $118.5^\circ\text{C}$  and a peak temperature of  $124^\circ\text{C}$ . Because the melting or crystallization of PEMA/nanocomposites shows a broad temperature range, the DSC curves were analyzed at temperature between  $60$  and  $130^\circ\text{C}$ . It is apparent that the onset temperature and the peak center decrease with the silicate filler content, even though the amount of these changes is minimal. The percentage crystallinity of nanocomposites was estimated based on the reference value of  $290$  J·g<sup>-1</sup> for 100% crystalline polyethylene [21]. The crystallinity of the PEMA/silicate nanocomposite from the DSC measurement is shown in Fig. 5. The crystallinity of nanocomposites ranges from 22 to 26%, which is somewhat lower than that from the XRD peak profile [23]. And the crystallinity of the silicates nanocomposites shows about a 15% drop by adding only 0.5 vol%, but the crystallinity remains nearly constant with a further increase of silicate content.

The thermal expansion of PEMA/silicate nanocomposites is shown in Fig. 6. The expansion value was calculated by the ratio of the elongation length to the initial length ( $L/L_0$ ). All composites show an increase of thermal expansion and thermal expansion rate with an increase in temperature. The thermal expansion values appear to remain constant for a

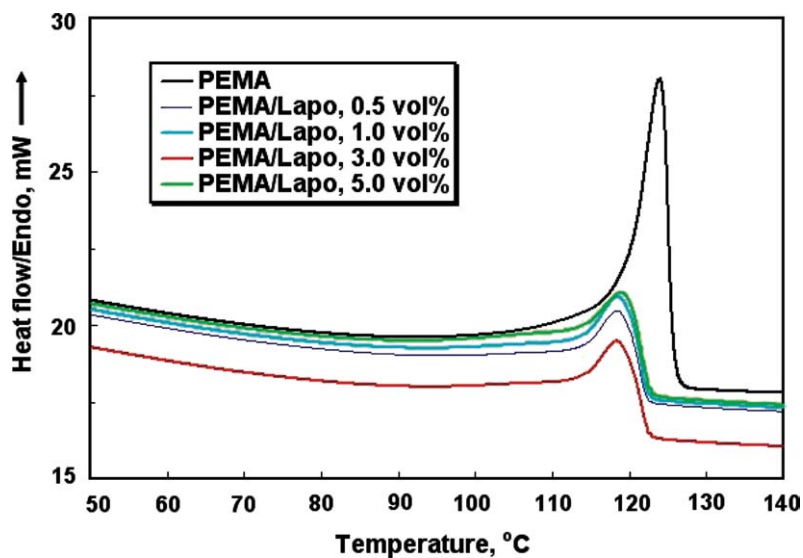


Fig. 3. Melting behavior thermogram of PEMA/Lapo nanocomposites.

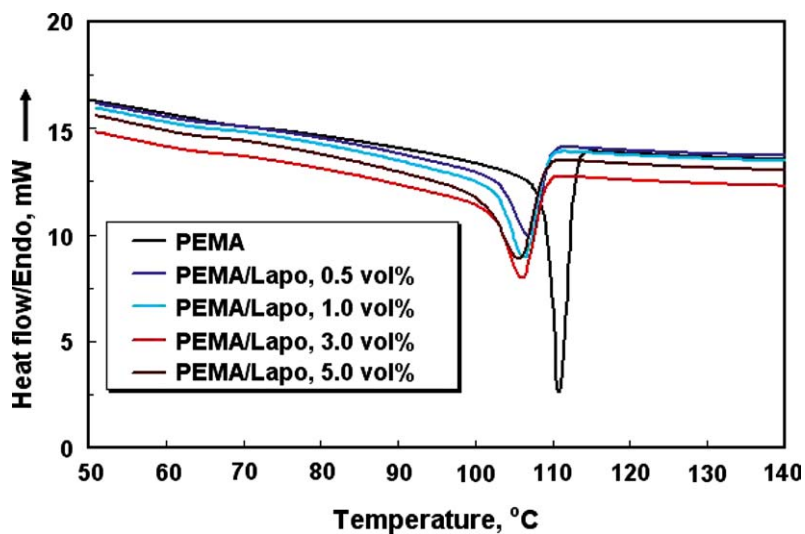


Fig. 4. Crystallization behavior thermogram of PEMA/Lapo nanocomposites.

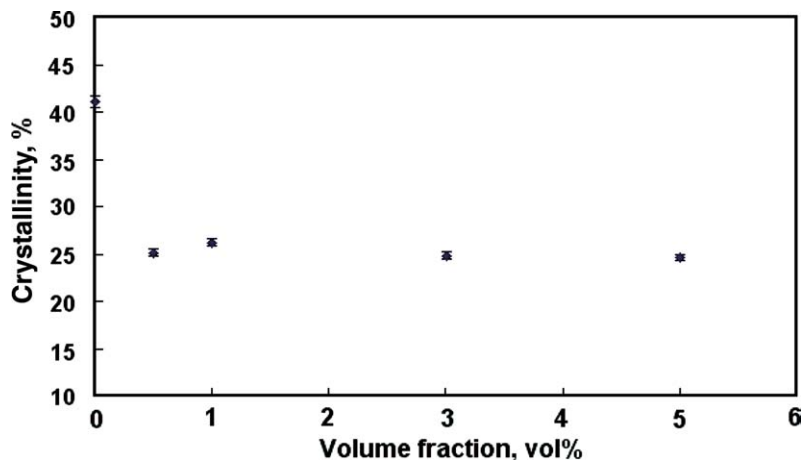


Fig. 5. Crystallinity of PEMA/Lapo nanocomposites.

variation of silicate content from 0.5 to 3 vol%, but that for a silicate content of 5 vol% clearly decreases to a value lower than that of PEMA. The coefficient of thermal expansion (CTE) of PEMA at room temperature was  $16.11 \times 10^{-5} \text{ K}^{-1}$ , which agrees well with reported data for PE,  $10 \times 10^{-5} \text{ K}^{-1}$  to  $22 \times 10^{-5} \text{ K}^{-1}$  [24]. The CTE of PEMA/Lapo nanocomposites at  $30^\circ\text{C}$  is  $12.59 \times 10^{-5}$ ,  $12.01 \times 10^{-5}$ ,  $12.46 \times 10^{-5}$ , and  $11.50 \times 10^{-5} \text{ K}^{-1}$  for 0.5, 1.0, 3.0, and 5 vol%, respectively. The thermal expansion of the pure PEMA at  $80^\circ\text{C}$  is almost 3 times as large as that of PEMA/Lapo of 5 vol%. As the amount of silicate filler increases, the thermal expansion rate decreases. The effective reduction in thermal expansion observed in the PEMA/silicate nanocomposites is believed to stem from the nature of the filler, e.g., high modulus, high aspect ratio, two-dimensional reinforcement, and low CTE [18].

The thermal conductivities of the PEMA and PEMA/silicate nanocomposites are shown in Table II and Fig. 7. The thermal conductivity of PEMA at 300 K was  $0.61 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . This value is slightly higher than the reference value of PE, which is 0.3 to  $0.53 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  [24]. In general, most polymers show thermal conductivities ranging from 0.1 to  $0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  and the thermal conductivity of polymers filled with inorganic fillers shows incremental change. In crystalline polymers, the thermal conductivity gradually decreases with an increase in temperature, as long as the temperature is maintained below the melting temperature. However, in amorphous polymers, the thermal conductivity increases slowly with an increase in temperature. Figure 7 shows the thermal conductivity

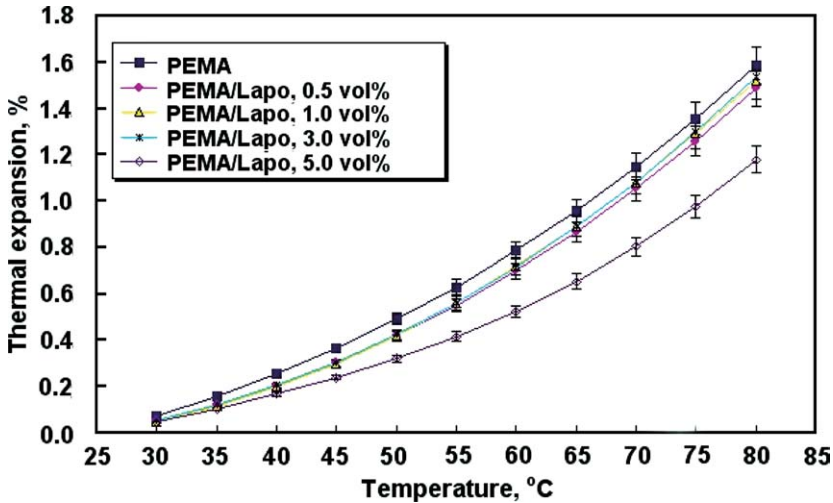


Fig. 6. Thermal expansion of PEMA/Lapo nanocomposites.

of the nanocomposites. The curves show that the thermal conductivity of PEMA/silicate nanocomposites decreases linearly with temperature. We also note that the thermal conductivity decreases with an increase of silicate content. The thermal conductivity of silicate is  $1.37 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  [23], which is higher than that of PEMA. Therefore, the addition of an organic filler should result in an increase of the thermal conductivity with an increase of the loading volume. The results observed in our PEMA/silicate nanocomposites are the opposite to this expectation. We speculate that the thermal conduction of the nanocomposite may be affected by the orientation of chain segments, crystallinity, and other structure factors. However, we are not certain yet about the origin of such unusual results. A more systematic study is warranted. We estimated our apparatus uncertainty level is about 5%, but the uncertainty of the  $3\omega$  method was found to be larger. The round-robin test results by VAMAS (Versailles project on Advanced Materials And Standards) to measure the thermal conductivity by the  $3\omega$  method show a scatter of  $\pm 25\%$  [25]. On the other hand, the thermal conductivity of polyurethane/layered clay nanocomposites decreased slightly with an increasing mass fraction of layered clay [3], which is similar to our results. Figure 8 shows the relation between thermal conductivity and volume fraction of silicate filler at 300 K. These data for the nanocomposites showed a scatter of about  $\pm 8.6\%$ . By increasing the volume fraction of layered silicate, the thermal conductivity decreased slowly rather than increases.



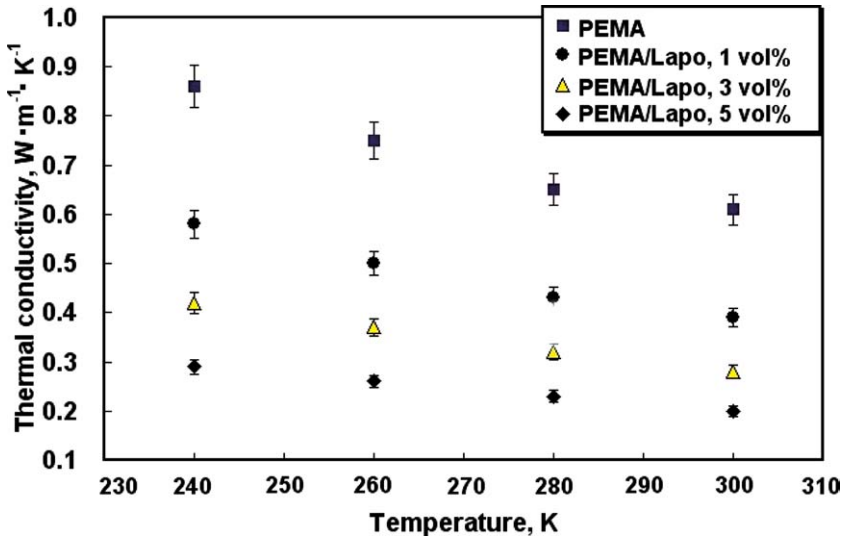


Fig. 7. Thermal conductivity of PEMA/Lapo nanocomposites.

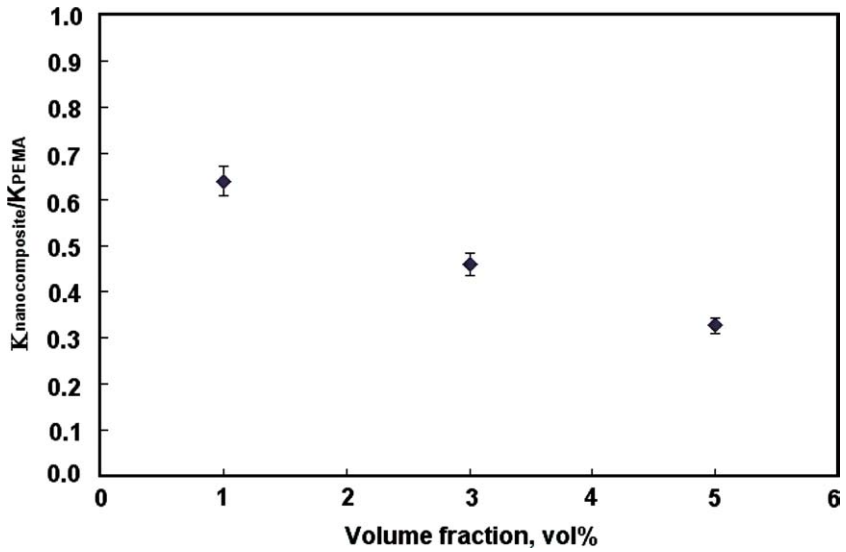


Fig. 8. Thermal conductivity vs. volume fraction for PEMA/Lapo nanocomposites.

**Table II.** Thermal Conductivities of PEMA/Lapo Nanocomposites

Temperature (K)	$\lambda(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$ PEMA <sup>a</sup>	$\lambda(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$ PEMA/Lapo (vol%) <sup>a</sup>		
		1%	3%	5%
240	0.86	0.58	0.42	0.29
260	0.75	0.50	0.37	0.26
280	0.65	0.43	0.32	0.23
300	0.61	0.39	0.28	0.20

<sup>a</sup>Uncertainty:  $\pm 5\%$ .

## 5. CONCLUSIONS

The thermophysical properties of PEMA/silicates nanocomposites, including melting and crystallization, thermal conductivity, and coefficient of thermal expansion, were investigated by the DSC, TMA, and  $3\omega$  methods. The onset and peak center of melting and crystallization decreased with an increase of silicate filler content. The crystallinity of PEMA/silicate nanocomposites decreased linearly with an increase of the silicate volume fraction. The rate of thermal expansion was not affected by the silicate content from 0.5 to 3 vol%, but shows a clear decrease to a value lower than that of PEMA when the content is 5 vol%. The thermal conductivity of the nanocomposites decreased linearly with an increase in temperature and with an increase of silicate content, even though the pure silicate particles exhibit a higher thermal conductivity than that of PEMA. The crystallinity and the crystal morphology of the PEMA/silicate nanocomposite may be the reasons for such an unusual result. It appears that the thermophysical properties of nanocomposites could only be accurately characterized on the basis of a detailed knowledge of structure and morphology.

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