

# Influences of Graphene Nanoplatlet aspect ratio and Thermal Treatment on Dielectric Performances of Poly(methyl methacrylate) Composites

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## Abstract

The dielectric property and percolated behavior of polymer matrix composites largely depend on the morphology of conductive fillers and external stimulations especially when the composites are processed by melting blending and extrusion injection way. In this study, the poly(methyl methacrylate) (PMMA) matrix composites incorporated by two kinds of graphene nanoplalets (GNP), G5 and G150 with different aspect ratios (the ratio of diameter and thickness) are prepared to study the influence of GNP morphology on the dielectric performances close to percolation threshold ( $f_c$ ). After annealing at glass transition temperature ( $T_g$ ) for 1 h, the dielectric permittivities of PMMA/G5 and PMMA/G150 near  $f_c$  increase 43% and 38%, respectively while the dielectric loss change little. This improvement on the dielectric property is possibly attributed to the slight change of the distance between adjacent GNPs after annealing at  $T_g$  which enables to arouse stronger polarization by tunneling effect.

**Key words: aspect ratio, thermal annealing, dielectric property, percolation threshold**

## Introduction

The percolated behavior is a classical topic when discussing the dielectric property of the composites with conductive fillers since when the volume fraction is approaching to a certain value, known as percolation threshold ( $f_c$ ), the dielectric performance of the composite will change thoroughly.<sup>[1, 2]</sup> Thus, researchers usually take advantages of this percolated transition to achieve the composite for high dielectric properties.<sup>[3-6]</sup> Huge amounts of reported studies have shown that various factors influence the percolation behavior of composites and their dielectric properties,<sup>[7-9]</sup> such as the morphology of the filler, the nature of the polymer matrix and processing methods which makes the obtained property hard to duplicate. Even the composites with same components and processed by the same method may also have different dielectric properties near  $f_c$ . Especially when reinforced by conductive fillers with a large aspect ratio such as carbon nanotubes (CNT) or graphene nanoplatlets (GNP), the dielectric properties of composites are various and sensitive to the external stimulation.<sup>[10-13]</sup> One of the possibilities for this sensitivity is that when a composite is processed by a general way such as extrusion-injection or filming, the conductive fillers migrate and orientate during the flow. Once the polymer matrix has an external stimulation such as the thermal treatment or electrical field, the original conductive network will be reformed easily and change the original dielectric properties when approaching to  $f_c$ .<sup>[14, 15]</sup>

If the external stimulation can be taken advantage effectively, the composite's dielectric property will be improved and finally reach to the stability. In the previous studies, we have already reported the annealing effect on dielectric properties for a linear semi-crystalline polymer, polyvinylidene fluoride (PVDF) incorporated by a CNT hybrids structure.<sup>[16, 17]</sup> When the composite is annealed at PVDF's crystalline temperature, 150 °C, for enough duration and after cooling to the room temperature, the dielectric permittivity ( $\epsilon'$ ) will have a three times' improvement while the dielectric loss ( $\tan\delta$ ) still keeps at low level compared with the results before annealing. This improvement is possibly attributed to the slight change of the distance between two adjacent CNTs caused by the shrinkage of PVDF's amorphous region and the increase of  $\beta$  polymorph in crystalline region after the thermal treatment which enables to induce the tunneling effect and arouse strong interfacial polarization.

Actually besides PVDF (a kind of semi-crystalline polymer), the composites with the matrix of the amorphous polymer may also have this improvement on the dielectric property after annealing at the certain temperature. The glass transition temperature,  $T_g$ , is one of the most important temperatures in the viscoelasticity of polymers. It is widely accepted that when the polymer is heated to the  $T_g$ , the molecule chains start to move due to the expansion of the free volume around.<sup>[18, 19]</sup> If the composite close to the  $f_c$  is annealed at the  $T_g$  for enough duration, it is highly possible that the dielectric property may also be different since the slight change of the free volume around

the molecule chains in the interfacial region enables to induce the shrinkage of the distance between adjacent conductive fillers. Therefore, with this suppose, we use poly(methyl methacrylate) (PMMA), a widely used amorphous polymer in the industry as the polymer matrix to prepare the composite. The conductive fillers chosen are two kinds of GNPs with different aspect ratios (the ratio of diameter and thickness), G5 and G150, respectively. Two kinds of composites, PMMA/G5 and PMMA/G150 are prepared by melting blending and extrusion injection way with different volume fractions. The influence of GNP's morphology on  $f_c$  for two kinds of composites will be firstly discussed. Then based on the results of the dynamic mechanical analysis (DMA), the interaction in the interfacial region of GNP and PMMA are analyzed and finally the effect of thermal treatment on the dielectric properties for the two kinds of PMMA/GNP composites approaching their  $f_c$  will be well studied.

## **2 Experiments and characterizations**

### **2.1 Preparation of GNPs/PMMA composites**

Two kinds of GNPs, G5 and G150, were directly purchased from KNANO Science Inc., China and commercial PMMA beads (melt flow index = 1.22 g/min, density = 1.18 g/cm<sup>3</sup>) were bought from LG PMMA Corporation (Korea). The composites with a series of different GNP volume fractions were processed by melting blending in a twin-screw micro-extruder/compounder (Micro 5 cc twin screw compounder, DSM) for 30 min at 230 °C with the speed of 60 rpm. The bone-shaped slab with 1.5 mm thickness was fabricated via the extrusion-injection method (Micro 5cc Injection Molder, DSM at 1.3 MPa). The temperatures of the injection nozzle and mould holder were set at 235 °C and 55 °C, respectively.

### **2.2 Characterization of the GNPs/PMMA composites**

The morphology of GNP and the fracture surface of GNPs/PMMA composites were characterized by the scanning electron microscope (SEM) (Quanta 200 FEG, FEI Company) at 5 kV. Herein, the fractures of composites were obtained after immersed in the liquid nitrogen for 5 min.

Dynamic mechanical analysis (DMA) was conducted in tension mode by Netzsch DMA 242C. The measurement was conducted from 30 °C and 150 °C with 2 °C/min heating rate at frequency of 1 Hz. The size of specimen was 20mm×5mm×1.5mm. The loss tangent for the modulus is defined as  $\tan \theta = \frac{E''}{E'}$ , where  $E'$  and  $E''$  correspond to the real and imaginary parts of the dynamical (complex) modulus  $E^*$ , respectively. The dielectric properties of composites were characterized as a function of frequency by an impedance analyzer (Solartron 1260) at room temperature (25 °C) from 100 Hz to 10<sup>7</sup> Hz. Before the measurement, silver pastes were applied on both sides of the sample for easy contacting. Samples are considered as plane capacitors and described by parallel

resistor-capacitor (RC) circuit systems. The complex dielectric permittivity ( $\epsilon^*$ ) is calculated as follows:  
 $\epsilon^* = \epsilon' - j\epsilon''$ , where  $\epsilon'$  and  $\epsilon''$  correspond to the real and imaginary parts of the complex  $\epsilon$ , respectively.  $\omega = 2\pi f$  is the angular frequency, and  $j = (-1)^{\frac{1}{2}}$ . The dielectric loss tangent ( $\tan\delta$ ) is defined as  $\tan\delta = \frac{\epsilon''}{\epsilon'}$ .

### 3. Results and discussion

#### 3.1 Morphology characterization for two kinds of GNP and fractures of their PMMA composites

As shown in the Fig. 1 (a) and (b), it can be found that the average diameter of G5 is larger than that of G150 while G5's thickness is thinner than that of G150 by the semi-transparent layer of G5 in the Fig. 1 (a). Thus, G5's aspect ratio is much larger than that of G150. The morphology of the fracture surface for PMMA/G5 and PMMA/G150 are presented in the Fig. 1 (c) and (d), respectively. Two kinds of GNPs can be dispersed in PMMA matrix compatibly without large agglomerates by the micro-compounder. But with larger aspect ratio, it can be found in (c) that G5 can form the network of fillers more easily in PMMA matrix than G150 though the volume fraction is 3%. Thus, PMMA/G5 composites may reach  $f_c$  with a lower volume fraction than that of PMMA/G150 which we will discuss more in the following parts.

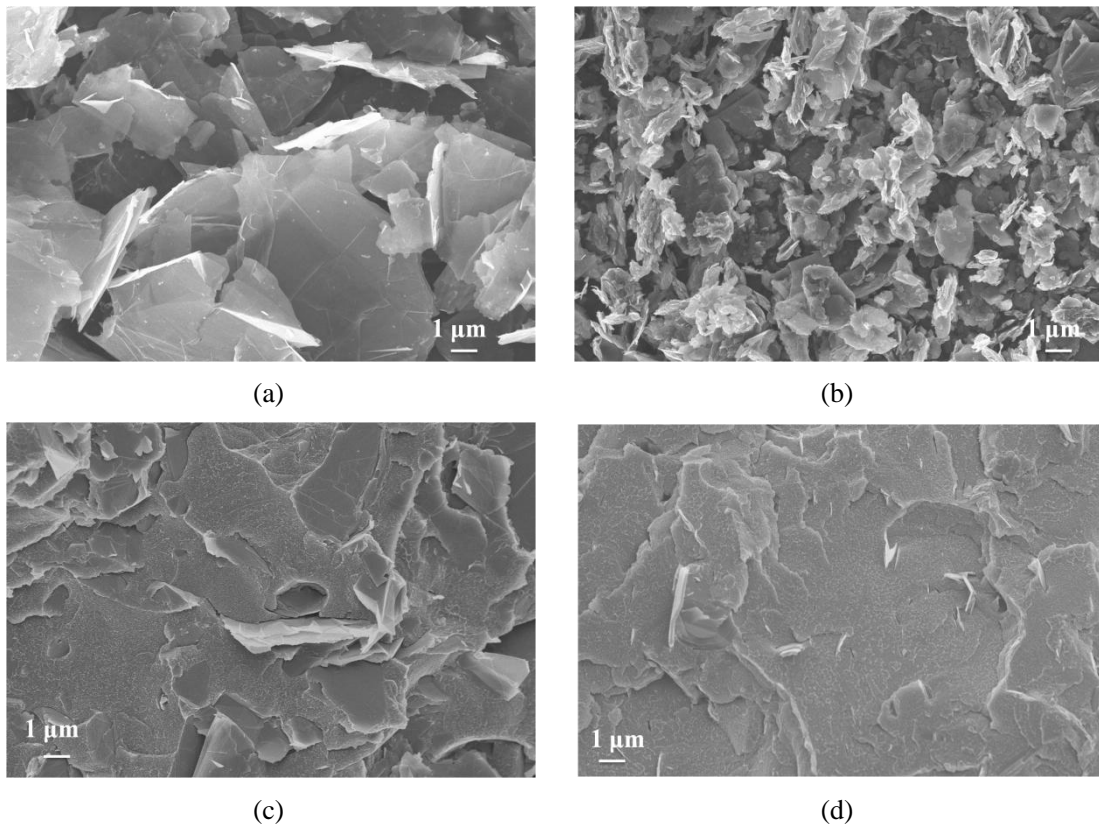


Fig. 1 (a) and (b) are SEM images for G5 and G150. (c) and (d) are SEM images for the fracture surface for PMMA/G5-3% and PMMA/G150-3%, respectively.

### 3.2 Dielectric properties of PMMA/G5 and PMMA/G150 before the thermal treatment

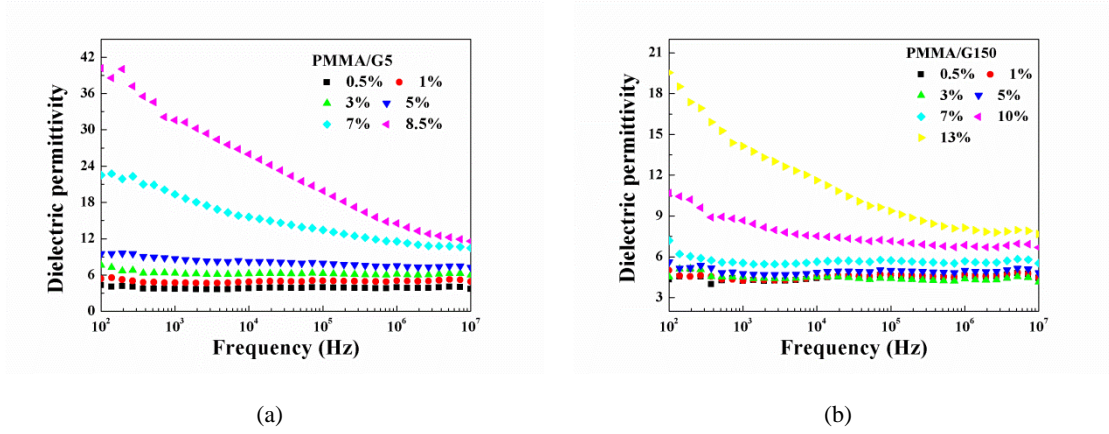


Fig.2 Frequency dependence of dielectric permittivity for composites with different GNP's volume fractions. (a) for PMMA/G5 and (b) for PMMA/G150

The results of frequency dependence of  $\epsilon'$  for PMMA/G5 and PMMA/G150 are presented in Fig. 2 (a) and (b), respectively. It can be found that the values of  $\epsilon'$  increase gradually in both figures as the volume fractions of GNP increasing. Moreover, based on the results, we can divide the increasing trend of  $\epsilon'$  into two stages. Namely, when the volume fractions of G5 and G150 are small, neither the increase of  $\epsilon'$  nor the dependence of frequency is clear in two composites. But once the volume fraction approaches to  $f_c$ , the increase of  $\epsilon'$  becomes very clear and the values of  $\epsilon'$  also show a strong frequency-dependent in both two cases. But the improvement on  $\epsilon'$  and the possible value of  $f_c$  are different between PMMA/G5 and PMMA/G150 as we have mentioned due to the different aspect ratios. In the case of PMMA/G5, an obvious increase of  $\epsilon'$  occurs when the volume fraction of G5 is over 7%, while for PMMA/G150, G150's volume fraction needs to be over 10%. Besides, the values of  $\epsilon'$  approaching to  $f_c$  achieved by G5 is nearly double times larger than that of G150 when the frequency is low. These phenomena of dielectric performances are related to composite's percolated transition. In order to study the percolation behaviors of PMMA/G5 and PMMA/G150 further, the linear fit is employed to calculate the theoretical  $f_c$  for these two kinds of PMMA/GNP composites:

$$\epsilon_{\text{eff}} \propto \epsilon_m |f - f_c|^{-q} \quad \text{for } f < f_c \quad (1)$$

where  $\epsilon_{\text{eff}}$  is the dielectric permittivity of composite;  $\epsilon_m$  is the one of PMMA (4.5 at 100 Hz) and  $f$  is the volume fraction of G5 or G150, respectively.

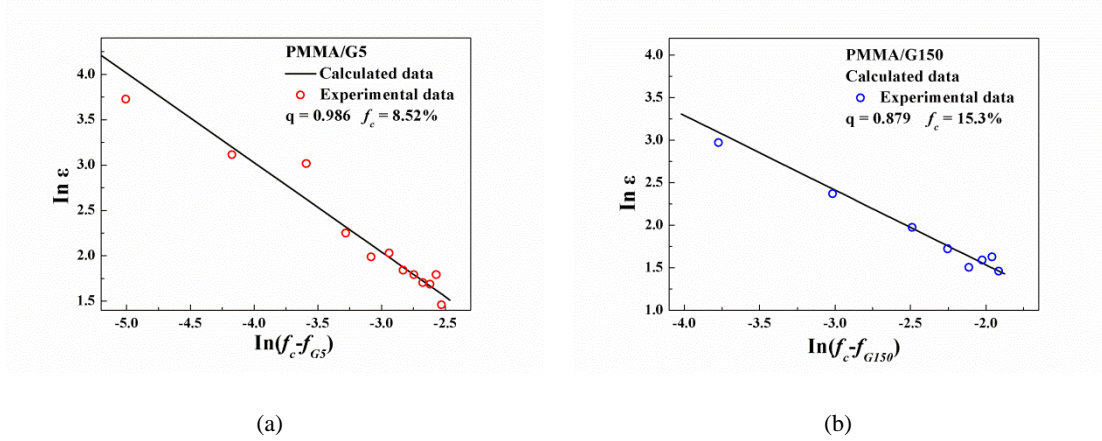


Fig. 3 Best linear fits for  $\epsilon'$  at 100 Hz of PMMA/G5 (a) and PMMA/G150 (b) composites with different volume fractions by percolation theory shown in equation (1).

The results of linear fitting for  $\epsilon'$  at 100 Hz of PMMA/G5 and PMMA/G150 are shown in Fig. 3 (a) and (b) and the best linear fittings give  $q = 0.935$  and  $0.879$  for PMMA/G5 and PMMA/G150, respectively which agree with the universal one (in the range from 0.8 to 1).<sup>[1]</sup> Furthermore, obtained by linear fitting,  $f_c$  for PMMA/G5 is 8.52% while for PMMA/G150 is 15.3%.  $f_c$  for PMMA/G150 is nearly double times higher than PMMA/G5 which is possibly attributed to the smaller aspect ratio since conductive filler's morphology influences the micro-capacitor's network in the polymer matrix. In our experimental system, G5 has much larger aspect ratio than that of G150 which makes micro-capacitor of G5-PMMA to mutually contact by an easier way and consequently arouses stronger interfacial polarization at low frequency due to the tunneling effect. Thus, not only  $f_c$  for PMMA/G5 is much smaller than that of PMMA/G150 but also the improvement on  $\epsilon'$  at low frequency of PMMA/G5 is higher than that of PMMA/G150. As we have already discussed in the introduction, annealing for the sample near  $f_c$  can improve dielectric property for the polymer matrix composite incorporated by conductive fillers. The PMMA/GNP composites are not exceptions and we choose PMMA/G5-7% and PMMA/G150-13% as two candidates since both of them are approaching to  $f_c$  and meanwhile, their values of  $\epsilon'$  before thermal treatment are similar which benefits to make the comparison.

### 3.2 Dynamic mechanical analysis for PMMA/G5 and PMMA/G150

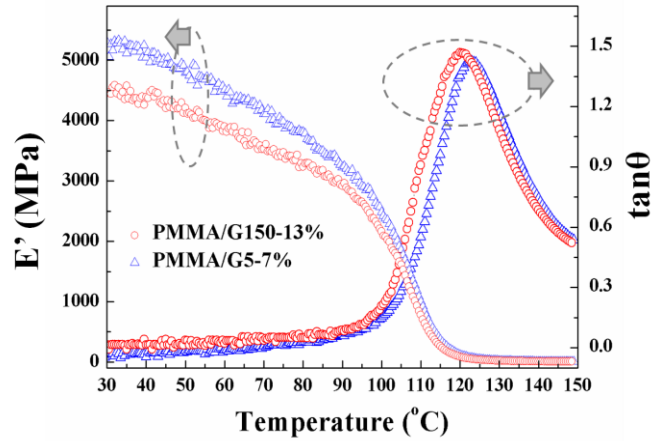


Fig. 4 DMA measurement PMMA/G5-7% and PMMA/G150-13% from 30 to 150 °C at 1 Hz.

According to the theory of viscoelasticity, polymer's  $T_g$  can be thought as the temperature of loss tangent's peak ( $\tan\theta$ ) by DMA method. Presented in the Fig. 4, obtained  $T_g$  for PMMA/G5-7% and PMMA/G150-13% are 123 and 120 °C and the  $E'$  for PMMA/G5-7% and PMMA/G150-13% are over 5200 MPa and 4500 MPa, respectively. Generally, the  $E'$  and  $T_g$  of a composite may infer that the interfacial interaction between fillers and polymer matrix and higher values mean a stronger interaction in the interfacial region of fillers and matrix. The results in Fig. 4 demonstrate that the addition of G5 and G150 in PMMA's molecule chain network work can form strong interactions for both composites due to the attractive interfaces. Thus, the great reinforcement in the storage modulus ( $E'$ ) appears for both PMMA/G5 and PMMA/G150. But still from Fig.4, it can also be figured out that PMMA/G5 shows a higher  $E'$  than that of PMMA/G150 which may also be attributed to its larger aspect ratio. The thinner thickness of G5 makes them to enter into the PMMA's molecule chains and form inter-penetrated network with PMMA more easily than that of G150 with a thicker thickness. Forming an inter-penetrated network effectively plays an essential role in the reinforcement of the mechanical property for polymer matrix composite when the filler's content is high. Therefore, the  $E'$  of PMMA/G5-7% is higher than that of the PMMA/G150-13%. After obtaining  $T_g$  for the two samples, a thermal treatment will be conducted and the dielectric property will be discussed then.

### 3.3 Dielectric properties for PMMA/G5-7% and PMMA/G150-13% after the thermal treatment

Before discussing, the details about the thermal treatment are presented as follows: as shown in the Fig. 4,  $T_g$  for these two samples, PMMA/G5-7% and PMMA/G150-13% are about 120 °C. Hence, both two samples are putting into an oven and heated at 120 °C. After annealing for 1 h, two samples are taken out and the dielectric

measurement is conducted again after the two samples cooling naturally to the room temperature. Frequency-dependent dielectric properties including  $\epsilon'$  and  $\tan\delta$  between before and after the thermal treatment for PMMA/G5-7% and PMMA/G150-13% are presented in Fig. 5 (a) and (b), respectively.

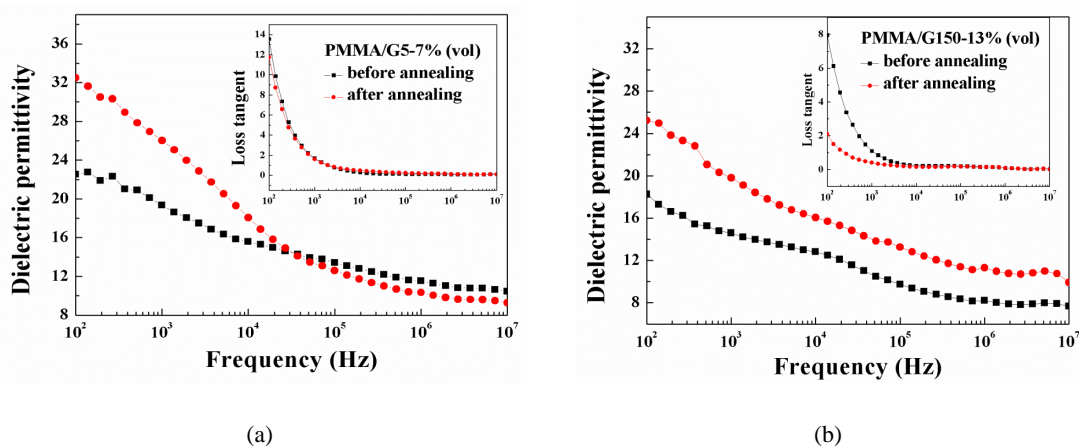


Fig. 5 Frequency dependence of dielectric properties for PMMA/G5-7% (a) and PMMA/G150-13% (b) before and after the thermal treatment. The large graph is for dielectric permittivity and the insert graph is for dielectric loss.

As shown in the Fig. 5, it can be found that after annealing at 120 °C for 1 h, the values for  $\epsilon'$  of both PMMA/G5-7% and PMMA/G150-13% have an increase especially at low frequency. It is possibly attributed to the reformation of the GNP conductive network in PMMA matrix. It is known that when the composite approaching to  $f_c$ , the dielectric behavior is very sensitive due to the distance between adjacent conductive fillers close to the critical value for the tunneling effect. When the samples processed by excursion-injection, the migration and orientation of GNP happen unavoidably under the flow during injection molding. If annealing at  $T_g$  for enough duration, some PMMA's molecule segments may move due to the expansion of the free volume in the interfacial region between PMMA and GNP. But after cooling to the room temperature, the free volume shrinks and PMMA molecules are stiff again. This procedure of the expansion and afterwards shrinkage provides the possibility for reforming the original migration of GNP conductive network in the interfacial region becomes more randomly. Thus, after the annealing, the values of  $\epsilon'$  at low frequency have an increase due to the interfacial polarization aroused by a more random GNP network in the PMMA. But the dielectric loss ( $\tan \delta$ ) in the insert graphs decreases after annealing which means this reformation of the conductive network due to polymer molecules does not consume more energy for the heat. Hence, this annealing treatment can be viewed as a method for increasing  $\epsilon'$  and keeping  $\tan\delta$  at low level. In addition, if we compare two graphs in Fig. 5, we can find that  $\epsilon'$  of PMMA/G5-7% has a bit decrease



when the frequency increases after the thermal treatment while  $\epsilon'$  of PMMA/G150-13% always increases in the whole frequency. This is also caused by the different aspect ratio of two kinds of GNPs. Polymer's orientation polarization occurs at high frequency and G5 with larger aspect ratio is easy to form inter-penetrated network with PMMA molecule chains as aforementioned. Hence, after annealing, this inter-penetrated network may be reinforced and consequently limits the dipoles of PMMA molecule chains orientation polarization which decreases  $\epsilon'$  a bit at high frequency. Therefore, an effectively annealing treatment can improve the dielectric property of the PMMA/GNP approaching to  $f_c$  and a possible reason is attributed to the reformation of GNP conductive network and the interaction between GNP and PMMA in the interfacial regions.

## Conclusion

GNP aspect ratio has an obvious influence on dielectric and dynamic mechanical property for the PMMA composites. G5 with a larger aspect ratio can easily enter into the PMMA molecule chains to form the inter-penetrated network, and consequently reduces the  $f_c$  and achieve a higher  $\epsilon'$  compared with G150 of a smaller aspect ratio. Moreover, the improvement on  $E'$  for both PMMA/G5 and PMMA/G150 infers that an attractive interface forms between GNPs and PMMA in the interfacial region of the composites processed by melting blending. Besides, after the thermal treatment at  $T_g$ , due to the slight change of the distances between adjacent GNPs in the interfacial region, the values of  $\epsilon'$  for both PMMA/G5 and PMMA/G150 near  $f_c$  have increases while dielectric loss still changes little compared with their dielectric properties before the thermal treatment.

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