Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 281–289

polymer

www.elsevier.com/locate/polymer

Effect of ultrasound on HDPE/clay nanocomposites: Rheology, structure and properties

Sarat K. Swain [b], Avraam I. Isayev [a,]*

[a] Institute of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, USA
[b] Department of Chemistry, North Orissa University, Baripada 757003, India

Received 1 May 2006; received in revised form 1 November 2006; accepted 3 November 2006
Available online 27 November 2006

Abstract

High density polyethylene (HDPE)/organoclay nanocomposites of varying concentrations of clay were prepared by a single screw compounding extruder with the attached ultrasound die operating at various amplitudes. The die pressure and power consumption due to ultrasound were measured at different feed rates of nanocomposites of various clay concentrations. The structure and morphology of nanocomposites were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and infrared spectroscopy. It was found that ultrasonic treatment enhanced the intercalation of HDPE into lattice layers of clay by increasing *d*-spacing up to 50%. Mechanical and rheological properties of these nanocomposites were investigated as a function of clay concentration and ultrasonic amplitude. Complex viscosity, storage and loss moduli of nanocomposites were increased after ultrasonic treatment. Mechanical properties such as the elongation at break, yield stress, toughness and impact strength of ultrasonically treated nanocomposites increased in comparison with the untreated nanocomposites. A reduction in oxygen permeability of nanocomposites was observed after ultrasonic treatment at an amplitude of 10 μm with the highest reduction by 20% at 2.5% clay concentration and a residence time of 21 s. This reduction in permeability was achieved even though results indicate that the crystallinity of ultrasonically treated nanocomposites was reduced.

Keywords: HDPE; Sonication; Nanocomposites

1. Introduction

The incorporation of particulate fillers into polymer matrices is a well-known technique to improve or modify some properties of neat polymers. However, from a reinforcing point of view, fibres, or at least fillers with laminate particles having a high aspect ratio are more effective as reinforcing agents. Polymer nanocomposites have opened a new horizon for a promising class of hybrid materials by the incorporation of particulate nanofillers into polymer matrices to improve the properties of neat polymers. In recent years, layer silicate based polymer nanocomposites have attracted considerable technological and scientific interest for their changes in thermal [1], rheological [2], mechanical [3] and physical [4] properties of polymers. In general, the layer silicate is modified with alkyl-ammonium, which is hydrophilic and this facilitates its interaction with the polymer. The layers in montmorillonite are arranged in stacks, which leads to a regular van der Waals gap or interlayer. Al^{3+} is replaced with Mg^{2+} in the octahedral sheet, and a negative charge is thus generated within the layer [5]. To counterbalance the negative charge, Ca^{2+} and Na^{+} are located in the gallery [6,7]. By replacing the charge-balancing interlayer-cations with alkyl-ammonium ions, for example, the compatibility between the clay mineral and the organic phase may be substantially enhanced. The alkyl-ammonium cations lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer [8].

When a thermoplastic polymer is mixed with an organoclay, it either intercalates or exfoliates the layer silicate aggregates. In general, the intercalation is obtained when the

---

* Corresponding author. Tel.: +1 330 972 6673; fax: +1 330 258 2339.
E-mail addresses: swainsk2@yahoo.co.in (S.K. Swain), aisayev@uakron.edu (A.I. Isayev).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.11.002

polymer matrix and layer silicates do not have sufficient attractive interactions, while exfoliation is observed when they have strong attractive interactions.

Polyethylene is one of the most widely used polymers, but does not have any polar groups in its backbone to interact with the clay surface for dispersion. However, by incorporating a compatibilizer into the system, it is possible to improve the dispersion of clay within the polymer matrix [9]. Although these methods have been proved to be capable of forming nanocomposites, the exfoliation of the clay silicate layers is incomplete and thus, the reinforcement effect is limited especially for polyolefins like HDPE.

Several studies on the application of ultrasound in nanocomposite preparation were reported within recent years [10−12]. The most recent attempts to develop polymer/clay nanocomposites via melt intercalation in an intensive batch mixer [13−16] with power ultrasound were reported. However, a prolonged ultrasonic treatment (10−20 min) was used in these studies, evidently leading to a substantial degradation of the polymer matrix. Despite the considerable number of studies concerned with the preparation, characterization and properties of polyethylene/clay nanocomposites, no report has been published regarding the processing of HDPE/clay nanocomposites using continuous ultrasonic assisted extrusion.

Over the past several decades, a number of studies of the effects of ultrasound on polymers have been performed and reported. It was observed that long-chain polymer molecules can be ruptured by high intensity ultrasound during melt extrusion [17] leading to the formation of long-chain radicals. In polymer/clay systems, polymeric radicals may combine with the surface modifying agent of the clay by forming a chemical bond. Another important aspect of the ultrasound assisted process was to facilitate the break up and delamination of layer silicate, which is essential for the nanoscale dispersion of clays during melt mixing in a batch mixer [18] and extruder [19]. In this paper, we have studied the effect of continuous ultrasonic treatment during the melt intercalation of HDPE/clay nanocomposites on their structural, mechanical, rheological and oxygen barrier properties.

2. Experimental

2.1. Materials and methods

The HDPE used was HMN 4550-03-Marlex (Chevron Phillips). Cloisite® 20A natural montmorillonite, modified with quaternary ammonium salt (dimethyl, hydrogenated tallow, quaternary ammonium chloride), with a cation exchange capacity of 95 meq/100 g and *d*-spacing of 2.42 nm was supplied by Southern Clay Product, Inc. HDPE/clay nanocomposites with varying clay content of 2.5 wt%, 5.0 wt% and 10.0 wt% were prepared using a single screw compounding extruder with the ultrasonic slit die attachment having two horns operating at a frequency of 20 KHz and amplitudes of 5 μm, 7.5 μm and 10 μm [20]. In contrast to conventional screw used in Ref. [20] the screw of the present setup was equipped with two mixing sections: the Maddock mixing section followed by a melt star mixing section. The screw speed was set at 100 rpm and temperatures were 180 °C, 190 °C, 200 °C and 200 °C from the feeding section to the die zones. The gap in the slit die was 4 mm. The material was ultrasonically treated in the molten state [20] at three different flow rates 0.25 g/s, 0.50 g/s and 0.75 g/s, corresponding to the residence time of 21 s, 10 s and 7 s, respectively.

2.2. Measurement of properties

Tensile bars were prepared using a Van Dorn 55 HPS 2.8F injection molding machine at a melt temperature of 190 °C, mold temperature of 40 °C, injection speed of 40 mm/s, holding pressure of 13.8 MPa, holding time of 20 s and cooling time of 20 s. The tensile tests of nanocomposites were carried out according to ASTM D-638 using an Instron testing machine Model 5567 at a crosshead speed of 50 mm/min with 10 KN load cell without the use of an extensiometer. The impact strength of nanocomposites was performed using an Izod impact tester with a 5 lb load at room temperature on notched samples. Five specimens for each composition were used for measurement and average values were reported.

The rheological properties were measured using ARES by TA Instruments with a dynamic mode frequency sweep (strain control) process at 200 °C. Parallel plate geometry with a diameter of 25 mm and a gap size of 1.7 mm was used.

Thermal behaviors of nanocomposites were measured by differential scanning calorimeter (DSC) on a TA Instruments, Model Universal V3.0G. Samples were heated from room temperature to 250 °C at a rate of 20 °C/min, then cooled down to room temperature and heated again at the same rate to 250 °C under nitrogen atmosphere. The crystallinity data were obtained from the second heating run.

X-ray diffraction (XRD) patterns were obtained, using a Rigaku X-ray machine operating at 40 kV and 150 mA, to determine the mean interlayer spacing of the (001) plane (d_{001}) for the organoclay and its nanocomposites with HDPE.

Transmission electron microscope (TEM) was used to study the morphology of nanocomposites. The ultra thin sections of specimens were cut by cryoultramicrotome below the glass transition temperature of HDPE. A Reichert Ultracut S low-temperature sectioning system equipped with a diamond knife was used. Thin sections of 75 nm were transferred into a copper grid. A transmission electron microscope (TECNAI 12, Philips) operating at 120 kV was used.

Fourier transform infrared spectra were obtained using a FTIR spectrometer (16 PC FTIR, Perkin−Elmer) with a 4 cm^{-1} resolution. A thin film suitable for FTIR was prepared by compression molding and the film thickness was adjusted such that the maximum absorbance of any band was less than 1.0, maintaining the validity of the Beer−Lambert law.

Oxygen permeability was measured on an oxygen permeation analyzer by Illinois Instrument Inc., Model 8001. Films of 0.5 mm thickness for testing were prepared by compression molding at a pressure of 27.5 MPa and at a temperature of 200 °C. To prevent sticking of materials to the molding plates, Teflon foil was used. All sample films were cut into a 10 cm diameter circle. Measurements were carried out in the presence of nitrogen gas with purge rate setup of 10 units. Oxygen permeability of nanocomposites in $cm^3\,day\,m^{-2}$ units was measured.

3. Results and discussion

3.1. Process characteristics

The die pressure (a) and power consumption (b) due to ultrasonic treatment were recorded and are shown in Fig. 1 as a function of feeding rate. It was observed that the die pressure increases with increased flow rate for HDPE/clay nanocomposites at all clay concentrations (Fig. 1a). This is because the die pressure, characterizing the resistance to flow, is a function of the average residence time of the polymer/clay in the treatment zone. The mean residence time is inversely proportional to the flow rate and directly proportional to the die gap [21]. The ultrasonic power consumption is due to both the dissipation of energy transferred to heat and that utilized to disperse clay filler and promotes polymer intercalation into the clay gallery. It was found that power consumption increased with increased feeding rate for all concentrations of clay, indicating that more energy is being transmitted into the system (Fig. 1b). However, the specific energy consumption, calculated as power consumption divided by feeding rate, is reduced with feeding rate. It was also observed that the ultrasonic treatment of pure HDPE required more energy than that of the HDPE/clay nanocomposites. The latter was apparently due to a higher pressure that was imposed in the treatment zone in case of pure HDPE as seen from Fig. 2a. Accordingly, the higher pressure would require the higher ultrasound power consumption.

As shown in Fig. 2, the die pressure decreases substantially with the application of ultrasound and decreases further with the increase of amplitude. This may be due to the reduction in friction between the HDPE/clay melt and the die walls due to ultrasonic vibration [22]. In all sets of experiments, the die pressure of neat polymer is always higher than that of the polymer/clay nanocomposites. There are two possible reasons for such a behavior, namely, a permanent change in the melt viscosity caused by a possible degradation of polymer chains and/or a temporary change of viscosity caused by a thixotropic effect. Both of these effects are evidently enhanced by the presence of clay causing enhanced cavitation. The thixotropic changes of viscosity occurring during ultrasonic treatment will recover after the ultrasonic waves are ceased. This is the reason why the die pressure is higher for the neat polymer than for nanocomposites. This also explains why the viscosity of the neat polymer after treatment is lower than that of the nanocomposites as shown below (see Section 3.4).

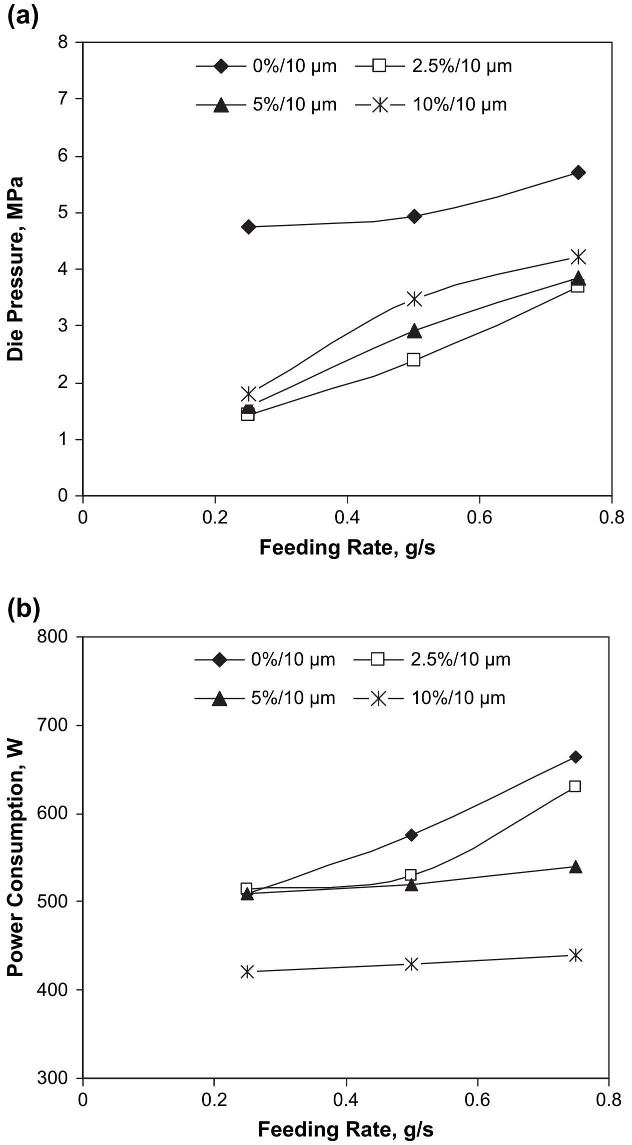

Fig. 1. Die pressure (a) and power consumption (b) as a function of feeding rate at different clay concentrations and an ultrasonic amplitude of 10 μm.

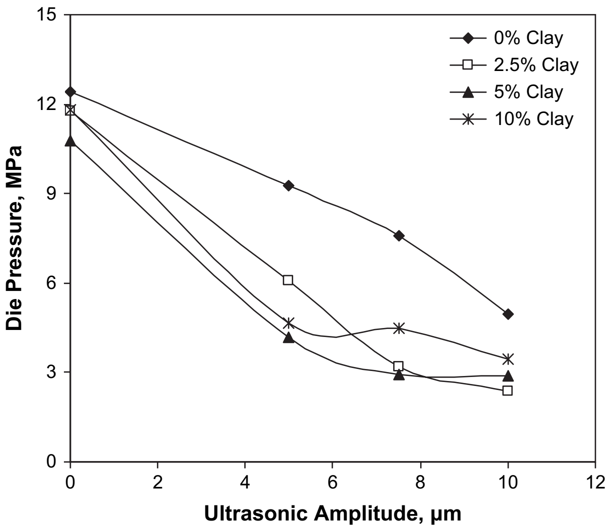

Fig. 2. Die pressure as a function of ultrasonic amplitude at different clay concentrations and a feeding rate of 0.5 g/s.

3.2. Structural properties

The XRD patterns of HDPE/clay nanocomposites are shown in Figs. 3–5. The interlayer distances and parameters are calculated by Bragg's law ($n\lambda = 2d \sin\theta$). As seen in Fig. 3 the (001) plane peaks of nanocomposites without sonication were shifted to lower angles, showing that the interlayer distance was enlarged (from 2.40 nm to 3.56 nm at 2.5 wt% clay concentration). The increased *d*-spacing of about 50% indicates that macromolecular chains had intercalated into the interlayers of Cloisite® 20A. However, the *d*-spacing decreased with increasing clay concentration. XRD patterns of nanocomposites of 5% clay at different amplitudes of ultrasound are shown in Fig. 4. The 2θ value corresponding to peak of the intensity of the sample treated at 5 μm amplitude is seen to be shifted to a lower value as compared to the untreated sample, but there was a slight increase in the 2θ value and a significant reduction in the intensity of peak at higher amplitudes of ultrasound. Apparently, a competition between the effects of ultrasound to introduce both intercalation and exfoliation is leading to these two observations. Moreover, the interlayer spacing of clay also undergoes changes with residence time of samples in the treatment zone (Fig. 5). It was also found that the intensity of the peaks was substantially decreased with increase of residence times. The latter is a direct evidence of the tendency of clay to exfoliate with increase of residence times. In particular, the nanocomposite of 2.5% clay treated at 10 μm amplitude and a mean residence time of 21 s showed a disappearance of this peak indicating an exfoliation of clay by HDPE matrix (Fig. 5).

The results of XRD studies were supported further by TEM analysis. TEM micrographs are demonstrated in Fig. 6. The regular layers of structure of untreated 5% clay samples (Fig. 6A) were disrupted by high power ultrasound showing that the polymer has entered into the intergallery spacing wherein individual clay layers are dispersed in the polymer matrix, as shown in Fig. 6B. This may be due to a partial exfoliation that occurs under treatment by ultrasound.

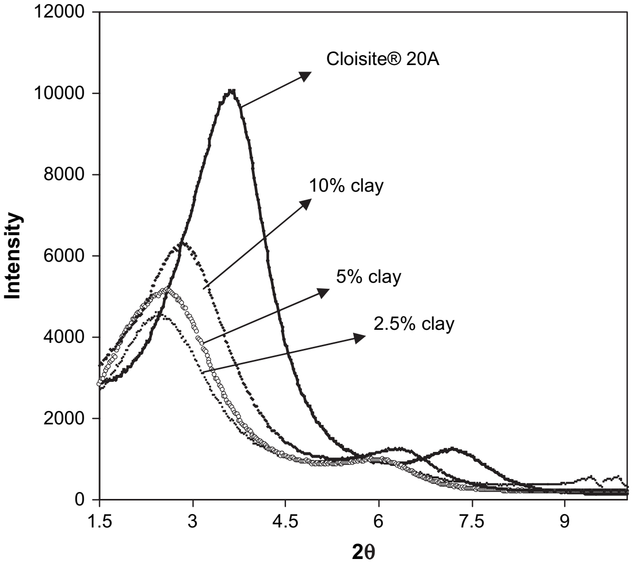

Fig. 3. XRD patterns of clay and nanocomposites of different clay concentrations obtained without sonication at a feeding rate of 0.5 g/s.

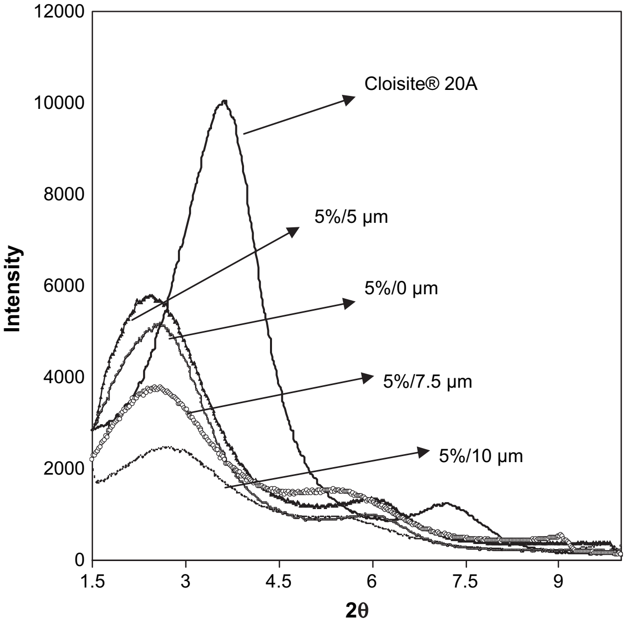

Fig. 4. XRD patterns of clay and nanocomposites of 5% clay concentration obtained at different ultrasonic amplitudes and a feeding rate of 0.5 g/s.

FTIR study was performed to describe changes in the molecular structure due to the application of ultrasound. Fig. 7 shows IR spectra of ultrasonically treated and untreated nanocomposites at 2.5% clay concentration. It was found that all the peaks were similar, except the peaks within the region of 1025–1100 cm^{-1} which have been assigned to the asymmetric stretching of C–C single bonds [23]. The broad peak in the untreated nanocomposites at 1072–1085 cm^{-1} was due to CH_2–CH_2 asymmetric stretching and CH_2 wagging of the HDPE chain. This peak became less intense for the

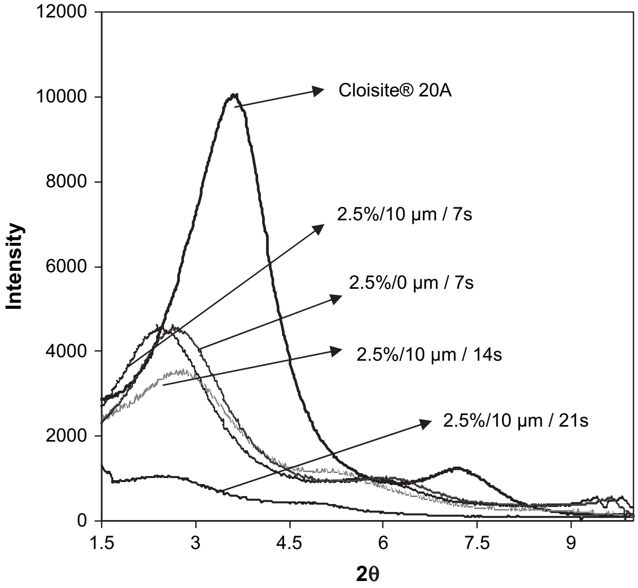

Fig. 5. XRD patterns of clay and nanocomposites of 2.5% clay concentration obtained at an ultrasonic amplitude of 10 μm and different residence times.

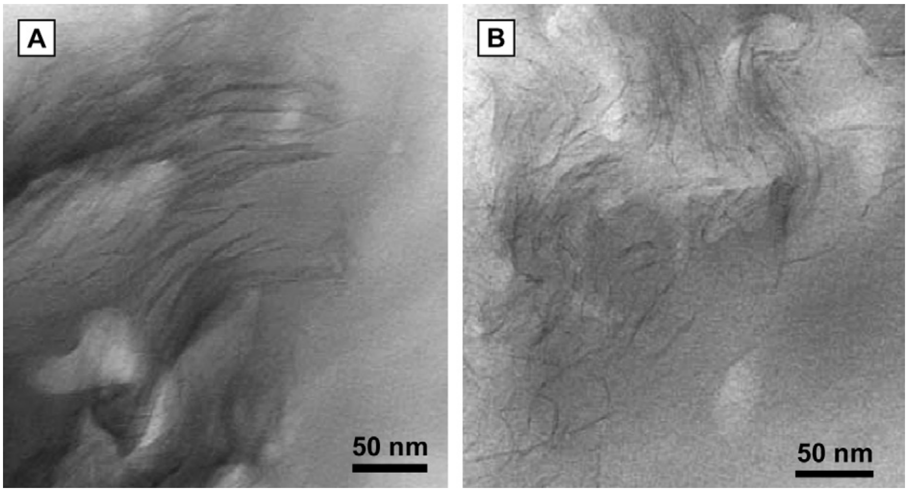

Fig. 6. TEM micrographs of nanocomposite of 5% clay concentration obtained at a feeding rate of 0.5 g/s without (A) and with (B) ultrasonic treatment at an amplitude of 5 μm.

ultrasonically treated sample. This may be due to structural deformation in the HDPE polymeric chain by sonication at amplitude of 10 μm. These changes in vibrational spectra with sonication were related to the structural modification of HDPE chain. It should also be noted that a similar structural modification of the HDPE chain was found to occur in the treated HDPE matrix in the absence of clay.

3.3. Mechanical properties

The mechanical properties, including the yield stress (a), yield strain (b), elongation at break (c) and toughness (d) of HDPE and all the nanocomposites prepared in this study have been plotted in Fig. 8. Values are also summarized in Table 1. The Young's modulus of the untreated nanocomposites increased significantly at clay loadings of 5% and 10% and decreased slightly with increasing ultrasonic amplitude (Table 1). For the treated nanocomposites, the Young's modulus is decreased with its variation with amplitude being not monotonic. In particular, the lowest value of the Young's modulus is seen at an amplitude of 7.5 μm. The yield stress (Fig. 8a) of ultrasonically treated nanocomposites was more than that of the untreated samples. The yield strain (Fig. 8b) of untreated samples decreased monotonically with the increase of clay concentration and also with ultrasonic amplitude for concentrations up to 5 wt%. Due to their rigidity, clay filler particles cannot be deformed by external stress in the specimen but act only as stress concentrators during the deformation process [24]. At the same time, the yield strain at 10 wt% clay increases with ultrasonic amplitude. Generally, the elongation at break (Fig. 8c) and toughness (Fig. 8d) of nanocomposites decreased tremendously with increasing clay content. However, in some cases, the elongation at break and toughness of the ultrasonically treated samples increased by more than two times with an increase of amplitude compared to the untreated samples. From Fig. 9, the impact strength of the untreated nanocomposites increased slightly with an increase of clay concentrations at 2.5% and 5%, then decreased at 10% clay concentration. It was found that the impact strength of treated nanocomposites was increased slightly with ultrasonic treatment at the amplitude of 5 μm whereas the impact strength of pure HDPE increased continuously with increasing ultrasonic amplitude. However, the impact strength at 10% clay concentration increased by more than two times at the amplitude of 5 μm. Therefore, from results of mechanical properties, it was concluded that ultrasound played a vital role in the dispersion of clay in HDPE by creating strong interfacial adhesion of clay with the matrix and by increasing extensibility of nanocomposites during tensile deformation.

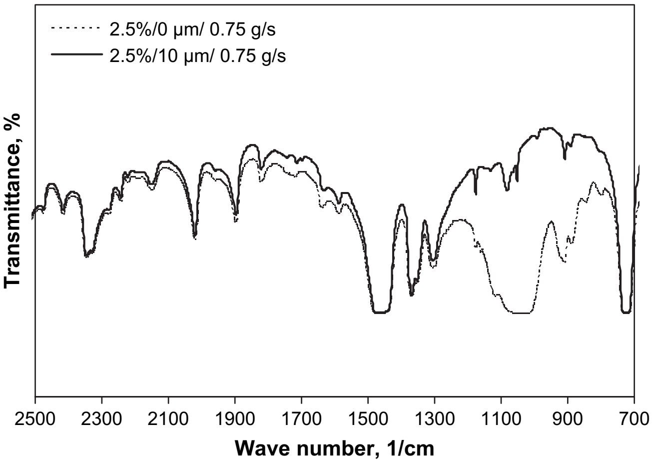

Fig. 7. IR spectra of HDPE/clay nanocomposites of 2.5% clay concentration obtained at a feeding rate of 0.75 g/s without and with ultrasonic treatment at an amplitude of 10 μm.

3.4. Rheological properties

The complex viscosity of nanocomposites as a function of frequency at various clay contents and at various ultrasonic amplitudes for 10% clay nanocomposite is illustrated in Fig. 10. It was found that the complex viscosity of nanocomposites

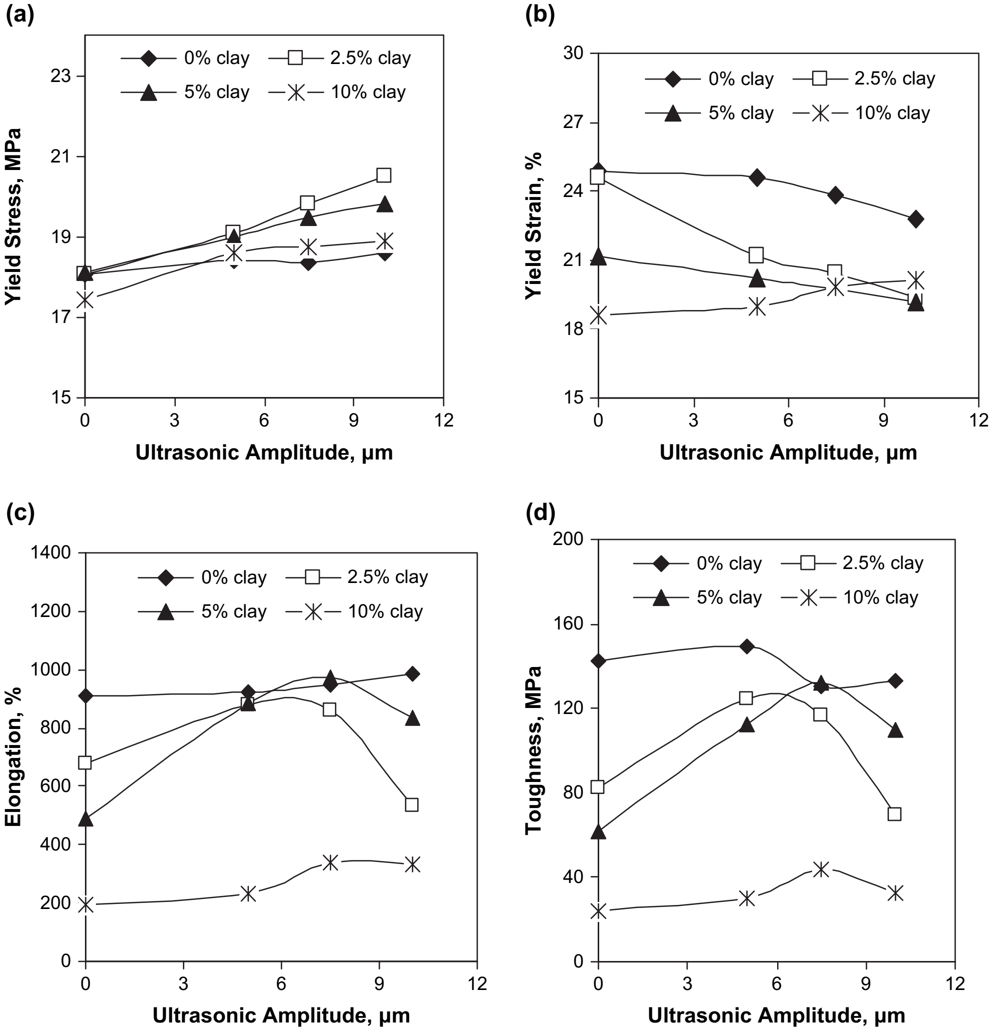

Fig. 8. Yield stress (a), yield strain (b), elongation at break (c) and toughness (d) as a function of an ultrasonic amplitude at different clay concentrations and a feeding rate of 0.5 g/s.

increases with increased clay concentration. The complex viscosity increased further with ultrasonic treatment and attained its maximum level at an amplitude of 5 μm. At an amplitude of 7.5 μm the complex viscosity is still higher than that of the untreated nanocomposite. The complex viscosity decreased at an amplitude of 10 μm. Similar trends have been obtained for all concentrations of clay. The great enhancement of complex viscosities of ultrasonically treated nanocomposites was attributed to the nanoscale dispersion of clay within HDPE, which improved the compatibility between the polymer matrix and layered silicate. The results of the storage, G', and loss, G'', moduli as a function of frequency at different concentrations of clay with different amplitudes of ultrasound are shown in Fig. 11a and b, respectively. The storage and loss moduli increased with an increase of clay concentration. After ultrasonic treatment, a sudden increase in moduli was obtained at 5 μm amplitude. Subsequently, a slow decrease was observed at higher amplitudes. At low frequencies, the storage, G', and the loss, G'', moduli were widely separated, while they were only slightly separated at high frequency region. An increase of viscosity of the treated nanocomposites at low frequency in comparison with the untreated ones at the same concentration

Table 1
Mechanical properties of HDPE/clay nanocomposites of different clay concentrations and ultrasonic amplitudes (flow rate 0.5 g/s)

Clay (%)	Ultrasonic amplitude (μm)	Young's modulus (MPa)	Elongation at break (%)	Toughness (MPa)	Yield strain (%)	Yield stress (MPa)
0	0	317 ± 23	908 ± 45	142.7 ± 9.8	24.8 ± 1.8	18.1 ± 0.7
2.5	0	324 ± 27	679 ± 48	82.4 ± 6.2	24.6 ± 1.2	18.1 ± 0.9
5	0	459 ± 37	487 ± 28	62.1 ± 5.3	21.1 ± 1.6	18.1 ± 1.0
10	0	445 ± 29	193 ± 17	23.9 ± 1.2	18.6 ± 1.1	17.4 ± 1.1
5	5	423 ± 24	887 ± 58	112.4 ± 7.3	20.2 ± 1.2	19.0 ± 1.1
5	7.5	400 ± 26	973 ± 62	132.3 ± 6.8	19.7 ± 0.9	19.5 ± 0.8
5	10	425 ± 32	835 ± 44	109.5 ± 5.5	19.1 ± 0.7	19.8 ± 0.9

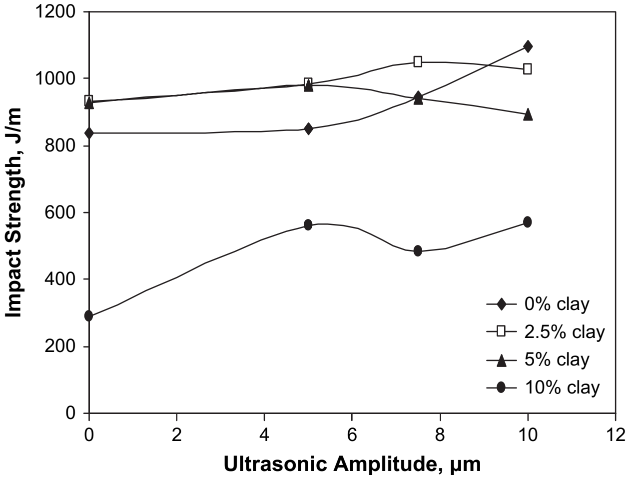

Fig. 9. Impact strength of nanocomposites as a function of an ultrasonic amplitude at different clay concentrations and a feeding rate of 0.5 g/s.

is evidently caused by a better interaction between clay and HDPE matrix. Accordingly, this is believed to be a result of the improved compatibilization effect of ultrasound on HDPE/clay nanocomposites leading to an increase of their viscosity and a reduction in the mobility of the polymer chains. In turn, the restricted mobility of the polymer chains leads to a decrease of crystallinity in HDPE/clay nanocomposites, as shown below.

3.5. Oxygen permeability

Polymer layered silicate nanocomposites, which have shown to inhibit oxygen permeation, are being studied for use in food packaging applications. HDPE/clay nanocomposites are suitable for manufacturing packaging films, because of their nanodispersed structure as compared to conventional composites. Polymer/clay nanocomposites have highly-ordered nanolayered structure which creates a tortuous path for oxygen penetration [25] whereas conventional composites have a less restrictive path for oxygen penetration in their microstructure [26] (Fig. 12). Oxygen permeability tests of HDPE/clay nanocomposites were conducted to measure the combined effect

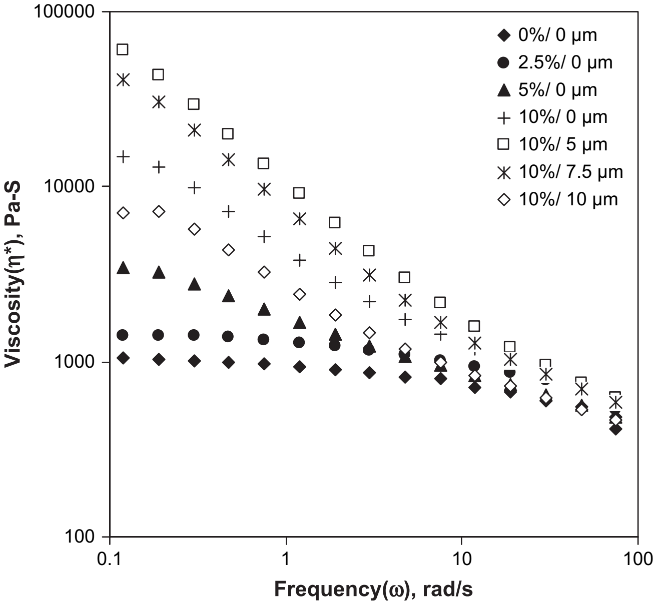

Fig. 10. Complex viscosity of nanocomposites as a function of frequency at different clay concentrations, ultrasonic amplitudes and a feeding rate of 0.5 g/s.

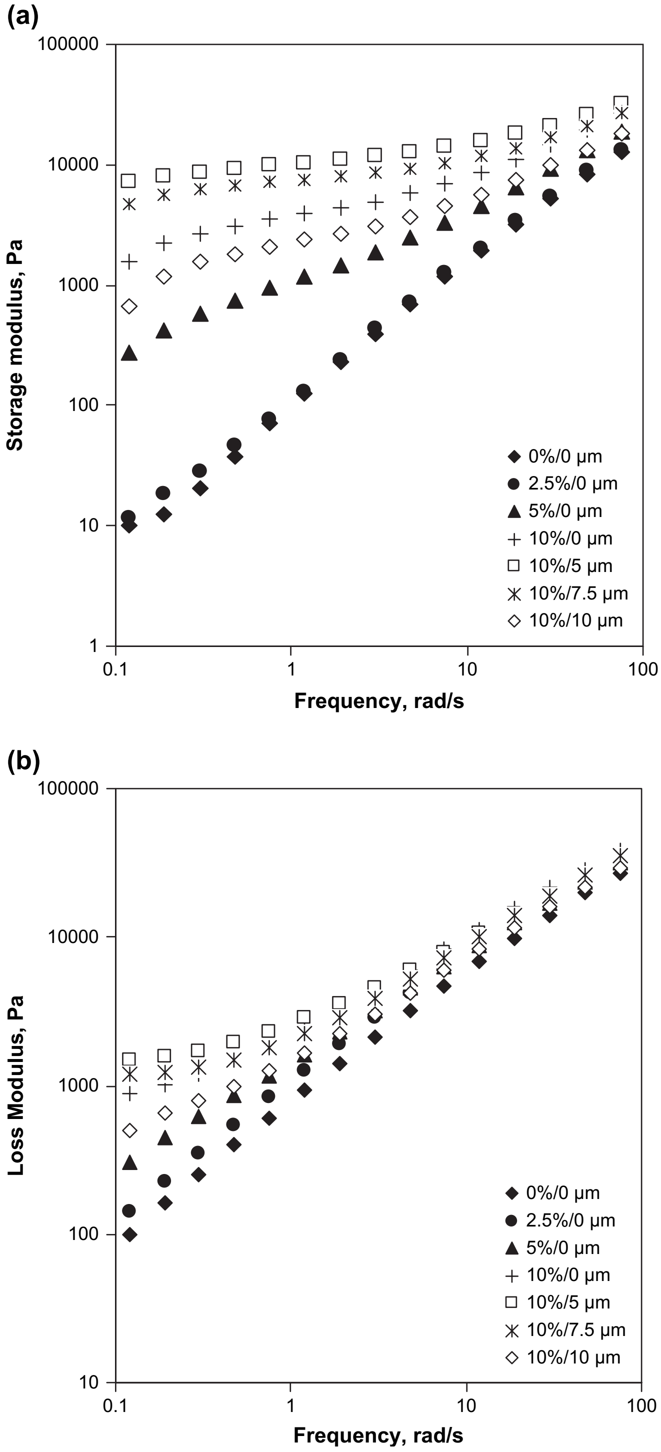

Fig. 11. Storage (a) and loss (b) moduli as a function of frequency at different clay concentrations without ultrasonic treatment and 10% clay concentration without and with ultrasonic treatment at different amplitudes at feeding rate of 0.5 g/s.

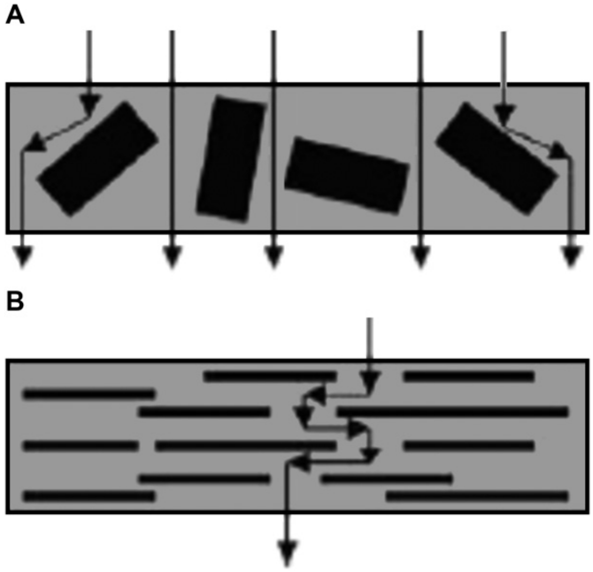

Fig. 12. Tortuous diffusion path of conventional composites (A) [26] and polymer/clay nanocomposites (B) [25].

of clay concentration and ultrasonic amplitude at different feeding rates (Table 2). It was found that oxygen permeability of nanocomposites slightly increased with clay loading, but substantially decreased by application of high amplitude ultrasound (at 10 µm). The nanocomposites of 2.5% clay with treatment of ultrasound at an amplitude of 10 µm with a feeding rate of 0.25 g/s (residence time of 21 s) have an oxygen permeability of 20% less than that of neat HDPE. It is clear that oxygen permeability of treated nanocomposites at higher amplitude and longer residence times is better even at a low concentration of clay of 2.5%.

3.6. Crystallinity

DSC melting and crystallization curves of untreated and ultrasonically treated HDPE and its nanocomposites were studied. Results are summarized in Table 3. The crystallinity data of HDPE were corrected for the presence of clay. The degree of crystallinity (Φ_c) was determined by the equation: $[(\Phi_c)\% = H_m/H_c \times 100]$, where H_m is the heat of fusion of the polymer and H_c is the enthalpy corresponding to the melting of a 100% crystalline sample. H_c for HDPE was reported to be equal to 292 J/g [27]. Results showed that the degree of crystallinity of nanocomposites tends to decrease slightly with increase of clay contents. But crystallinity decreased considerably at the ultrasound amplitude of 5 µm and increased at higher amplitudes. This is due to the creation of higher interfacial area between the polymer matrix and the clay, which acts to reduce the mobility of polymer chains. Similar trends have also been reported to occur in polyethylene/vermiculite nanocomposites [28]. Apparently, the interaction of polymer matrix and clay may be increased by ultrasonic treatment, and thus decreasing crystallinity. The effect is due to a decrease of mobility of the polymer chains, as earlier mentioned.

Table 2
Oxygen permeability of HDPE/clay nanocomposites at different clay concentrations and ultrasonic amplitudes

Sample	Clay (%)	Amplitude (µm)	Feeding rate (g/s)	Oxygen permeability (cm^3 day m^{-2})
1	0	0	0.75	75.9
2	2.5	0	0.75	76.2
3	5	0	0.75	76.4
4	10	0	0.75	79.7
5	2.5	5	0.75	76.8
6	2.5	7.5	0.75	80.6
7	2.5	10	0.75	69.7
8	5	10	0.75	71.2
9	10	10	0.75	73.3
10	2.5	10	0.5	65.9
11	2.5	10	0.25	61.8

Table 3
Absolute crystallinity of HDPE/clay nanocomposites at different clay concentrations and ultrasonic amplitudes (feeding rate 0.5 g/s)

Sample	Clay (%)	Amplitude (µm)	T_m (°C)	H_m (J/g)	Φ_c (%)
1	0	0	131.4	179.5	61.5
2	2.5	0	132.6	173.9	61.1
3	5	0	132.8	165.5	59.7
4	10	0	132.8	153.8	58.5
5	5	5	134.6	118.1	40.4
6	5	7.5	134.1	159.9	54.8
7	5	10	134.5	163.7	56.1

4. Conclusion

High dispersion of HDPE/clay nanocomposites without any chemical modification of the polymer matrix was achieved by ultrasonic treatment. Accordingly, a continuous ultrasonic extrusion method to achieve a rapid intercalation and a partial exfoliation of HDPE/clay nanocomposite without a chemical modification of the matrix was developed. This is supported by a TEM study showing a partial exfoliation and XRD study indicating an increase of *d*-spacing. Mechanical properties of HDPE/clay nanocomposites were substantially improved after ultrasonic treatment. Rheology is strongly affected by ultrasonic treatment. Viscosity of the obtained nanocomposites was found to be highest at an amplitude of 5 µm. Crystallinity of HDPE is decreased after ultrasonic treatment and with addition of clay. Oxygen permeability was substantially decreased with ultrasonic treatment at high amplitudes and residence times.

Acknowledgement

Authors express their appreciation to the Department of Science and Technology, Government of India for awarding BOYSCAST fellowship to S. K. Swain for this research at The University of Akron.

References

[1] Lee SH, Kim JE, Song HH, Kim SW. Int J Thermophys 2004;25(5):1585–95.
[2] Choi S, Lee KM, Han CD. Macromolecules 2004;37:7649–62.

[3] Maiti P, Nam PH, Okamoto M. Macromolecules 2002;35:2042–5.
[4] Rana PK, Swain SK, Sahoo PK. J Appl Polym Sci 2004;93:1007–11.
[5] Ray SS, Okamoto M. Prog Polym Sci 2003;28:1539–641.
[6] Krook M, Morgan G, Hedenqvist MS. Polym Eng Sci 2005;45:135–41.
[7] Giannelis EP. Adv Mater 1996;8:29–35.
[8] Giannelis EP, Krishnamoorti R, Manias E. Adv Polym Sci 1999;138:107.
[9] Liang G, Xu J, Bao S, Xu W. J Appl Polym Sci 2004;91:3974–80.
[10] Kumar R, Koltypin Y, Palchik O, Gedanken A. J Appl Polym Sci 2002; 86:160–5.
[11] Xia H, Wang Q. J Appl Polym Sci 2003;87:1811–7.
[12] Isayev AI, Hong CK, Kim KJ. Rubber Chem Technol 2003;76(4): 923–47.
[13] Ryu J, Lee P, Kim H, Lee J. In: SPE ANTEC; 2001. p. 2135–9.
[14] Ryu J, Kim H, Lee J. In: SPE ANTEC; 2002. p. 2240–4.
[15] Ryu J, Kim H, Lee J. Macromol Res 2002;10(4):187–93.
[16] Lee EC, Mielewski DF, Baird R. J Polym Eng Sci 2004;44(9):1773–82.
[17] Isayev AI, Wong CM, Zeng X. Adv Polym Technol 1990;10(1):31–45.
[18] Ryu JG, Kim H, Lee JW. Polym Eng Sci 2004;44(7):1198–204.
[19] Lapshin S, Isayev AI. SPE Tech Papers 2005;51:1911–5.
[20] Oh JS, Isayev AI, Rogunova MA. Polymer 2003;44(8):2337–49.
[21] Tapale M, Isayev AI. J Appl Polym Sci 1998;70(10):2007–19.
[22] Tukachinsky A, Schworm T, Isayev AI. Rubber Chem Technol 1996;69: 92–103.
[23] Prasad K, Grubb DT. J Polym Sci Part B Polym Phys 1989;27:381–9.
[24] Wang KH, Choi MH, Koo CM, Xu M, Chung J, Jang MC, et al. J Polym Sci Part B Polym Phys 2002;40:1454–63.
[25] Yano K, Usuli A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci Part A Polym Chem 1993;31:2493–8.
[26] Nielsen LE. J Macromol Sci (Chem) 1967;A1(5):929–42.
[27] Brandrup J, Immergut EH. Polymer handbook. 3rd ed. John Wiley & Sons Inc.; 1989. p. V-23.
[28] Tjong SC, Bao SP. J Polym Sci Part B Polym Phys 2005;43:253–63.