Clay-Assisted Dispersion of Carbon Black in Thermoplastic Nanocomposites

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ABSTRACT: The poor dispersion of carbon black (CB) in thermoplastic polymers has provided a space for improving the various properties of nanocomposites. In this study, nanoclay (NC) was introduced into CB/thermoplastic composites to improve the dispersion of CB and, finally, to improve the thermal or mechanical performance. We noticed that there was a simultaneous enhancement in the mechanical and thermal performances of the nanocomposites because of the combination of the NC and CB. The information obtained from the mechanical and thermal studies indicated that the properties were improved to an appreciable extent because of the plastic–plastic/CB/NC combination. The tensile strength of polycarbonate (PC) was observed to be enhanced by 9.4% only because of the addition of CB, although when poly(methyl methacrylate) (PMMA) was used as a matrix material along with PC, the tensile strength improved by 25%, although the tensile strength of PMMA is much lower than that of PC. This confirmed that the tensile properties of the polymer composites also depended on the plastic–plastic interaction phenomenon. Moreover, the tensile strengths of the different blended nanocomposites system increased by around 42.5% with the addition of NC. A significant improvement of 22% was achieved in the thermal stability of the PMMA composites with the addition of CB. However, the addition of NC provided further improvement in the thermal decomposition temperature by only 3.7%. This showed that the thermal stability of the polymer nanocomposites was slightly affected by the addition of NC. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41477.

INTRODUCTION

Polymer-based composites have been extensively used for decades because of their high stiffness-to-weight ratio. Generally, the polymers may be either thermosetting or thermoplastic polymers, and accordingly, the composites are known as thermoplastic- or thermosetting-polymer-based composites.[1] Nanofillers in polymer–matrix composites (PMCs) act as reinforcing materials and their applicability in different fields, such as military and commercial aircraft, the automotive industry, sporting goods, packaging materials, and health care products, has been proven.[2–5] This has mainly been due to the high aspect ratio of the nanomaterials.[6–9]

The fabrication of composites involving the combinations of a matrix and nanofillers may be done through *in situ* polymerization, exfoliation–adsorption, and template synthesis and melt intercalation. Melt intercalation is a powerful new approach for the preparation of polymer nanocomposites. It has been proven to be the most efficient and environmentally friendly alternative to the other available methods.[10,11] In this process, nanoclay (NC) layers are directly dispersed in molten polymers with conventional melt-processing techniques. Thermoplastic polymers

reinforced with NCs as nanofillers have been synthesized extensively with this technique.[12–14] Polymer nanocomposites can be produced by the melt intercalation of polymers followed by compression molding, extrusion molding, injection molding, or plastic molding to obtain desirable properties.[15] However, compression molding is most commonly preferred after melt intercalation for the preparation of polymer nanocomposites.

Carbon black (CB) has been proven to have excellent capability for use as a reinforcing material for future polymer nanocomposites because of its good electrical and thermal properties and high aspect ratio. In addition, CB can be homogeneously dispersed in a layer of nanometer scale thickness; this has increased interest in the reinforcement of CB in polymer composites.[16–18] However, the poor solubility and dispersability of CB, which are due to the strong van der Waal's attractions, limit CB's applications in polymer composites.[19] NC-reinforced nanocomposites were first introduced by Toyota in 1980s, and they have shown to significantly improve the heat distortion and modulus for nylon–clay nanocomposites. These properties increase with increasing amounts of clay.[2] It has been noted that the addition

Table I. Composite Samples and Their Respective Codes

Code	Component
Sample A	PC
Sample B	PC + CB
Sample C	PMMA
Sample D	PMMA + CB
Sample E	PC + PMMA + CB
Sample F	PC + PMMA + CB + clay

of NC improves the dispersion and solubility of nanofillers in polymer matrix due to its high surface area, aspect ratio and possibilities of being dispersed as individual particles in matrices.[20] Also, a significant improvement in the mechanical properties of nanocomposites was noticed with the use of clay nanoparticles in CB-reinforced polymer nanocomposites.[21] The introduction of a small quantity (1–5 wt %) of NC to the polymer matrix resulted in a considerable improvement in the mechanical strength because of its nanometric dimensions and high aspect ratio.[22] The specific properties of NC, such as their ability to expand to layered silicates, intercalation and exfoliation into nanocomposites, natural abundance, and low cost of NC have broadened its industrial value.[23] In comparison to conventionally filled polymers, exfoliated nanocomposites have attained a higher degree of stiffness, strength, and barriers properties with a lower NC content.[24] Furthermore, the use of NCs in PMCs has shown enhancements in the mechanical properties, thermal stability, electrical conductivity, fire retardancy, corrosion resistance, and gas-barrier properties.[25,26] The electrical conductivity of carbon-nanotube (CNT)-based nanocomposites was improved by several orders without any reduction in the modulus or glass-transition temperature with the addition of 2 wt % NCs. Liu and Grunlan[27] found that the electrical conductivity percolation threshold of CNTs could be reduced by a factor of five through the addition of NC particles into epoxy/single-walled CNT composites.

In this study, the melt intercalation technique and compression molding were used sequentially to prepare thermoplastic polymer composites with the help of nanofillers; that is, polycarbonate (PC) and poly(methyl methacrylate) (PMMA) were used here for matrix materials with CB and NC as nanofillers. Our main aim was to study the effect of the addition of NC to polymer–matrix nanocomposites and to observe the importance of plastic–plastic interactions on the mechanical properties of these nanocomposites for their applications in transportation systems and automobile accessories with lightweight components.

EXPERIMENTAL

Materials
CB (PC-503), used as a reinforcing nanomaterial, was purchased from Phillips CB, Ltd., with a particle size less of than 20 nm, and organically modified NC (Cloisite 25A) was provided from Southern Clay Products, Inc. For this study, both materials were used without any modification. PC pallets (Iupilon S 3000UR 16.5 MFI, UV stabilized PC with release) were purchased from

Mitsubishi Engineering Plastics, and PMMA (IG840) was obtained from LG Chemicals.

Composite Preparation
In this study, different composites were prepared through PC and PMMA as matrix materials. CB and NCs were used as reinforcing materials with these matrix materials to prepare nanocomposites.

All of the samples were prepared in a two-step process, where the matrix material and reinforcement were initially mixed during heating inside an internal mixture rotating at 30 rpm until the matrix material came to its semisolid state, and the reinforcing material was homogeneously dispersed inside the matrix. The composites in the semisolid state were then transferred to a compression-molding machine and cured with less than a 3-ton load until the mold pallets attained room temperature. Table I shows the various combinations of matrix and reinforcing materials used for the preparation of the composites.

Characterization
Tensile Testing. All specimens for tensile testing were prepared from the semisolid composites obtained from the internal mixture. These materials were transferred to compression molding machine with a mold with dumbbell-shaped cavities. All of the specimens were prepared according to ASTM D 638-10. Tensile testing was conducted with a universal tensile testing machine (Instron 5582) at room temperature ($25 \pm 2^\circ$C). The initial gauge length of the specimens were 50 ± 5 mm, and the cross-head speed was maintained at 2 mm/min. The tensile strength, elongation at break, and deformation were recorded from the stress–strain data.

X-ray Diffraction (XRD). The XRD patterns were obtained with an X-ray diffractometer (Bruker AXS Diffraktometer D8) equipped with Cu Kα radiation ($\lambda = 0.1540$ nm). Scans were taken in the range of diffraction angle (2θ) of 10–90°, which varied with a scanning rate of 2°/min. The operating voltage and current were maintained at 40 kV and 20 mA, respectively. The distance between the detector and sample was maintained 177 mm. All samples for wide-angle XRD were prepared through compression molding technique having thickness of 2 mm.

Field Emission Scanning Electron Microscopy (FESEM). Studies related to the morphology of the tensile fracture surfaces of the composites were carried out with FESEM (model Zeiss-Ultra Plus, Gemini Co.) under a pressure of 10^{-6} m Bar. The fractured ends of the specimens were mounted on aluminum stubs, and a secondary electron (SE) detector was used to analyze the electrons. The gold coating on the abraded surface was used to make the surface conductive for the morphological analysis of the fractured surface.

Thermogravimetric Analysis (TGA). The thermal characteristics of the plastic–plastic/CB/NC blended nanocomposites were studied with TGA (TGA SII 6300 Exstar Instrument). TGA was used to study the thermal decomposition behavior of the nanocomposites. All of the tests were done in a nitrogen atmosphere at a scanning rate of 10°C/min in the temperature range
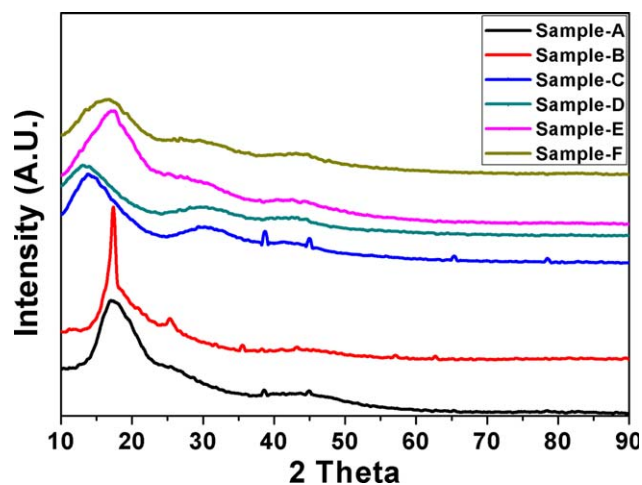
Figure 1. XRD spectra of the different nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

32–700°C. The weight of the samples was varied from 5 to 10 mg for different composite specimens.

RESULTS AND DISCUSSION

XRD Analysis

XRD analysis was used for the characterization of polymer nanocomposites. Figure 1 shows the XRD patterns for different polymers reinforced with CB and NC. Only one major peak was obtained for all of the polymers at different values of the diffraction angles; this showed the effect of the reinforcement on the crystallization characteristics of the thermoplastic polymer composites. A single peak at $2\theta = 17.5°$ was obtained for pure PC.[28] With the addition of CB, the peak sharpened; this signified the reduction in crystallinity of PC. Also, one more peak at $2\theta = 25°$ was observed; this was assigned to CB.[29] A similar trend was obtained with CB-reinforced PMMA nanocomposites. Two peaks at $2\theta = 13.86$ and $30°$ were obtained;[30] this showed the crystalline behavior of PMMA and the presence of CB, respectively. The additional peak of CB disappeared in the NC-reinforced CB/PC/PMMA nanocomposites. This was due to the improved dispersion of the CB nanoparticles in the polymer matrix.[31] As there were no additional peaks obtained with addition of NC, this indicated that exfoliated structures were produced.[32]

Morphological Characterization

The surface morphology of the polymer–matrix nanocomposites was investigated with the help of a field emission scanning electron microscope. The FESEM micrographs of various thermoplastics blends are shown in Figure 2. The examination of the impact-fractured surfaces provided information on the nanocomposites about their interfacial properties and the dispersion of the reinforcing phase in the matrix materials. It is clear from Figure 2(b,d) that the dispersion of nanoparticles in the polymers was highly inhomogeneous, and clusters were formed at a few sights; this indicated that the agglomeration of nanomaterials within the matrix and, hence, resulted in a lack of improvement in the properties of polymer composites. A similar trend for the agglomera-

tion of nanoparticles was also observed in the case of the PC/PMMA/CB nanocomposites, as shown in Figure 2(e).

An improvement in the dispersion of filler particles was noticed with the addition of NC loadings.[33–35] The fractured surface of the PC/PMMA/CB/NC nanocomposite is shown in Figure 2(f). We observed that the CB nanoparticles were homogeneously dispersed in the polymer matrix, and the surface experienced ductile fracture. Furthermore, the nanocomposites with 3 wt % NC showed a CB-rich area; this signified the improvement for the dispersion of CB in the polymer matrix. Simultaneously, the networking CB particles became strong because of better contact among the CB particles.

Thermal Analysis

The thermal stability of all of the composites was tested in the presence of a nitrogen atmosphere and is shown through the TGA curves in Figure 3. All of the composites decomposed completely between 305 and 540°C. We found that thermogravimetry curves shifted toward a higher temperature with the addition of CB and NC. These shifts toward the higher temperature indicated that the thermal stability of the hybrid nanocomposites increased.[36,37] We also observed that organically modified NC with 3% addition strongly affected the thermal degradation temperature because of the specific properties of the NC layers, where it acted as a good barrier. This improved the thermal stability of the polymer/clay nanocomposites.[38,39]

For the pure polymer and PC–CB, the weight loss was constant up to 310°C, whereas for samples having a combination of PMMA and CB, the weight loss was constant up to 430°C. The thermal degradation temperatures of PC (sample A), PMMA (sample B), and PC–CB (sample C) were found to be very close. This showed that there was a very small effect of the addition of CB to PC. However, PMMA–CB (sample D) showed around a 22% increase in the thermal decomposition temperature; this showed a noticeable effect of the addition of CB to the PMMA composites. A slight enhancement in the degradation temperature was observed with sample E (~8%) compared with that of sample D. This increase may have been due to the better plastic–plastic interaction. Further, because of the addition of NC, the decomposition temperature increased by 3.7%; this may have been due to the better dispersion of CB in the plastic–plastic matrix; this indicated that the highest thermal stability was achieved by the dispersion of CB in the presence of NC.

Mechanical Characterization

The mechanical properties of the thermoplastic composites were investigated with tensile testing to determine the influence of the filler and NC. The tensile strength and elongation at break were found to be enhanced with the use of CB as a reinforcing material. Table II summarizes the mechanical properties of the melt-blended thermoplastic composites based on CB and NC. We observed that at room temperature (25°C), the addition of 3% CB improved the tensile strength of the PC composites by 9.4% and that of the PMMA composites by 40.5%. A similar improvement in the elongation at break and a reduction in elongation were observed for both thermoplastics. Moreover, when PC and PMMA were used together as a matrix with CB
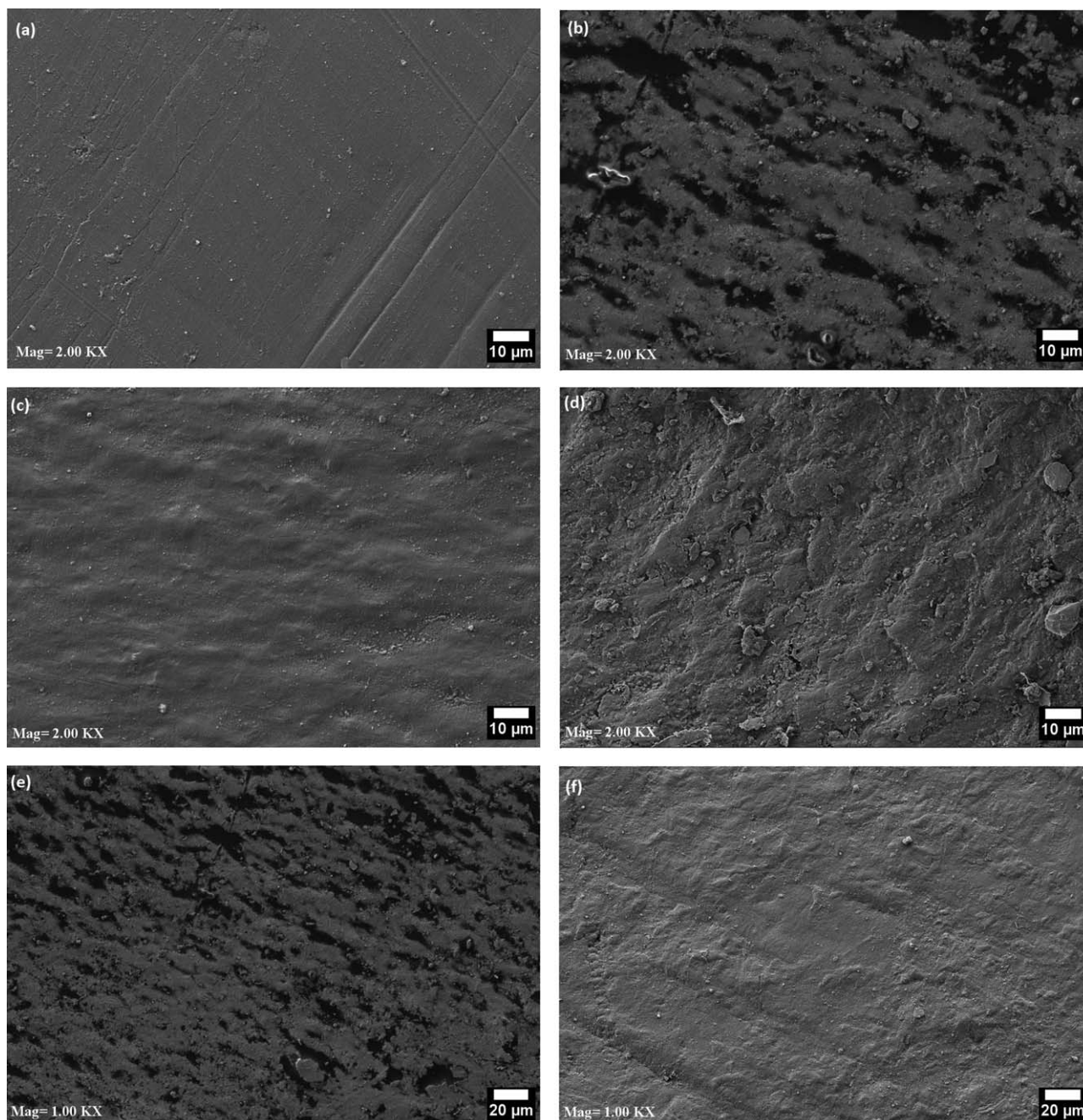
Figure 2. FESEM analysis of different nanocomposites: (a) sample A for PC, (b) sample B for PC + CB, (c) sample C for PMMA, (d) sample D for PMMA + CB, (e) sample E for PC + PMMA + CB, and (f) sample F for PC + P MMA + CB + NC.

as a reinforcing material; both properties were highly improved. The tensile strength and elongation at break for PC/PMMA/CB increased by 52 and 43.27% in comparison to sample D (PMMA/CB). This must have been due to the better plastic–plastic interaction. However, the properties were still found to not be up to the mark because of the bundling or agglomeration of particles at different sites, as shown clearly through the FESEM images.

We noticed many times that the mechanical properties of the composites were improved with enhanced uniformity in the dispersion of the fillers.[40,41] Many authors have already achieved

enhancements in the mechanical properties through improved homogeneous dispersion.[42] The addition of 3% NC resulted in a 42.41% increase in the tensile strength compared to the PC/PMMA/CB nanocomposites. However, the elongation at break was reduced by 53.69% because of the reduction in the ductility of composites with the addition of NC; this denoted the enhanced brittleness of nanocomposite.[43] We observed that brittle fracture turned to ductile fracture with the addition of NC particles, and brittle fracture could no longer be seen as the clay content in the nanocomposites, as a result of which the strong ductile nature of the composite was observed. This was yet an
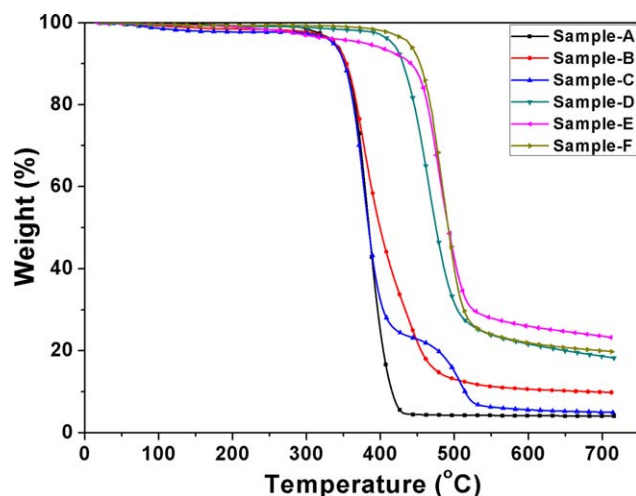
Figure 3. TGA results of the thermoplastic nanocomposites showing the effects of the addition of CB and NC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indication of good dispersion of nanoparticles; this brought out a maximum improvement in the mechanical properties at 3 wt % NC loading.[44] The improvement in the properties was attributed to the two factors; one was the homogeneous dispersion of CB in the matrix because of the addition of NC, and the other was the existence of exfoliated silicate layers. This resulted in better interaction among the matrix and reinforcing phases because of the formation of hydrogen bonds.[45] Also, the improved interaction between the polymer chains and NC surface caused the promotion of the tensile strength and the yield stress.

CONCLUSIONS

In this study, the mechanical, thermal, and morphological properties of the thermoplastic/CB blend reinforced with NC were studied. From XRD analysis, we observed that the additional peak of CB disappeared in the NC-reinforced CB/PC/PMMA nanocomposites because of the improved dispersion of CB nanoparticles in the polymer matrix. Furthermore, we also noticed that the addition of NC produced exfoliated structures. The homogeneous morphologies obtained due to addition of NC in the CB-reinforced polymer–matrix nanocomposites were ascertained with FESEM studies. From TGA, we observed that

the thermogravimetry curves shifted toward a higher temperature with the addition of CB and NC. The decomposition temperature of all of the composites remained between 305 and 540°C. We also found that there was a very small effect of NC in the degradation temperature with the pure polymer. However, the PMMA/CB composite presented a 22% increment in the thermal degradation temperature and because of better plastic–plastic interaction. Furthermore, the decomposition temperature increased by 3.7% with the addition of NC. Also, the mechanical properties with 3 wt % NC and CB increased to a great extent as compared to those of the neat blend samples. We observed that the tensile strengths of PC and PMAA with CB improved by 9.4 and 40.5% compared to those of the pure polymer. Furthermore, a 42.41% increase in the tensile strength and a 53.69% reduction in the elongation at break were observed with the addition of NC (3 wt %) compared to those of the PC/PMMA/CB composites. These observations confirmed that the use of NC in the PMCs considerably improved the mechanical properties of the nanocomposites through homogeneous dispersion of reinforcing nanoparticles in the matrix.

REFERENCES

1. Bayar, S.; Delale, F.; Liaw, B. M. *J. Aerospace Eng.* **2014**, *27*, 491.

2. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **2005**, *8*, 185.

3. Kumar, S.; Rath, T.; Mahaling, R. N.; Das, C. K. *Compos. A* **2007**, *38*, 1304.

4. Dang, Z. M.; Yuan, J. K.; Zha, J. W.; Zhou, T.; Li, S. T.; Hu, G. H. *Prog. Mater. Sci.* **2012**, *57*, 660.

5. Hofmann, F.; Maier, G. *Compos. Sci. Technol.* **2008**, *68*, 2056.

6. Paul, D. R.; Robeson, L. M. *Polymer* **2008**, *49*, 3187.

7. Bera, O.; Pilic, B.; Pavlicevic, J.; Jovicic, M.; Hollo, B.; Szecsenyi, K. M.; Spirkova, M. *Thermochim. Acta* **2011**, *515*, 1.

8. Al-Saleh, M. H.; Gelves, G. A.; Sundararaj, U. *Mater. Des.* **2013**, *52*, 128.

9. Chen, C.; Samaniuk, J.; Baird, D. G.; Devoux, G.; Zhang, M.; Moore, R. B.; Quigley, J. P. *Polymer* **2012**, *53*, 1373.

10. Wang, S.; Hu, Y.; Wang, Z.; Yong, T.; Chen, Z.; Fan, W. *Polym. Degrad. Stab.* **2003**, *80*, 157.

11. Liebscher, M.; Blais, M. O.; Potschke, P.; Heinrich, G. *Polymer* **2013**, *54*, 5875.

12. Filippi, S.; Mameli,; Marazzato, C.; Magagnini, P. *Eur. Polym. J.* **2007**, *43*, 1645.

13. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.

14. Vaia, R. A.; Ishii, H.; Giannelis, E. P. *Chem. Mater.* **1993**, *51*, 694.

15. Li, Z. M.; Li, S. N.; Yang, M. B.; Huang, R. *Carbon* **2005**, *43*, 2397.

16. Yasmin, A.; Luo, J. J.; Daniel, M. I. *Compos. Sci. Technol.* **2006**, *66*, 1182.

Table II. Mechanical Properties of the Different Samples

Sample	Composition	Tensile strength (MPa)	Elongation at break (%)	Deformation (mm)
A	PC	23.08	1.91	0.75
B	PC + CB	25.25	1.98	0.58
C	PMMA	13.48	0.93	0.29
D	PMMA + CB	18.94	1.04	0.27
E	PC + PMMA + CB	28.86	1.49	0.72
F	PC + PMMA + CB + NC	41.10	0.69	0.31

17. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. *Compos. Sci. Technol.* **2007**, *67*, 2045.

18. Shen, J. W.; Chen, X. M.; Huang, W. Y. *Appl. Polym. Sci.* **2003**, *88*, 1864.

19. Xueli, W. U.; Jianhui, Q.; Liu, P.; Sakai, E.; Lei, L. *J. Polym. Res.* **2013**, *20*, 167.

20. Galimberti, M.; Coombs, M.; Cipolletti, V.; Giannini, L.; Conzatti, L. *Appl. Clay. Sci.* **2013**, *83*, 449.

21. Rooj, S.; Das, A.; Morozov, I. A.; Stockelhuber, K. W.; Stocek, R.; Heinrich, G. *Compos. Sci. Technol.* **2013**, *76*, 61.

22. Leszczynska, A.; Njugna, J.; Pielichowski, K.; Banerjee, J. R. *Thermochim. Acta* **2007**, *453*, 75.

23. Qin, H.; Zhang, S.; Zhao, C.; Feng, M.; Yang, M.; Shu, Z.; Yang, S. *Polym. Degrad. Stab.* **2004**, *85*, 807.

24. Powell, C. E.; Beall, G. W. *Curr. Opin. Solid. State. Mater. Sci.* **2006**, *10*, 73.

25. Jang, B. N.; Costache, M.; Wilkie, C. A. *Polymer* **2005**, *46*, 10678.

26. Zhao, C.; Qin, H.; Gong, F.; Feng, M.; Zhang, S.; Yang, M. *Polym. Degrad. Stab.* **2005**, *87*, 183.

27. Liu, L.; Grunlan, J. C. *Adv. Funct. Mater.* **2007**, *17*, 2343.

28. Battaglia, M.; Piazza, S.; Sunseri, C.; Inguanta, R. *Electrochem. Commun.* **2013**, *34*, 134.

29. Athreya, S. R.; Kalaitzidou, K.; Das, S. *Compos. Sci. Technol.* **2011**, *71*, 506.

30. Zhang, Y.; Xiang, J.; Zhang, Q.; Liu, Q.; Frost, R. L. *Thermochim. Acta* **2014**, *576*, 39.

31. Abdelaziz, M. *J. Thermoplast. Compos. Mater.* **2013**, *26*, 1.

32. Yeha, J. M.; Changa, K. C.; Penga, C. W.; Lai, M. C.; Hunga, C. B. *Mater. Chem. Phys.* **2009**, *115*, 744.

33. Uday, K.; Gautam, D.; Niranjan, K.; Mesua, F. L. *J. Appl. Polym. Sci.* **2011**, *121*, 1076.

34. Guo, J.; Han, X. H.; Zhao, K. C. *Polym. Plast. Technol. Eng.* **2011**, *50*, 1035.

35. Song, Z.; Li, Z.; Yan-Ying, W.; Yi, Z.; Shi-Bo, G.; Yu-Bao, L. *Polym. Plast. Technol. Eng.* **2011** *50*, 1047.

36. Gaur, M. S.; Singh, R.; Tiwari, R. K. *J. Electrostat.* **2014**, *72*, 242.

37. Xiong, J.; Zheng, Z.; Song, W.; Zhou, D.; Wang, X. *Compos. A* **2008**, *39*, 904.

38. Zhao, C.; Qin, H.; Gong, F.; Feng, M.; Zhang, S.; Yang, M. *Polym. Degrad. Stab.* **2005**, *87*, 183.

39. Qin, H.; Zhang, S.; Zhao, C.; Feng, M.; Yang, M.; Shu, Z. *Polym. Degrad. Stab.* **2004**, *85*, 807.

40. Etika, K. C.; Lei, L.; Hess, L. A.; Grunlan, J. C. *Carbon* **2009**, *47*, 3128.

41. Tang, H.; Dong, L. S.; Zhang, J.; Ding, M. X.; Feng, Z. L. *J. Appl. Polym. Sci.* **1996**, *60*, 725.

42. Ma, H. Y.; Tong, L. F.; Xu, Z. B.; Fang, Z. P. *Nanotechnology* **2007**, *18*, 375.

43. Martino, V. P.; Jimenez, A.; Ruseckaite, R. A.; Averous, L. *Polym. Adv. Technol.* **2011**, *22*, 2206.

44. Chakradhar, K. V. P.; Subbaiah, K. V.; Kumar, M. A.; Reddy, G. R. *MPJ* **2011**, *6*, 109.

45. Taghizadeh, E.; Naderi, G.; Razavi-Nouri, M. *Polym. Test.* **2011**, *30*, 327.