Ultra-High Enhancement in the Toughness of Polyethylene by Exfoliated Natural Clay Nanosheets

Dongyu Cai, Mo Song

Department of Materials, Loughborough University, Loughborough, Leicestershire, United Kingdom LE11 3TU
Correspondence to: M. Song (E-mail: m.song@lboro.ac.uk)

ABSTRACT: The full exfoliation of inorganic natural clay was engineered in a nonpolar polyethylene following a novel method without the involvement of any chemical modification to the surface of silicate layers. Tensile results showed that the toughening effect was dependent of strain rates, and the toughness of polyethylene was substantially improved by nearly five times with 0.5 wt % natural clay nanosheets at a strain rate of 0.15 s^{-1}. Toughening mechanism was also discussed based on this new exfoliated system. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41314.

INTRODUCTION

The combination of nanomaterials and polymer has generated a new group of interesting materials known as polymer nanocomposites (PNCs).[1–3] The contribution of two-dimensional clay nanosheets to the PNCs is historical because the term "PNCs" was created as nylon/clay nanocomposites came out as the first commercial products in 1990.[4] In general, the dispersion of nanoclay in polymer matrices follows several established techniques including melt compounding, solution blending and in-situ polymerization. Natural clay minerals have rich resources in the world of nature, but they cannot be well-dispersed in organic polymers particularly nonpolar ones such as polyolefin due to inorganic-organic incompatibility. In these methods, pre-treatment of nanoclays namely surface modification is necessary to improve the compatibility between polymers and inorganic clay.[4] Nowadays, commercial clay products for PNCs (normally named as organoclays) are commonly made by chemically modifying natural clay minerals. However, the use of chemical modifiers produces huge impact on manufacturing cost, safety, processing and recycling of the PNCs.

Polyethylene (PE) is one of leading thermoplastic materials that have been utilized in a variety of commercial applications such as protective liners, pipes, packaging and heavy duty sacks. It generates a great deal of interests in using nanofillers (e.g., nanoclays, carbon nanotubes, mica, and calcium carbonate) to enhance the mechanical performance. Melt compounding is the most popular method for fabricating PE nanocomposites. Swain and Isayev[5] reported the use of a single screw extruder attached with an ultrasound die for producing high density polyethylene

(HDPE)/organoclay (Cloisite_20A) nanocomposites. The results showed that the stiffness of HDPE was improved, but the elongation and toughness dramatically decreased with the addition of 2.5 wt % organoclays. Tanniru et al.[6] used a twin screw extruder to mix HDPE copolymer with a natural montmorillonite clay modified with dimethyl dialkyl ammonium. They also observed that the elongation substantially decreased with the incorporation of 4 wt % nanoclays. Some reserachers attempted to use compatibilizer such as oxidized PE,[7] PE-g-MA,[8] and PP-g-MA[9] to improve the interaction between PE matrix and nanoclay. However, the toughness still decreased with the addition of nanoclay.

In this communication, we report that full exfoliation of a natural clay can be achieved by a simple method in HDPE that is a typical nonpolar polyolefin with poor wetting ability and inactive backbone. The chemical modification of nanoclay is not involved in this process, which demonstrates the advantages in manufacturing clay-based PNCs in future. Furthermore, we observe that the HDPE is significantly toughened by these unmodified clay nanosheets, and meanwhile toughening mechanism is discussed along with our observation.

EXPERIMENTAL

Fabrication of Exfoliated HDPE/Clay Nanocomposites

The natural hectorite clay (Benton®HC) and HDPE powder was supplied by Elementis Specialties (Belgium) and ICO Polymer (UK), respectively. Making exfoliated HDPE/clay nanocomposites followed several steps. The clay powder was added into water, in a weight proportion of 2%. To ensure the exfoliation
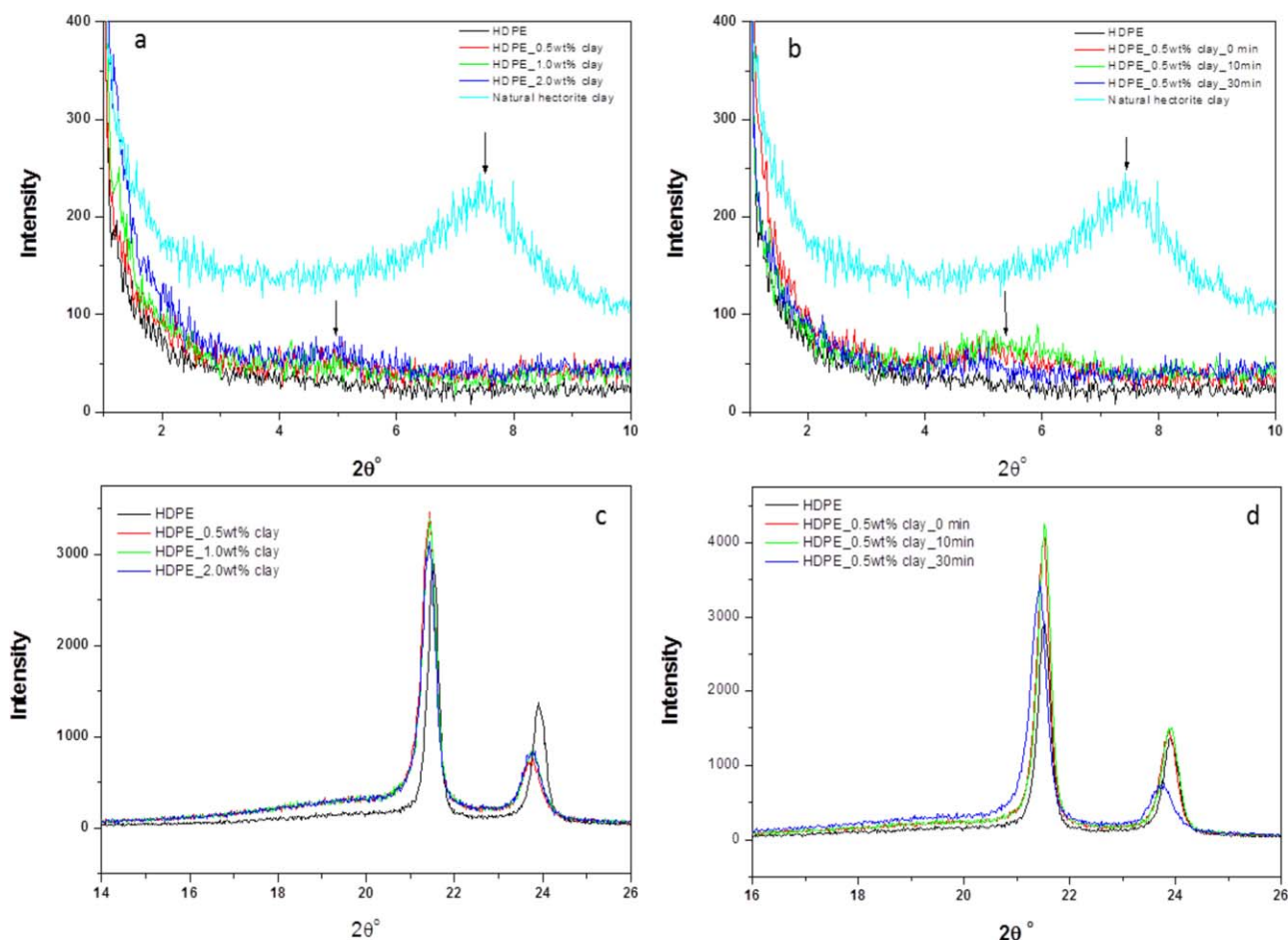
Figure 1. XRD patterns of (a,c) the exfoliated HDPE/clay nanocomposites with 0.5, 1, and 2 wt % natural clay nanosheets, and (b,d) the HDPE/(0.5 wt %) clay nanocomposites treated with different sonication time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

of the clay the mixture was then subjected to ultrasound for 30 min using 300 w ultrasonic horn at 20 kHz. The suspension of exfoliated clay was then mixed with twice the initial quantity of water, and HDPE powder was added, such that the weight ratio of HDPE powder to clay was 98 to 2 (2 wt % clay). This mixture was stirred vigorously while being heated in a pressure vessel to 121°C at elevated pressure, and maintained at that temperature for 10 min with continuous stirring using a magnetic stirrer. During this period, the clay nanosheets adhere to the surfaces of the HDPE powder. The mixture was then cooled to 50°C and the water was separated from clay coated HDPE powder using a filter. The wet HDPE/clay powder was further dried in an oven at 65°C for 12 h. Finally dried HDPE/clay powders were fed into a Haake Polylab mixer (Thermo Scientific) at 170°C for 5 min to form the exfoliated HDPE/clay nanocomposites.

Characterization

X-ray diffraction (XRD) patterns were obtained using Philip-X' Pert X-ray diffractometer (anode 40 kV, filament current 35 mA) with nickel-filtered CuK_α ($\lambda = 0.1542$ nm) radiation at a scan speed of $1°$ min^{-1}. Transmission electron microscopy (TEM) analysis was conducted using a JEOL 2100 FX instru-

ment. The nanocomposite samples were microtomed to the slices of 100–150 nm thickness using Huxley-Pattern Ultramicrotome (Cambridge Scientific instruments, UK), and then placed into standard TEM copper grids. Tensile tests were performed on the specimens (gauge length = 25 mm) using a Hounsfield tensile tester (Hounsfield test equipment, UK) at a crosshead rate of 50 mm/min (0.03 s^{-1}) and 250 mm/min (0.15 s^{-1}), respectively. The DumbBell specimens were cut from a 1-mm thick HDPE or nanocomposite sheet that was made using hot compression. Five specimens were tested for each sample. Nonisothermal crystallization was performed using a TA Instrument DSC 2920 calorimeter. About 10 mg sample was melted at 170°C for 2 min to ensure the complete removal of pre-existing crystals. Afterward, the melted sample was cooled to 20°C at a rate of 5°C/min and then heated to 170°C at a rate of 5°C/min. Reflective optical microscopy (MeF3, Reichert-Jung, Wien, Austria) was used to image the surface of the sample directly after tensile tests.

RESULTS AND DISCUSSION

Firstly, XRD and TEM techniques were both utilized to prove the exfoliation of the clay in the HDPE matrix. Figure 1(a) shows the XRD patterns of the natural hectorite clay and
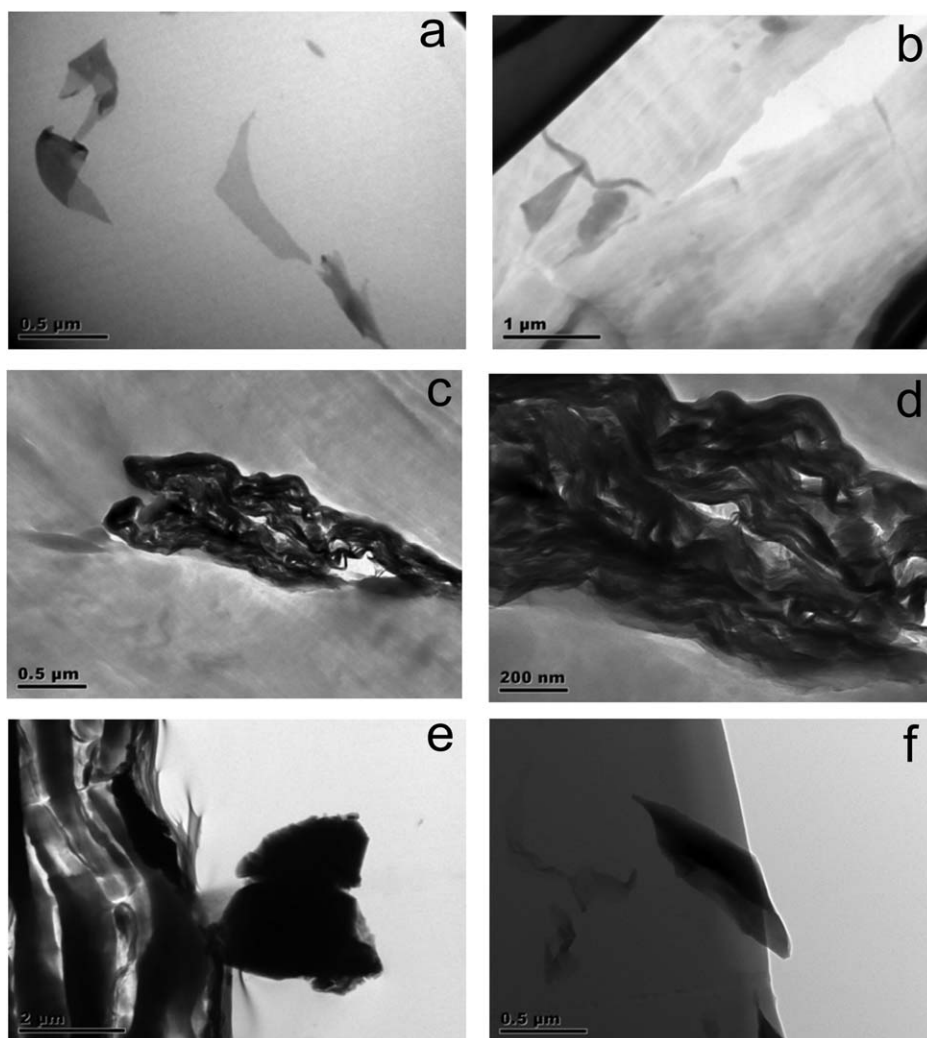
Figure 2. TEM images of (a,b) the exfoliated HDPE/(0.5 wt %) clay nanocomposite, (c,d) the exfoliated HDPE/(2 wt %) clay nanocomposite, and (e,f) nonexfoliated HDPE/(0.5 wt %) clay nanocomposite without sonication.

exfoliated HDPE/clay nanocomposites. The layered structure of the natural hectorite clay is reflected by the diffraction peak of 7.5°. The vanishing of this peak in the XRD patterns of the nanocomposites indicates the destruction of layered structure and the exfoliation of the clay in the HDPE matrix. However, a very tiny bumping peak is observed around 5° at 2 wt % clay. It means a highly exfoliating state is acheived while a small proportion of clays are intercalated due to the factor of clay concentration. Figure 2(a,b) show the TEM images of the HDPE/(0.5 wt %) clay nanocomposite, in which single layer clay nanosheets are clearly observed. Figure 2(c,d) present an intercalated clay with layered structure in the HDPE/(2 wt %)clay nanocomposite. It could be claimed that full or high exfoliation of the natural inorganic clay in the HDPE matrix was achieved by our method without any chemical modification. As disclosed in experimental section, 30 min sonication is the key step for ensuring the exfoliation of nanoclays in our method. A broad peak centered at 5.5° can be seen in the XRD patterns [Figure 1(b)] as the sonication time is shortened or no sonication is applied. The TEM images in Figure 2(e) also show that the

natural clay cannot be completely exfoliated into single layer nanosheets in the HDPE matrix without proper sonicating treatment. As shown in Figure 2(f), it should be admitted that a few exfoliated clay nanosheets can be produced in the HDPE matrix even without the ultrasonic treatment.

It has been widely recognized that the nanofillers can make substantial contribution to the stiffness of polymers.[10,11] But the nano-toughening effect is much more complex, particularly for semi-crystalline polymers with two-phase microstructures.[12] It is well-known that the toughness of semi-crystalline polymers is related to the rate of external deformation and enviromental temperature. Toughening semi-crystalline polymer by micro-sized hard particles was experimentally discovered by Argon and his coworkers.[13] The toughening effect of hard particles was attributed to the oriented polymer crystalline layers induced around the hard particles. These oriented layers with reduced plastic shear resistance initiated the debonding of the hard particles from the polymeric matrix and the formation of cavity, resulting in the improvement in the toughness. When it comes
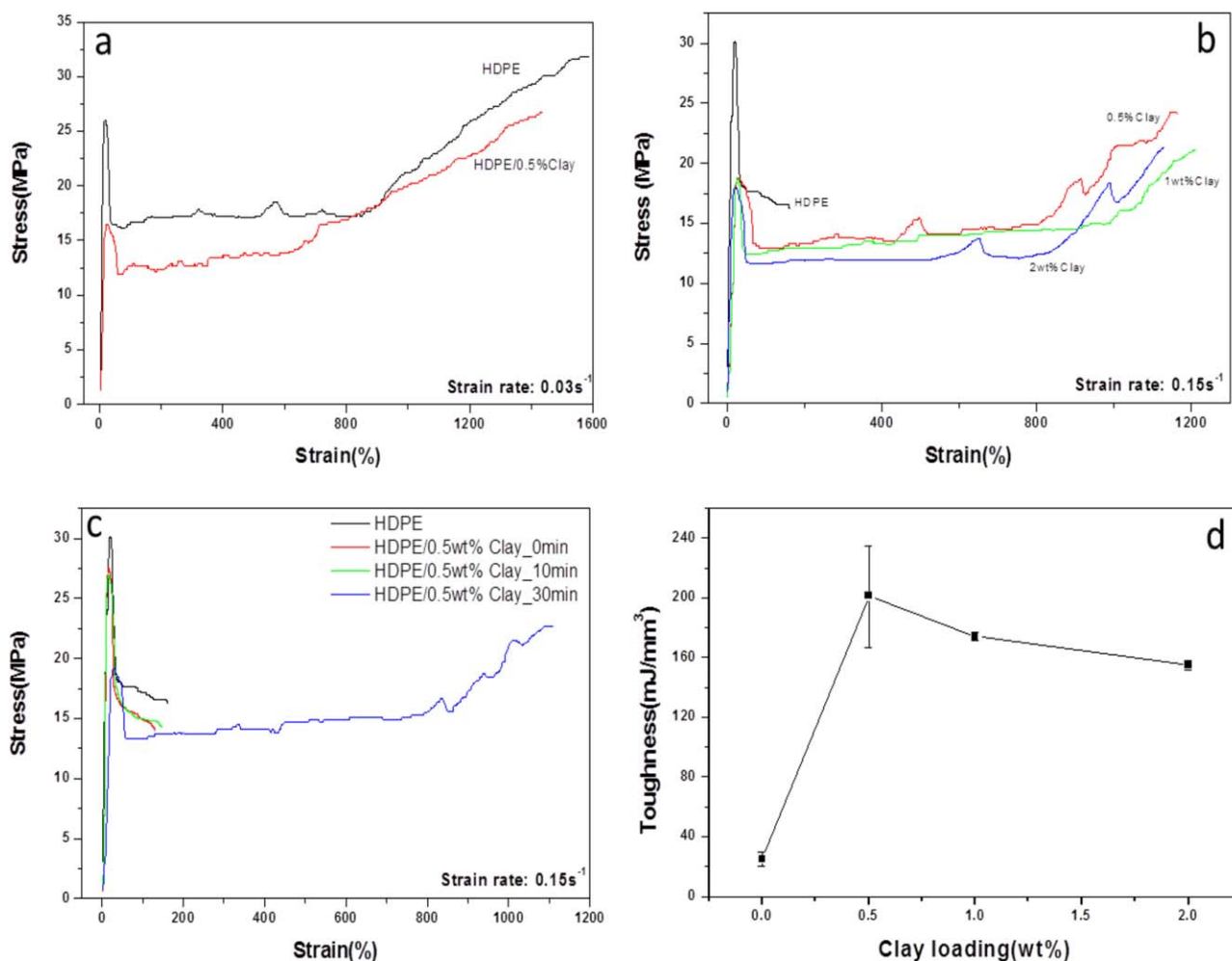
Figure 3. Tensile properties of the HDPE/clay nanocomposites. (a,b) stress–strain curves of the exfoliated HDPE/clay nanocomposites (a: strain rate = 0.03 s^{-1}; b: strain rate = 0.15 s^{-1}); (c) stress–strain curves of the HDPE/(0.5 wt %) clay nanocomposites against sonication time (strain rate = 0.15 s^{-1}); (d) The average toughness (the area under stress–strain curves) of the exfoliated HDPE/clay nanocomposites against clay loading at the strain rate of 0.15 s^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to nanofillers, the nanofillers with higher surface energy will form stronger adhesion with the matrix than that of micro-sized fillers and the debonding of the nanofillers from the matrix become more difficult. This is why the nanofillers generally show modest impact on the toughness of semi-crystalline polymers, sometimes even make the situation worse.[12] However, nano-toughening effect can be found in some cases providing that the interface is specifically tailored. If the interaction between the nanofillers and the matrix is significantly enhanced via surface modification of the nanofillers, the improvement of toughness results from the substantial energy dissipation taking place during the debonding of the nanofillers from the matrix.[14] This circumstance is generally observed at a low loading of nanofillers in which the stiffness and strength of polymers is increased with limited loss in plasticity.[15,16] In addition, the improvement of the toughness is brought by new crystalline structure of polymers induced by nanofillers such as ductile fiber-like crystals.[17,18] The improved toughness is mainly due to the increase in the plasticity of polymers rather than the

stiffness. In some specific cases,[19] it has been found that the mobility of nanofillers in polymeric matrices facilitates the enhancement in the energy dissipation and plasticity. The mobility can be enhanced via softening the matrices at certain temperatures, therefore this nano-toughening mechanism is only available when the materials are tested above glass transition temperature. Our work demonstrates that the exfoliated natural clay nanosheets provides a new route to toughen semi-crystalline polymers. It is considered that a very weak interface formed due to inorganic-organic compatibility could possibly benefit the debonding of the clay nanosheets from the matrix.

Tensile tests were carried out at two different strain rates of 0.03 and 0.15 s^{-1} to evaluate the toughness of the exfoliated HDPE/clay nanocomposites. As shown in Figure 3(a), exfoliated clay nanosheets fails to toughen the HDPE at a low strain rate of 0.03 s^{-1}. The HDPE performs as typical ductile materials with large plastic deformation because polymer chains have enough time to reptate to dissipate external stress and the concentration of internal stress is avoided under low strain rate extension. The

Table I. Summary of DSC and Tensile Results (Strain Rate = 0.15 s^{-1}) of HDPE/Clay Nanocomposites

	Heat of fusion (J/g)	Melting temperature (°C)	Yield stress (MPa)	Tensile modulus (MPa)	Elongation (%)
HDPE	157	128	30.6 ± 0.6	269 ± 24	138 ± 27
HDPE/0.5% clay	156	128	19.0 ± 0.2	105 ± 10	1225 ± 141
HDPE/1% clay	152	128	18.9 ± 0.5	164 ± 18	1197 ± 16
HDPE/2% clay	154	129	18.5 ± 0.8	173 ± 15	1128 ± 16

decrease in tensile modulus and yield stress is clearly illustrated from the strain–stress curves, indicating that the stiffness of the HDPE is reduced by the clay nanosheets. Figure 3(b) shows the strain–stress curves at a higher strain rate of 0.15 s^{-1}. The values of yield stress, tensile modulus and elongation are summerized in Table I. The HDPE performs like a brittle material because there is no enough time for polymer chains to reptate. The yield stress and tensile modulus decrease with the addition of the clay nanosheets. Figure 3(d) reveals that the toughness of the nanocomposites with 0.5–2 wt % clay nanosheets is nearly six times that of pure HDPE. Apparently, the exfoliated nanocomposites exhibit ductile behavior in comparison with brittle HDPE under high strain rate extension. The relation between exfoliation and toughness is also investigated. As said above, the exfoliation is partly determined by sonication time in our method. Tensile stress–strain curves in Figure 3(c) reveal that the tougheness of the HDPE fails to witness any improvement as the full exfoliation of the clay is not achieved. Therefore, fully or highly exfoliating natural clay into single layer nanosheets is a critical condition for switching on nano-toughening effect in the nanocomposites. After being stretched by the tensile tester, the samples were analyzed by reflective optical microscopy. The optical images in Figure 4 clearly show that a large number of micro-cracks are induced by the exfoliated clay nanosheets during tensile extension, but the formation of micro-cracks is hardly found in the pure HDPE. The formation of micro-cracks should be the reason of the nanocomposites with the enhanced elongation under external deformation. Now the question is that how these micro-cracks are formed in presence of the exfoliated clay nanosheets. As discussed before, the interface is one of the main issues determining the nano-toughening effect. Here, it is worthy investigating the interface in this exfoliated ssystem.

It is our belief that interaction is very weak in this exfoliated system because the clay nanosheets with inorganic surface are not compatible with nonpolar HDPE matrix. The reduction in the tensile modulus for all exfoliated HDPE/clay nanocomposites could be the evidence for this assumption. The formation of PE crystallites nucleated by the exfoliated clay nanosheets might be the chance for engineering a strong interface. DSC technique was used to measure the crystallization behavior of the exfoliated HDPE/clay nanocomposites at a cooling and heating rate of 5°C/min. Figure 5(a,b) shows that the exfoliated clay nanosheets impose negligible influence on the crystallization and melting behaviuor of the HDPE, indicating that the crystalline interface is not formed. The values of melting temperature

and heat of fusion are given in the Table I. XRD technique was used to study the crystalline structure of the HDPE/clay nanocomposites. The reflection at $2\theta = 21.5°$ and 23.9° corresponds to the index of refraction [110] and [200] planes of the orthorhombic unit cell in HDPE crystals, respectively.[20] Figure 1(c,d) discloses that the characteristic peaks shift to lower position by ~0.2° and also are broadened in all exfoliated nanocomposites, whilst nonexfoliated ones hardly observe any change. It implies that no new crystalline structure is formed, but the integrity of crystalline phases is slightly altered by the exfoliated clay nanosheets. This may explain reduced yield stress of the nanocomposites because the yield stress is related to the inter-attraction between crystalline lamella. As the interface is engineered to be very weak, it may be understandable that the interfacial
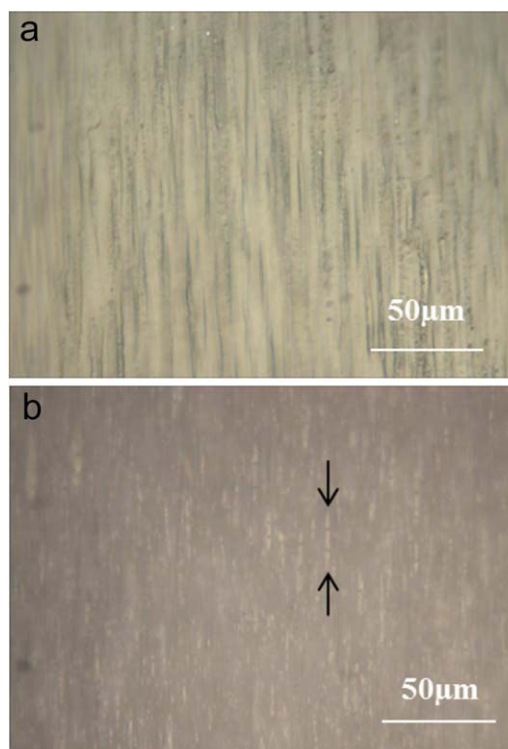

Figure 4. Optical images of (a) the HDPE, (b) the exfoliated HDPE/(0.5 wt %) clay nanocomposite after tensile extension at a strain rate of 0.15 s^{-1}. The white void indicated by arrows in the image (b) is a typical micro-crack formed during stretching the bulk sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
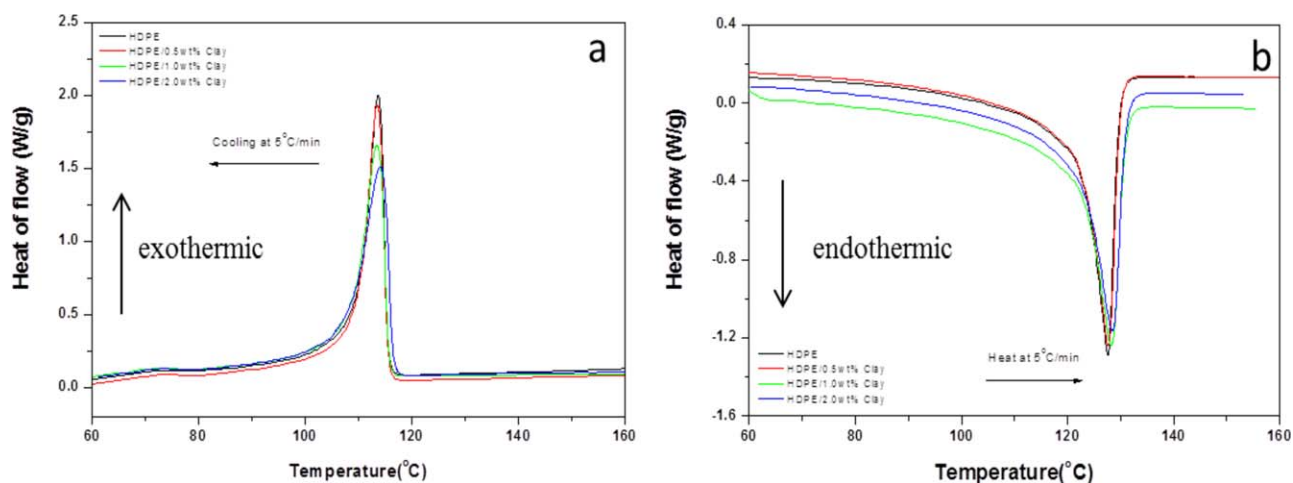
Figure 5. DSC curves of the exfoliated HDPE/clay nanocomposites at a cooling and heating rate of 5°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

debonding become easy and results in the formation of micro-cracks to avoid the concentration of internal stress.

CONCLUSION

This study disclosed that natural inorganic clays could be exfoliated in a nonpolar HDPE matrix without using any chemical treatment. The toughness of exfoliated HDPE/clay nanocomposites was substantially increased in comparison with that of the pure HDPE at a high strain rate. This exfoliated system had a weak interface due to the inorganic characteristic of the clay nanosheets. A possible mechanism was disscused to understand clay-enhanced energy dissipation in this exfoliated system, which was due to the formation of micro-cracks resulting from the debonding of the weak interface with low shear strength. In this system, the exfoliated natural clay nanosheets increased the plasticity but decreased the stiffness of the matrix. It was an interesting phenomenon different from the common reinforcing effect of hard nanoparticles. It was believed that this system provided new platform to understand nano-toughening mechanism and would offer a new angle for designing nanocomposite materials.

REFERENCES

1. Manias, E. *Nat Mater.* **2007**, *6*, 9.

2. Byrne, M.T.; Gun'ko, Y. K. *Adv. Mater.* **2010**, *22*, 1672.

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

4. Okada, A.; Usuki, A. *Macromol. Mater. Eng.* **2006**, *291*, 1449.

5. Swain, S. K.; Isayev, A. *Polymer* **2007**, *48*, 281.

6. Tanniru, M.; Yuan, Q.; Misra, R. D. K. *Polymer* **2006**, *47*, 2133.

7. Durmuş, A.; Woo, M.; Kaşgöz, A.; Macosko, C. W.; Tsapatsis, M. *Eur. Polym. J.* **2006**, *43*, 3737.

8. Pegoretti, A.; Dorigato, A.; Penati, A. *Express Polym. Lett.* **2007**, *1*, 123.

9. Lee, J. H.; Jung, D.; Hong, C. E.; Rhee, K. Y.; Advani, S. G. *Compos. Sci. Technol.* **2005**, *65*, 1996.

10. Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* **2006**, *44*, 1624.

11. Coleman, J. N.; Khan, U.; Gun'ko, Y. K. *Adv. Mater.* **2006**, *18*, 689.

12. Chen, B.; Evans, J. R. G. *Soft Matter* **2009**, *5*, 3572.

13. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. *Polymer* **1999**, *40*, 2347.

14. Sun, L.; Gibson, R. F.; Gordaninejad, F.; Suhr, J. *Compos. Sci. Technol.* **2009**, *69*, 2392.

15. Coleman, J. N.; Cadek, M.; Blake, R.; Nicolosi, V.; Ryan, K. P.; Belton, C.; Fonseca, A.; Nagy, J. B.; Gun'ko, Y. K.; Blau, W. J. *Adv. Func. Mater.* **2004**, *14*, 791.

16. Cai, D.; Yusoh, K.; Song, M. *Nanotechnology* **2009**, *20*, 85712.

17. Rafiq, R.; Cai, D.; Jin, J.; Song, M. *Carbon* **2010**, *48*, 4309.

18. Shah, D.; Maiti, P.; Gunn, E.; Schmidt, D. F.; Jiang, D. D.; Batt, C. A.; Giannelis, E. P. *Adv. Mater.* **2004**, *16*, 1173.

19. Shah, D.; Maiti, P.; Jiang, D. D.; Batt, C. A.; Giannelis, E. P. *Adv. Mater.* **2005**, *17*, 525.

20. Uehara, H.; Nakae, M.; Kanamoto, T.; Ohtsu, O.; Sano, A.; Matsuura, K. *Polymer* **1998**, *39*, 6127.