

## Preparation and Dielectric Properties of Poly( $\epsilon$ -caprolactone) Compounded with “Bucky Gels”-Like Mixture

Sang Won Yoon,<sup>1</sup> Xianqian Ren,<sup>2</sup> Guang-Xin Chen<sup>2</sup>

<sup>1</sup>Department of Automotive Engineering, Hanyang University, Seoul 133-791, Korea

<sup>2</sup>College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Correspondence to: G.-X. Chen (E-mail: gxchen@mail.buct.edu.cn)

**ABSTRACT:** Poly( $\epsilon$ -caprolactone) (PCL) was melt compounded with “Bucky gels”-like mixture that prepared by grinding multiwalled carbon nanotubes (MWNTs) and ionic liquids (ILs). Raman spectrum showed the significant interaction between ILs and MWNTs. The dielectric behavior of PCL nanocomposites based on unmodified and IL-modified MWNTs was studied from 40 Hz to 30 MHz. The addition of ILs significantly enhanced the dielectric property of PCL/IL/MWNT ternary nanocomposites, which was much higher than that of the sum of PCL/IL with PCL/MWNT binary nanocomposites. The dielectric properties of PCL/IL/MWNT nanocomposites were mainly influenced by ILs in low frequency and were dominated by MWNTs in high frequency. SEM results revealed that a more uniform and fine dispersion of MWNTs were achieved throughout the PCL matrix because of ILs. The addition of ILs in nanocomposites changed the crystallinity of PCL. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40231.

**KEYWORDS:** composites; ionic liquids; nanotubes

Received 21 October 2013; accepted 30 November 2013

DOI: 10.1002/app.40231

### INTRODUCTION

The carbon nanotubes (CNTs) possess a high aspect ratio, a large  $\pi$ -electronic surface, and complex 3D networks. Plenty of researchers have been attracted to have them functionalized or take advantage of their mechanical and electrical properties to modify polymers promptly.<sup>1,2</sup> Although the prospect for carbon nanotube-based nanocomposites is attractive, a fatal problem that the CNTs do not disperse well in the matrix exists. CNTs are ropes and bundles that are constantly entangled with one another, thereby restricting the development of carbon nanotube-based nanocomposites. Methods such as the modification of the surface of CNTs with covalent<sup>3–7</sup> or noncovalent<sup>8–12</sup> approaches have been attempted. However, noncovalent methods are preferred because these methods retain most of the properties of CNTs.

Ionic liquids (ILs) normally possess a high ionic conductivity with unique chemical stability, comprising a bulky organic cation and an organic or inorganic anion. Numerous kinds of ILs are being synthesized for special use in polymer science, such as solid polymer electrolytes,<sup>13–15</sup> solar cells,<sup>16–18</sup> and plasticizers.<sup>19,20</sup> Most studies on ILs are focused on the polarity of IL<sup>21–24</sup> or poly (IL)<sup>25,26</sup> solutions through the dielectric behavior of these solutions, or the solid electrolyte usually utilized in fuel cells. Computer simulations of ILs have rapidly developed such

as simulations of molecular motion and relaxation equations.<sup>27,28</sup> ILs used as plasticizers in polymer science have been studied in the past few years to improve the mechanical property of polymers. However, the dielectric property of ILs in a polymeric matrix has not received a similar amount of attention.

The special interaction between ILs and CNTs<sup>29–32</sup> garnered much attention since 2003. Aida et al.<sup>33,34</sup> reported that a physic interaction exists between the surface of CNTs and the imidazole ring via  $\pi$ -cation/ $\pi$ -electronic, and that “Bucky gels”<sup>35,36</sup> is a good example of this interaction. “Bucky gels” can be easily prepared through grinding or strong sonicating a mixture of CNTs and imidazolium ion-based ILs. Shang et al.<sup>29</sup> used a special ionic liquid in the CNTs/polyurethane conductive nanocomposites to gain a highly stretchable material through a new way of heating ILs with CNTs for pretreatment. Their results have indicated that ILs improved the electric property and the mechanical property of the nanocomposites. Given these interesting results between the CNTs and the ILs, we can expect that an interaction between the ILs and the CNTs affects the dielectric property of their polymeric nanocomposites.

In this study, pristine multiwalled carbon nanotubes (MWNTs) are blended with ILs for pretreatment to form a “Bucky gel”-like mixture. Using the melt processing method, we attempt to

blend together the “Bucky gel”-like mixture with poly( $\epsilon$ -caprolactone) (PCL) to form a well-distributed nanocomposite, and then investigate the co-operative effect of MWNTs and ILs on the dielectric properties of PCL-based nanocomposites in frequencies between 40 Hz to 30 MHz. The crystallization of the PCL/IL/MWNT nanocomposites is also discussed.

## EXPERIMENTAL

### Materials

Pristine MWNTs were purchased from Carbon Nanotechnologies, China. The diameter of the tubes range from 10 to 20 nm and the average length range from 10 to 15  $\mu\text{m}$ . Room temperature ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF<sub>6</sub>), 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM]BF<sub>4</sub>), and 3-allyl-1-methyl-1H-imidazol-3-ium hexafluorophosphate ([AMIM]PF<sub>6</sub>) (purity  $\geq 99\%$ ), were purchased from Shanghai ChengJie, China and dried in vacuum at 80°C for 3 days. The PCL was obtained from Union Carbide (USA) with a weight average molecular weight of  $1.1 \times 10^5$  g/mol as reported by the manufacturer. The content of adipate units in PCL was 0.5 moles/mole of 1,4-butane diol units. The PCL was dried in a vacuum oven at 60°C for 24 h before processing.

### Preparation of IL/MWNT “Bucky Gel”

Dried [BMIM]PF<sub>6</sub> was blended with MWNTs in an agate mortar, and was grinded with a pestle for 8 h to form the “Bucky gels”-like mixture. The mixture had a varied weight proportion of MWNTs in ILs and the concentrations of MWNT are shown in Table I.

### Preparation of Nanocomposites

The mixture of PCL and IL/MWNT gel were melt-compounded using a HAAKE Rotational Rheometer at 120°C for 5 min. The rotation speed used in this study was kept at 100 rpm. The films of the nanocomposites were hot pressed by a flat rheometer to obtain a smooth surface with a processing temperature of 120°C. The binary mixtures, namely, PCL/IL and PCL/MWNT nanocomposites, were prepared at the same condition with the ternary PCL/IL/MWNT nanocomposites. The sample names and the concentrations of IL and MWNT in PCL are listed in Table I.

### Characterization

Dielectric properties were measured by Agilent 4294A with 16451B fixture (40 Hz  $\sim$  110 MHz), at a constant temperature at 25°C. Samples were prepared by flat rheometer to obtain a thickness of about 1 mm and then measured by three different areas of samples from 40 Hz  $\sim$  30 MHz.

Scanning electronic micrographs for fracture plane samples were investigated by Field Emission Scanning Electron Microscope (FE-SEM, HITACHI S-4700). Samples were prepared by brittle fracture of the nanocomposite film in liquid nitrogen. Gold was sprayed on the surface of the sample, which successively mounted on stubs using electric adhesive tape paste, and then measured at an accelerating voltage of 20 kV.

Raman spectra were measured with a laser Raman microscope (Renishaw inVia) using a 514 nm Ar line as the excitation source. The laser power was 0.5 W. The spectra were measured

**Table I.** Concentrations of PCL/IL/MWNT Nanocomposites

Samples	PCL (wt %)	“Bucky gel”-like mixture	
		MWNT (wt %)	IL (wt %)
PCL-0-1	99	0	1
PCL-0-5	95	0	5
PCL-0-10	90	0	10
PCL-0-20	80	0	20
PCL-0.06-0	99.94	0.06	0
PCL-0.06-1	98.94	0.06	1
PCL-0.06-5	94.94	0.06	5
PCL-0.06-10	89.94	0.06	10
PCL-0.06-20	79.94	0.06	20
PCL-0.6-0	99.4	0.6	0
PCL-0.6-1	98.4	0.6	1
PCL-0.6-5	94.4	0.6	5
PCL-0.6-10	89.4	0.6	10
PCL-0.6-20	79.4	0.6	20
PCL-3-0	97	3	0
PCL-3-1	96	3	1
PCL-3-5	92	3	5
PCL-3-10	87	3	10
PCL-3-20	77	3	20
PCL-6-0	94	6	0
PCL-6-1	93	6	1
PCL-6-5	89	6	5
PCL-6-10	84	6	10
PCL-6-20	74	6	20

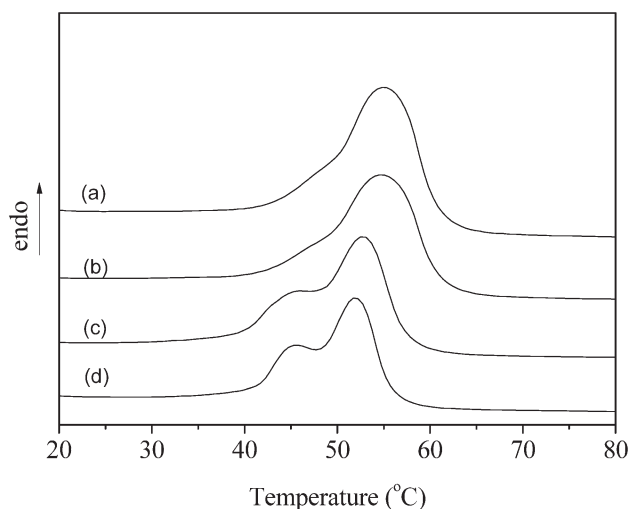
in a backscattering configuration with a triple monochromator at intervals of 1.5  $\text{cm}^{-1}$ .

The melting behaviors were studied by differential scanning calorimetry (DSC). The experiments were carried out in nitrogen atmosphere using 9 mg sample sealed in aluminum pans. The samples were first heated from room temperature to 200°C under 10 K/min and maintain at this temperature for 5 min to eliminate thermodynamic potential, and then measured again from  $-60$  to 200°C under 10 K/min. The melting temperatures are taken from second heating run in the calorimetric curves.

## RESULT AND DISCUSSION

### DSC Analysis

The DSC curves of the PCL and its nanocomposites are shown in Figure 1, from which an obvious effect from the addition of ILs in the nanocomposites can be observed. First, Figure 1 shows that the melting temperature ( $T_m$ ) of the PCL nanocomposites, including the IL, decreased compared with pure PCL. Second, the crystallinity, calculated through  $x_c = \Delta H_m / \Delta H_m^0$ , where  $\Delta H_m^0 = 136.08$  J/g, declined when IL was added in the matrix, especially with the nanocomposite of PCL/IL/MWNT. After an integral of molten enthalpy  $\Delta H_m$ , the pure PCL attained a crystallinity of 44.9%. The crystallinity of



**Figure 1.** DSC heating curve of (a) pure PCL, (b) PCL-0.06-0, (c) PCL-0-10, (d) PCL-0.06-10.

PCL-0.06-0, PCL-0-10, and PCL-0.06-10 was 41.3, 34.8, and 31.2%, respectively. The decrease in  $T_m$  and the crystallinity of PCL/IL nanocomposite is ascribed to the plasticizer effect of the nanocomposite. Meanwhile, the marked decrease in  $T_m$  and the crystallinity of the PCL/IL/MWNT nanocomposite is probably the combined result of the nucleating of the CNTs and the plasticizing of the ILs. The resultant imperfect polymer crystals in the nanocomposites melted at a lower temperature than the control polymer. The morphologies of the nanocomposites were investigated to find the cause of the lowest  $T_m$  and crystallinity shown by the PCL/IL/MWNT nanocomposite.

### Morphologies

The SEM images (Figure 2) show the cross-sections of the nanocomposites prepared by fracturing the PCL nanocomposites in liquid nitrogen to produce an intact fractured surface morphology. Figure 2(a,b) show that the bright regions in the SEM images are attributed to the MWNTs as a result of high electrical conductivity of the MWNTs. Aggregates were clearly observed in the PCL/MWNT nanocomposites as shown in Figure 2(a,b). The morphologies of the PCL nanocomposites with ILs are revealed in Figure 2(c,d), where the ILs are clearly homogeneously dispersed in the PCL/IL nanocomposites with the shape of small particles. The small particles indicate that some of the ILs were not dispersed in the PCL in molecular level. The diameter of the IL particles increased with the content of IL such as from about 50 nm in 5 wt % ILs to about 140 nm in 10 wt % ILs. As a result, the aggregated parts of the ILs cannot work as plasticizer of PCL. Interestingly, no IL particles were observed in the PCL/IL/MWNT nanocomposites shown in Figure 2(e,f). The SEM images also clearly reveal that an even dispersion of MWNTs was achieved throughout the PCL matrix without any aggregation. Most MWNTs were separated into individual tubes during the simple melt compounding; thus, the MWNTs were evenly dispersed in the matrix, which is of great practical importance in making polymer/CNT nanocomposites. A closer inspection reveals that most of the MWNTs are broken in the matrix upon failure, and loop-like MWNTs are observed

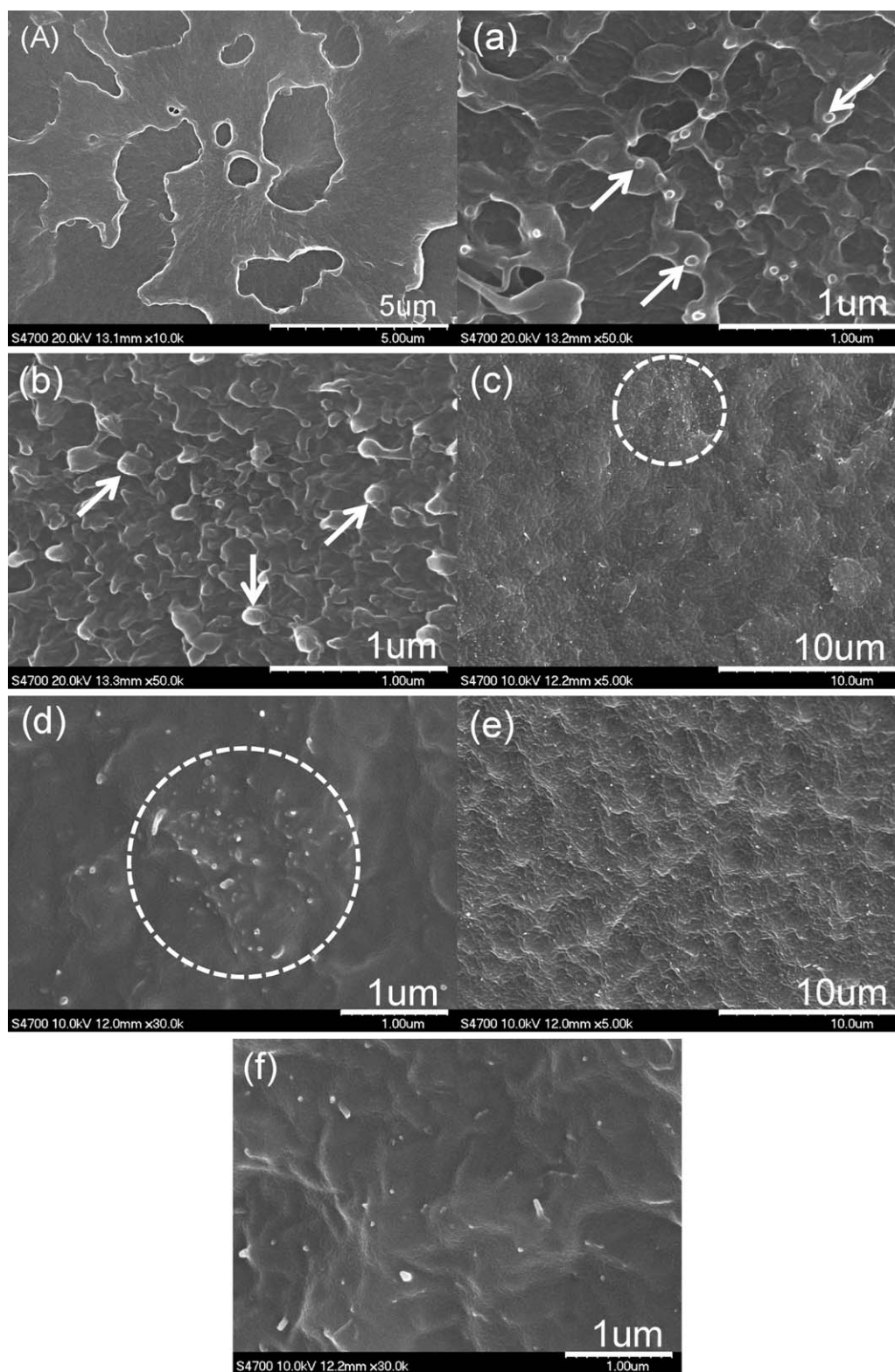
with their two ends still strongly embedded in the matrix. This typical breakage phenomenon of the MWNTs indicates that a strong interfacial adhesion exists between the MWNTs and PCL matrix. The well-dispersed MWNTs and the strong interfacial adhesion are believed to be caused by the “Bucky gel” prepared through grinding the ILs and MWNTs for long time. The interaction between the ILs and MWNTs are shown in Raman spectrum below.

### Raman Analysis

The Raman spectrum (Figure 3) revealed that a large interaction between IL and MWNT. The D band stands for the defects in the CNTs, and the G band stands for the  $sp^2$  carbon. Figure 3 shows that obvious Raman shifts of the MWNTs were observed both in the “Bucky gel”-like mixture and in the PCL/IL/MWNT nanocomposites compared with pure MWNT. The shift of the tangential mode frequency of the MWNTs observed suggests interactions between the IL and the MWNT. No obvious Raman shift in both the D and G bands were observed compared with “Bucky gel”-like mixture and PCL/IL/MWNT nanocomposite. The lack of Raman shift indicates that the interaction between the IL and MWNT in the matrix through melt processing did not further increase compared with the mixture of IL/MWNT through grinding processing. Table II shows the D/G intensity ratio ( $I_D/I_G$ ), always used as an indicator of the degree of crystallinity and purity of the CNTs, of MWNT, “Bucky gel”-like mixture, PCL/MWNT, and PCL/IL/MWNT nanocomposite. The  $I_D/I_G$  exhibits the degree of disorder in MWNTs.<sup>37</sup> The values of  $I_D/I_G$  of “Bucky gel”-like mixture and PCL/IL/MWNT nanocomposite, 0.74 and 0.70, is greater than that of pristine MWNTs (0.52), which indicates that the addition of IL can generate more defects on the MWNTs. However, the obvious difference of the Raman shift and  $I_D/I_G$  in the PCL/MWNT nanocomposite was not observed compared with pure MWNT.

### Dielectric Permittivity of Nanocomposites

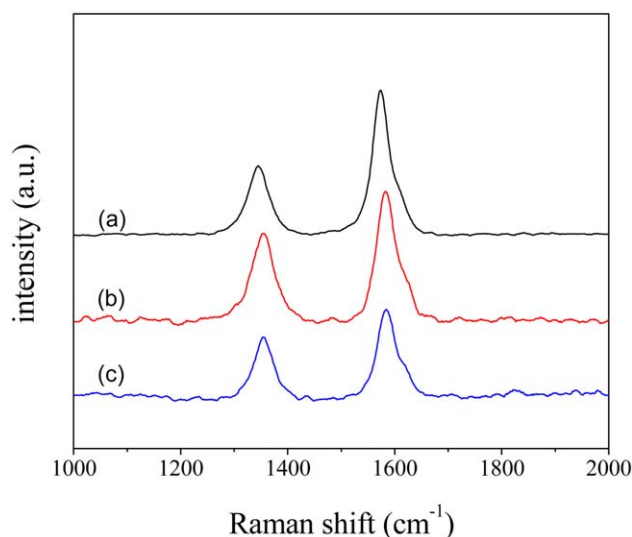
Figure 4 shows the dielectric permittivity and dielectric loss values of the PCL/MWNT nanocomposites as a function of the MWNT weight fraction ( $f_{MWNT}$ ) at 25°C and different frequencies. The dielectric permittivity was enhanced with the increase of  $f_{MWNT}$  and was rapidly enlarged when 6 wt % MWNT was added, as shown in Figure 4(a). The nanocomposites with a low percentage of MWNT did not make much of a difference in the dielectric property of pure PCL. The increasing dielectric permittivity of the nanocomposites can be attributed to the polarization of the Maxwell–Wagner–Sillars (MWS) effect. The MWS effect shows that charges accumulated at the interface between the two-materials interfaces with different relaxation times ( $\tau = \epsilon/\sigma$ , where  $\epsilon$  represents the dielectric permittivity and  $\sigma$  represents the conductivity). The relaxation time of the PCL was much larger than the MWNT, and the MWNT–PCL interfaces may block the charge flow, causing interfacial polarization (MWS effect), and high dielectric permittivity. The PCL/MWNT nanocomposites gained more interfacial polarization effects with the increase of the weight percentage of MWNT, and provided the main cause of the increasing dielectric permittivity of the nanocomposites. Figure 4(b) shows that the dielectric loss of the PCL/MWNT nanocomposites increased with the addition of MWNT, especially when  $f_{MWNT} = 6$  wt %.



**Figure 2.** SEM images of PCL and its nanocomposites prepared via melt compounding (A) pure PCL, (a) PCL-0-5, (b) PCL-0-10, (c, d) PCL-0.6-0, (e, f) PCL-0.6-10.

Figure 5 presents the relationship of the dielectric permittivity of the PCL/IL nanocomposites with different weight fractions ( $f_{IL}$ ) and frequencies at 25°C. Figure 5(a) shows that the dielectric

permittivity grows sharply as  $f_{IL}$  increases. The addition of the IL in the nanocomposites obviously changed the electronic property of PCL compared with pure PCL. The dielectric relaxation of the



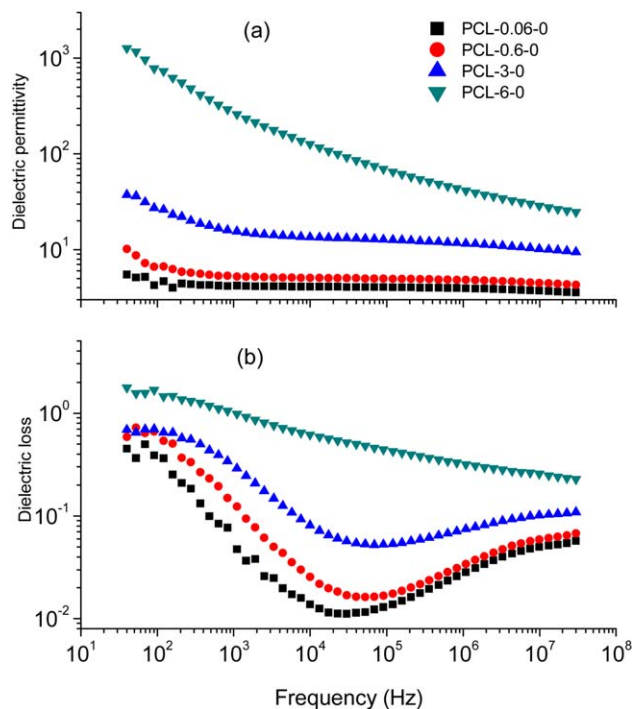
**Figure 3.** Raman shift of (a) pure MWNT, (b) “Bucky gel”-like mixture (MWNT/IL = 3 wt %), and the PCL-0.6-10. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

IL was partly dipolar and partly ionic because of its dipolar ions; thus, ionic relaxation polarization and ionic conductivity were the main influences of the dielectric property of the nanocomposites. The increase of the PCL amorphous region in the PCL/IL nanocomposites (shown in Figure 1) led to the increase of space for ILs to move and the ease in obtaining ionic relaxation polarization and ionic conductivity. The dielectric studies of the ion-omer system by Fragiadakis et al.<sup>38</sup> reveal that the ion-pair relaxation mode appears at frequencies lower than that of the polymer segmental relaxation mode, and accordingly enhances the dielectric permittivity significantly. The dielectric property of nanocomposites is similar to pure PCL in frequencies ranging from  $10^5$  to  $10^6$  Hz. The dielectric permittivity of the nanocomposites is nearly equal with the pure PCL at frequencies above  $10^7$  Hz, indicating that the main dielectric property is provided by the polymer segment of PCL at above  $10^7$  Hz.

The addition of IL in PCL increases the dielectric permittivity of the nanocomposites in 10–100 KHz, and the MWNTs in PCL may provide a large scale of interface, which changes the dielectric property of the PCL/MWNT nanocomposites. The PCL and “Bucky gel” nanocomposites were prepared to study the dielectric property of the PCL/IL/MWNT ternary system and the interaction of the MWNT and IL in PCL. The 0.6 wt % of MWNT in the ternary nanocomposites was selected to avoid the electric conduction of PCL/MWNT because of the percolation.

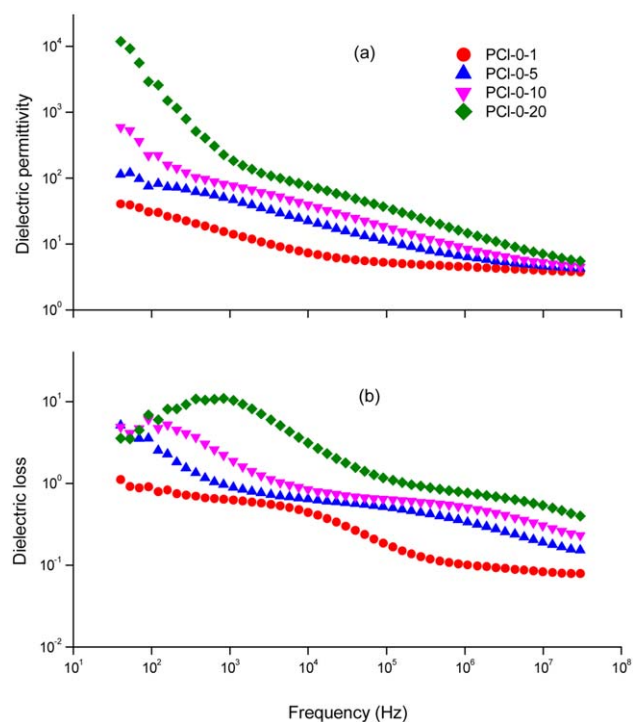
**Table II.** Raman Shift and D/G Intensity Ratio of MWNT in Bucky Gel and Nanocomposites

Samples	D band ( $\text{cm}^{-1}$ )	G band ( $\text{cm}^{-1}$ )	D/G intensity ratio
Pure MWNT	1350.6	1579.7	0.52
IL/MWNT	1359.2	1586.6	0.74
PCL-0.6-10	1359.5	1587.5	0.70

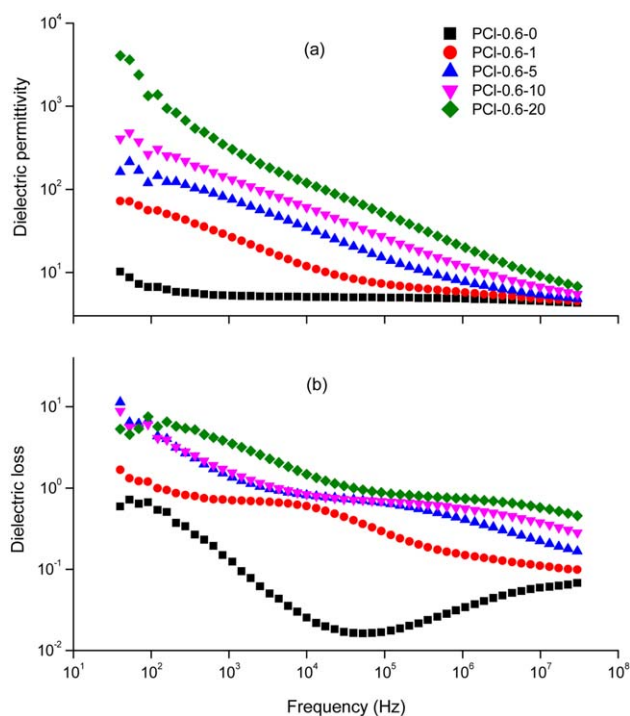


**Figure 4.** Dielectric permittivity (a) and dielectric loss (b) of PCL/MWNT nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Figure 6 shows the dielectric property of the PCL/IL/MWNT nanocomposites. The ternary nanocomposites gain the higher dielectric properties than binary PCL/IL and PCL/MWNT

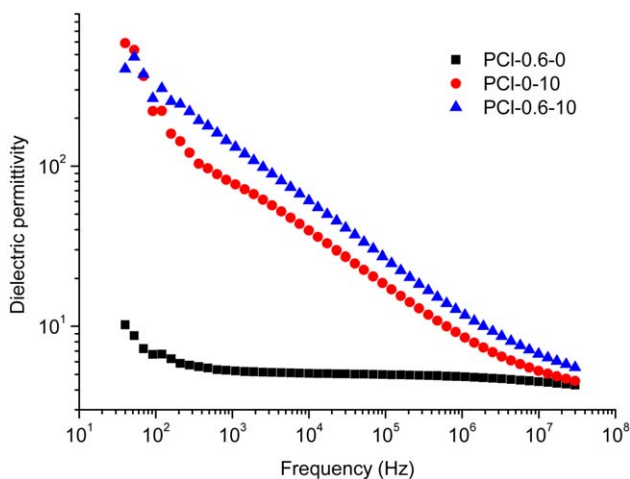


**Figure 5.** Dielectric permittivity (a) and dielectric loss (b) of PCL/IL nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

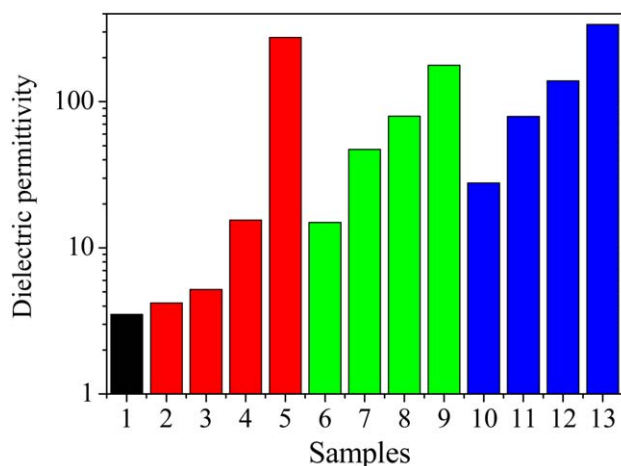


**Figure 6.** Dielectric permittivity (a) and dielectric loss (b) of PCL/IL/MWNT nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanocomposites.<sup>39</sup> Figure 7 exhibits a comparison of the dielectric property in the PCL, PCL-0.6-0, PCL-0-10, and PCL-0.6-10. Figure 8 exhibits the drift of increasing dielectric permittivity related to the percentage of IL and MWNT kept at 1 KHz and 25°C. The dielectric properties of the PCL/IL/MWNT nanocomposites are more than a simple addition of PCL/MWNT and PCL/IL nanocomposites. For example, the dielectric permittivity of PCL-0.6-0, PCL-0-10, and PCL-0.6-10 is 5.2, 79.8, and 138.6, respectively. The dielectric permittivity of ternary nanocompo-

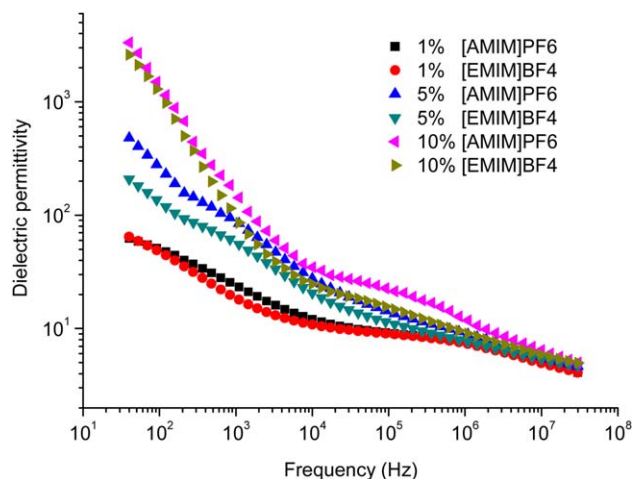


**Figure 7.** Comparison of the dielectric permittivity of PCL nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Dielectric permittivity of (1) PCL and nanocomposites at 1 KHz and 25°C, (2) PCL-0.06-0, (3) PCL-0.6-0, (4) PCL-3-0, (5) PCL-6-0, (6) PCL-0-1, (7) PCL-0-5, (8) PCL-0-10, (9) PCL-0-20, (10) PCL-0.6-1, (11) PCL-0.6-5, (12) PCL-0.6-10, and (13) PCL-0.6-20. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sites is attributed to the homogeneous dispersion both of ILs and MWNTs in the PCL matrix, which was proven in the SEM results. On one hand, the ILs attached to the surface of MWNTs enlarged the interphase between the MWNT and the PCL; thus, interfacial polarization increased. On the other hand, the dispersion of the ILs in the PCL/IL/MWNT nanocomposites was much better than in the PCL/IL nanocomposites. Thus, the amorphous region of the PCL in ternary nanocomposites was much larger than that of the binary nanocomposites. As a result, the ternary nanocomposites obtain a strong ionic relaxation polarization and ionic conductivity. The significantly enhanced dielectric permittivity of the PCL/IL/MWNT nanocomposites is attributed to the synergistic effect of interfacial polarization, ionic relaxation polarization, and ionic conductivity. The dielectric behavior of the PCL/IL/MWNT nanocomposites tends to be similar to the PCL/IL nanocomposites at lower



**Figure 9.** Dielectric permittivity of PCL/IL nanocomposites with different cation/anion and percentages. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

frequencies, and to the PCL/MWNT nanocomposites at higher frequencies.

Two more kinds of ILs, namely, [EMIM]BF<sub>4</sub> and [AMIM]PF<sub>6</sub>, are applied to compare with the previous [BMIM]PF<sub>6</sub>-based PCL/IL nanocomposites to find the relationship between the cation/anion and dielectric permittivity of nanocomposites. The dielectric permittivity is shown in Figure 9, which indicates the dielectric permittivity of different types of ILs in PCL seems to have the same tendency at above 10<sup>5</sup> Hz. Even the 1% IL added in the nanocomposites heavily increased the dielectric permittivity of nanocomposites. The dielectric loss of nanocomposites enlarged rapidly in low frequencies, and met pure PCL at higher frequencies. The gap of the dielectric loss between the nanocomposites and pure PCL can be provided through ionic conductivity and ionic relaxation. The dielectric strength of the PCL/IL tended to purify the PCL when the frequency was higher than 10<sup>6</sup> Hz, indicating that IL affects the dielectric property a little at a high frequency. Different types of cations or anions in the ILs have minimal influence in the dielectric property of the nanocomposites.

## CONCLUSIONS

A convenient method for preparing nanocomposites using the polymers and the “Bucky gels”-like mixture was developed. The resulting IL–MWNT gel reinforced the PCL nanocomposites efficiently through a simple melt compounding, and endowed the nanocomposites with excellent dielectric properties. The dielectric properties of the PCL/IL/MWNT nanocomposites were larger than that of the simple addition of the PCL/MWNT and PCL/IL nanocomposites, which were attributed to the synergistic effect of the interfacial polarization, ionic relaxation polarization, and ionic conductivity. The dielectric properties of the PCL/IL/MWNT nanocomposites were mainly influenced by the ILs at a low frequency and were dominated by the MWNTs at a high frequency. The type of ILs used in this research had minimal effect on the dielectric properties of the nanocomposites. The microscopic observations revealed that a more uniform and fine dispersion of MWNTs was achieved throughout the PCL matrix because of the strong interaction between the CNTs and the ILs. The DSC showed that the addition of ILs in nanocomposites changed the crystallinity of the PCL.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support of this work coming from Natural Science Foundation of China (NSFC) (No. 51173009).

## REFERENCES

1. Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science* **1994**, *265*, 1212.
2. Haggemueller, R.; Fischer, J. E.; Winey, K. I. *Macromolecules* **2006**, *39*, 2964.
3. Balasubramanian, K.; Burghard, M., *Small* **2005**, *1*, 180.
4. Prato, M.; Kostarelos, K.; Bianco, A. *Acc. Chem. Res.* **2007**, *41*, 60.
5. Chen, G.-X.; Shimizu, H. *Polymer* **2008**, *49*, 943.
6. Roy, N.; Sengupta, R.; Bhowmick, A. K. *Prog. Polym. Sci.* **2012**, *37*, 781.
7. Xu, Y.; Li, Q.; Sun, D.; Zhang, W.; Chen, G.-X. *Ind. Eng. Chem. Res.* **2012**, *51*, 13648.
8. Zhao, Y.-L.; Stoddart, J. F. *Acc. Chem. Res.* **2009**, *42*, 1161.
9. Chen, J.; Liu, H.; Weimer, W. A.; Halls, M. D.; Waldeck, D. H.; Walker, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 9034.
10. Satake, A.; Miyajima, Y.; Kobuke, Y. *Chem. Mater.* **2005**, *17*, 716.
11. Chen, G. X.; Li, Y. J.; Shimizu, H. *Carbon* **2007**, *45*, 2334.
12. Chen, G. X.; Miyauchi, M.; Shimizu, H. *Appl. Phys. Lett.* **2008**, *92*, 203113.
13. Nakajima, H.; Ohno, H. *Polymer* **2005**, *46*, 11499.
14. Bandara, T. M. W. J.; Mellander, B. E.; Albinsson, I.; Dissanayake, M. A. K. L. *Solid State Ionics* **2009**, *180*, 362.
15. Ueki, T.; Watanabe, M. *Macromolecules* **2008**, *41*, 3739.
16. Shankar, K.; Mor, G. K.; Prakasam, H. E.; Varghese, O. K.; Grimes, C. A. *Langmuir* **2007**, *23*, 12445.
17. Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Mater.* **2004**, *16*, 2694.
18. Freemantle, M. *Chem. Eng. News Arch.* **2002**, *80*, 6.
19. Scott, M. P.; Brazel, C. S.; Benton, M. G.; Mays, J. W.; Holbrey, J. D.; Rogers, R. D. *Chem. Commun. (Camb.)* **2002**, 1370.
20. Park, K.; Ha, J. U.; Xanthos, M. *Polym. Eng. Sci.* **2010**, *50*, 1105.
21. Lohse, P. W.; Bartels, N.; Stoppa, A.; Buchner, R.; Lenzer, T.; Oum, K. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3596.
22. Daguinet, C.; Dyson, P. J.; Krossing, I.; Oleinikova, A.; Slattery, J.; Wakai, C.; Weingärtner, H. *J. Phys. Chem. B* **2006**, *110*, 12682.
23. Stoppa, A.; Hunger, J.; Buchner, R.; Hefter, G.; Thoman, A.; Helm, H. *J. Phys. Chem. B* **2008**, *112*, 4854.
24. Krause, C.; Sangoro, J. R.; Iacob, C.; Kremer, F. *J. Phys. Chem. B* **2009**, *114*, 382.
25. Chen, H.; Elabd, Y. A. *Macromolecules* **2009**, *42*, 3368.
26. Nakamura, K.; Saiwaki, T.; Fukao, K. *Macromolecules* **2010**, *43*, 6092.
27. Petrowsky, M.; Frech, R. *J. Phys. Chem. B* **2009**, *113*, 16118.
28. Matsumiya, Y.; Uno, A.; Watanabe, H.; Inoue, T.; Urakawa, O. *Macromolecules* **2011**, *44*, 4355.
29. Shang, S.; Zeng, W.; Tao, X.-M. *J. Mater. Chem.* **2011**, *21*, 7274.
30. Cao, J.; Li, P.; Yi, L. *J. Chromatogr. A* **2011**, *1218*, 9428.
31. Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. *Science* **2003**, *300*, 2072.
32. Xing, C.; Zhao, L.; You, J.; Dong, W.; Cao, X.; Li, Y. *J. Phys. Chem. B* **2012**, *116*, 8312.

33. Lee, J.; Aida, T. *Chem. Commun. (Camb.)* **2011**, 47, 6757.
34. Wang, J.; Chu, H.; Li, Y. *ACS Nano* **2005**, 2, 2540.
35. Freemantle, M. *Chem. Eng. News Arch.* **2003**, 81, 7.
36. Fukushima, T.; Aida, T. In *Ionic Liquids in Polymer Systems*; American Chemical Society, **2005**; Chapter 11.
37. Yang, Y.; Wang, X.; Liu, L.; Xie, X.; Yang, Z.; Li, R. K. Y.; Mai, Y.-W. *J. Phys. Chem. C* **2007**, 111, 11231.
38. Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. *Macromolecules* **2008**, 41, 5723.
39. Oh, K.; Lee, J. Y.; Lee, S.-S.; Park, M.; Kim, D.; Kim, H. *Compos. Sci. Technol.* **2013**, 83, 40.