

## Study on the properties of polyethylene/montmorillonite nanocomposites prepared by a novel vane mixer

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**ABSTRACT:** A novel mixer-vane mixer which is based on elongation flow was used to prepare high-density polyethylene (HDPE)/montmorillonite (MMT) nanocomposites without any additives. The effect of elongation flow on MMT intercalating in HDPE matrix was studied in terms of rotor speed and mixing time. X-ray diffraction and transmission electron microscope analyses showed that exfoliated and intercalated nanostructures were obtained when the rotor speed was 40 and 50 rpm, and mixing time was 6 minutes. For all samples prepared by vane mixer, MMT layers showed fine intercalation in the nanocomposites. Differential scanning calorimetry and thermogravimetric analysis were used to study the thermal properties of the nanocomposites. The results showed that the addition of MMT can improve the crystallization of the HDPE. Tensile test revealed the relationships between the mechanical properties and process parameters. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42600.

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### INTRODUCTION

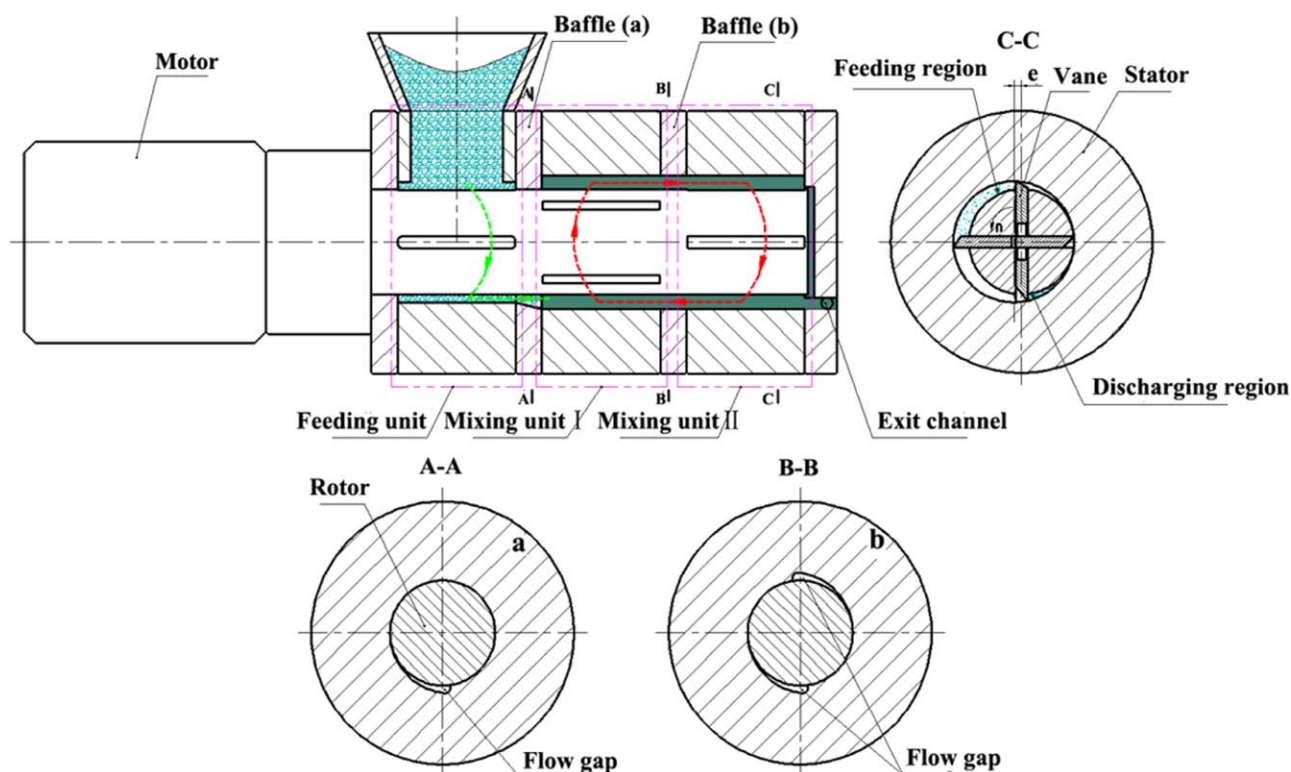
During the past few years, clays are wildly used as additives in reinforcing polymer materials.<sup>1,2</sup> Given the structure and widely sources in the nature, montmorillonite (MMT) has been one of the most commonly used clay for preparing polymer/clay nanocomposites.<sup>3</sup> A lot of research about polymer/MMT nanocomposites have been published, mainly about the improvement of the mechanical<sup>4,5</sup> and thermal<sup>6</sup> properties of the polymer matrix. However, researchers found that the unique properties of the polymer/MMT nanocomposites will only be achieved by dispersing the MMT layers in the polymeric matrices to have large surface area and aspect ratio.

Polyolefin is one of the most extensively used polymers. Preparing polyolefin/MMT nanocomposites with improved properties has attracted a large number of researchers. But the main challenge in the fabrication of the polyolefin/MMT nanocomposites is how to make MMT layers well disperse in the polyolefin matrix, due to the incompatibility between hydrophobic polyolefin matrix and hydrophilic MMT layers.<sup>7</sup> Thus there are numerous researchers who want to obtain exfoliated structure and enhance the properties by modifying the polyolefin/MMT nanocomposites with polar compatibilizer.<sup>5,8–18</sup>

Since the possibility of direct melt intercalation was investigated,<sup>19</sup> the melt intercalation method has become one of the most

important one for the fabrication of polymer/clay nanocomposites.<sup>3,20</sup> Ferreira *et al.*<sup>21,22</sup> studied the mechanical properties on the polypropylene/MMT nanocomposites prepared by injection molding. They found that fine intercalated nanostructures can be obtained during the injection process, and the addition of MMT can significantly improve the mechanical properties of the nanocomposites. Some works have been done on the theoretical analysis of thermodynamics<sup>23</sup> and kinetics.<sup>24,25</sup> However, there are few works about the effect of machining process on the properties of polymer/clay nanocomposites.<sup>26–34</sup> Sharma *et al.*<sup>32</sup> studied the effect of rotation speed on the mechanical properties of PP/MMT nanocomposites using a twin-screw extruder. They found that lower rotation speed can led better mechanical properties of the nanocomposites. They thought the reason is low rotation speed can led more residence time, gives more time to shear. In all these works, nanocomposites usually prepared by a conventional corotation twin-screw extruder, wherein the effect of shear stress on the exfoliation and intercalation of MMT is very limited.

The elongation flow is more effective than the shear flow in polymer processing. Polymer melt drops are more efficiently broken under elongation flow than under shear flow.<sup>35–37</sup> Therefore, in this research, high-density polyethylene (HDPE)/MMT nanocomposites were prepared by a vane mixer<sup>38</sup> which is based on elongation flow. The plasticizing and conveying mechanism of the vane mixer is dominated by elongation flow,



**Figure 1.** Schematic drawing of the vane mixer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

which is a better choice for the dispersive and distributed mixing of composites. Transmission electron microscopy (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile test were used to investigate the effect of elongation flow on the structure and properties of HDPE/MMT nanocomposites with respect to the rotor speed and mixing time independently.

## MATERIALS AND EXPERIMENTAL PROCEDURE

### Materials

HDPE [9001, density = 0.950 g/cm<sup>3</sup>, melt flow index = 0.05 g/10 min (190°C 2.16 kg)] was purchased from Formosa Plastics Co. (Taiwan). Commercial grade MMT is obtained from Nanocor, Arlington Heights, IL (Nanomer 1.44P). Nanomer 1.44P is an onium ion-modified MMT clay containing 60% clay (CAS No. 1318-93-0) and 40% dimethyl dialkyl (C14–18) ammonium organic modifier. HDPE was dried in an oven at 80°C for 5 h before compounding, while MMT was dried in an oven at 105°C for 5 h before mixing with the matrix.

### Description of the Mixer

The vane mixer is a novel polymer processing equipment which is completely different from traditional processing equipment in terms of structure.<sup>38</sup> As shown in Figure 1, the vane mixer is composed of one feeding unit and two mixing units. Each unit composed of a stator, a rotor, four vanes, and two baffles. The structure and working principle of the unit were introduced in detail in the previous study.<sup>39,40</sup> The baffles were used to establish a closed space and to control the material flow direction. Two types of baffles were used in this new mixing device to

generate circular flow. As shown in Figure 1, there is only one flow gap on the no-return baffle and there are two flow gaps on a circular baffle. The material flow will extrude only when the exit channel is open.

### Preparation of Nanocomposites

All nanocomposites were prepared by the novel vane mixer through melt compounding technique. The HDPE and MMT were dry mixed at first, then fed into the vane mixer, which has a mixing capacity of 50 g. In our previous work, the effect of MMT layers content on the properties of nanocomposites prepared by the novel vane mixer was studied. The results show that the best loading level of MMT is 3 wt %. So in this nanocomposites, the MMT content was 3 wt %. The temperature during the mixing was set as 210°C. The rotor speed and mixing time are listed in Table I. In all samples, the material was cooled to room temperature in air at the end of the mixing procedure.

The new vane mixer blends were used to characterize the phase morphology and thermal stability properties. The nanocomposites were dried again in an oven for 4 h at 80°C and then compression molded into flat plate with a thickness of 1 mm using a flat plate sulfide machine (QLB-25D/Q). The flat plates were molded at 210°C and a pressure of 15 MPa for 6 min. Then all flat plates were cut into dumbbell-shaped tensile test specimens for the tensile test.

### Characterization and Instruments

The interlayer distance (*d*-spacing) of the neat clay itself and the clay in the HDPE/MMT nanocomposites were measured at

**Table I.** Rotate Speed and Mixing Time

Samples	Rotor speed (rpm)	Mixing time (min)
A1	10	6
A2	20	6
A3	30	6
A4	40	6
A5	50	6
B1	30	1
B2	30	2
B3	30	4
B4	30	6
B5	30	8
B6	30	10

room temperature in the transmission mode with small-angle X-ray scattering (XRD; Bruker, D8 ADVANCE, Germany) with Cu K $\alpha$  radiation at a wavelength of 1.5418 at 40 kV and 40 mA and a scanning rate of 7.5/min. The  $d$ -spacing of organoclay was computed by the application of Bragg's equations:<sup>41</sup>

$$2d \sin \theta = n\lambda \quad (1)$$

where the variable  $d$  is the distance between clay layers, and  $\theta$  and  $\lambda$  are the certain angles and wavelength of incidence, respectively, and  $n$  is an integer.

TEM images were obtained from FEI (Tecnai F20) operating at accelerating voltage of 200 kV to indicate the location of clay particles and the intercalation of polymer molecules in the clay galleries. The nanocomposites were cut by an ultramicrotome to observe the particles on their edges. Ultramicrotomed slices 30 nm thick cut with a diamond knife were finally mounted on a copper grid.

DSC measurements were performed in a Netzsch DSC204 (Germany) in a nitrogen atmosphere.<sup>42</sup> Samples of 6–10 mg were heated to 200°C at a rate of 10°C/min, held at that temperature for 5 min, then cooled to 0°C at a rate of 10°C/min. The crystallization temperature ( $T_c$ ) was obtained from the cooling process.

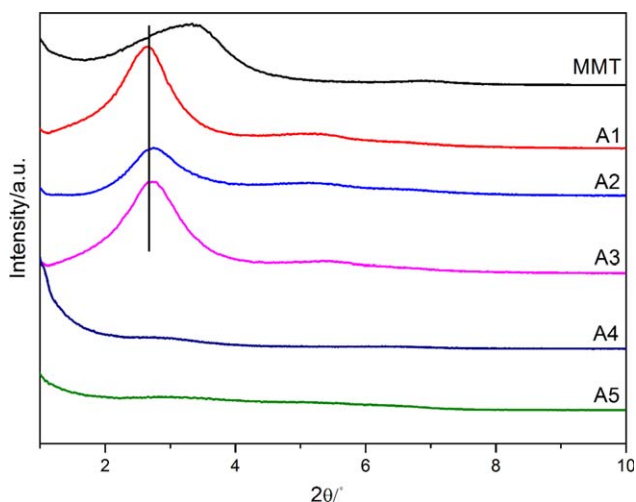
Thermal stability of HDPE/MMT composites samples was studied by using Netzsch TG209 TGA. The weight of the samples used was approximately 10.0 mg and were heated from 30°C to 600°C at a rate of 10°C/min. Nitrogen gas was used to protect the samples from being oxidized.

Tensile properties of the HDPE/MMT nanocomposites were tested using an Instron Universal Testing Machine (model 5566).<sup>43</sup> The crosshead speed of tensile test was 50 mm/min according to GB/T 1040.2 (2006). All of the data are the average from five determinations. All tests were performed at room temperature.

## RESULTS AND DISCUSSION

### Morphological Analysis

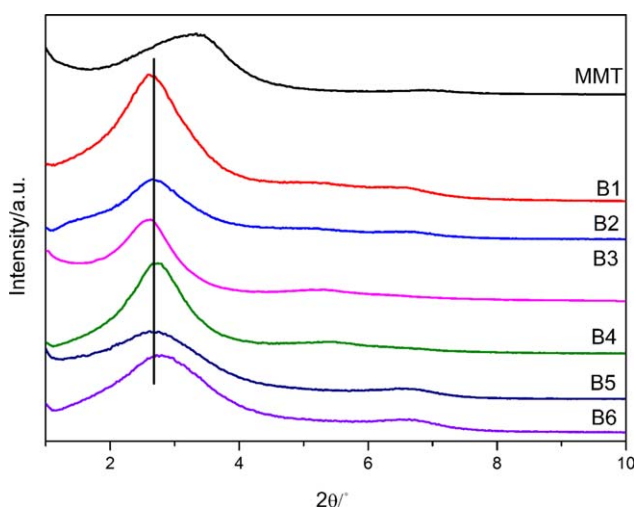
The morphological analysis of MMT layers in the HDPE/MMT nanocomposite was characterized by XRD patterns and TEM.



**Figure 2.** XRD patterns of MMT and the samples with different rotate speed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XRD is a very important measurement method to study the morphological analysis.<sup>44</sup> It is well known that XRD can provide a good way to determine the interlayer distance which is calculated using Bragg's law [eq. (1)] of the clay layers in the polymer/clay nanocomposites. The XRD curves of HDPE/MMT nanocomposites are shown in Figures 2 and 3. The  $2\theta$  value and  $d$ -spacing data are collected in Table II.

In Figure 2 and Table II, the primary (001) diffraction of neat MMT is located around 2, which means an interlayer distance ( $d$ -spacing) of 2.6 nm. For the samples with different rotor speed, the (001) diffraction position of MMT becomes weaker with the increase of rotor speed. This decreasing (001) diffraction position is because of an increase in interlayer distance between the different MMT layers, which means HDPE has intercalated into the MMT layers. When the rotor speed is set between 10 rpm and 30 rpm, the (001) diffraction position of



**Figure 3.** XRD patterns of MMT and the samples with different mixing time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table II.** XRD Data for All HDPE/MMT Nanocomposite Samples

Sample	$2\theta$ (°)	$d$ -spacing (Å)
MMT	3.339	26.4378
A1	2.668	33.0883
A2	2.77	31.8733
A3	2.729	32.3474
A4	-	-
A5	-	-
B1	2.627	33.5988
B2	2.648	33.5776
B3	2.648	33.3410
B4	2.729	32.3474
B5	2.627	33.5972
B6	2.77	31.8717

MMT changes to around 2, and the  $d$ -spacing changes to 3.2 nm, which shows a fine intercalated structure of MMT layers. The XRD curves show no obvious peaks when rotor speed increases to 40 rpm and 50 rpm, which means that the exfoliated and/or intercalated nanostructures occur in the nanocomposites when the rotor speed is 40 rpm and 50 rpm. Furthermore, intercalated nanostructures in various samples indicate that elongation flow is conducive for the occurrence of intercalation of MMT layers. When the rotor speed is high enough, the exfoliated structures can obtain in the nanocomposites even without compatilizers.

In Figure 3 and Table II, for the samples with different mixing time, with the increasing of mixing time, the (001) diffraction position of MMT does not change obviously. The (001) diffraction position of MMT is mainly around 2, and the  $d$ -spacing is about 3.2 nm, which shows a fine intercalated structure in the nanocomposites. The stable (001) diffraction position and  $d$ -spacing indicate the mixing time has little effect on the exfoliation of MMT layers in the nanocomposites. Both the decrease in (001) diffraction position and increase in  $d$ -spacing show that parameters which are set as 1 min for mixing time and 30 rpm for rotor speed is enough to obtain intercalated structure in the nanocomposites. After that, a longer mixing time has little effect on further exfoliation and intercalation of MMT layers. In previous work,<sup>34</sup> the effect of extrusion cycles on PP/MMT under shear stress was studied. In that work, the XRD analyses also show the increasing mixing time could not lead an exfoliated structure in the nanocomposites.

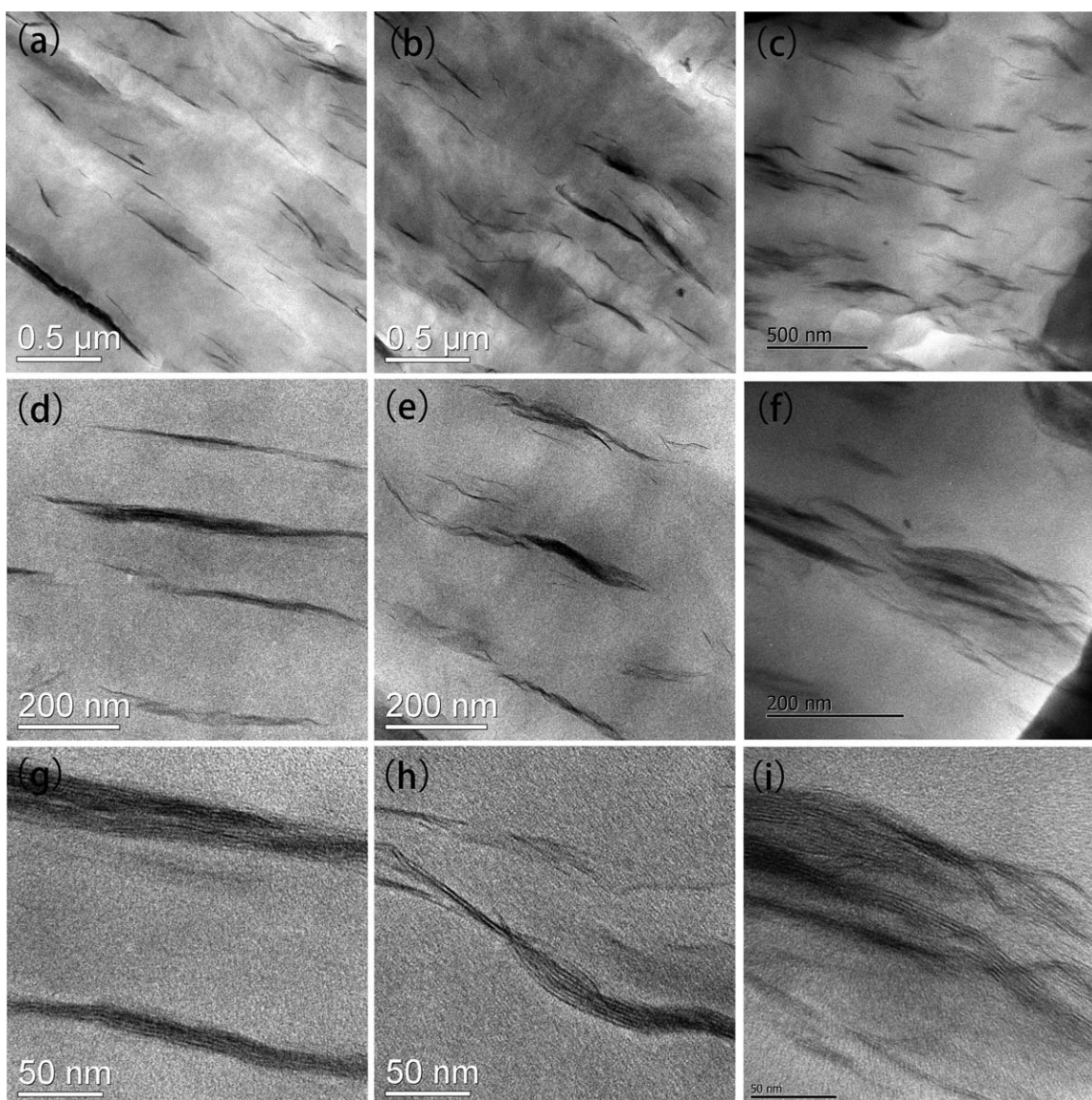
TEM was introduced to evaluate the detailed dispersion and distribution status of MMT in the nanocomposites. Figure 4 displays TEM micrographs of sample A3, A4, B1 with different magnifications. In these graphs, the dark lines represent MMT layers, while the white/grey base represents the HDPE phase. In Figure 4(a–c), the magnifications of TEM images are low, and we observed that stacked MMT layers were evenly distributed in the HDPE matrix, which means the distributions are good in those nanocomposites. This shows that both increasing rotor speed and mixing time have little effect on the distribution of

MMT in the nanocomposites. Figure 4(a,d,g) show the microstructure of the sample which was mixed for 6 min at 30 rpm. In Figure 4(d,g), it is obviously shown that the intercalated nanostructure has occurred in the nanocomposites. In Figure 4g, we can measure that the interlayer spacing of MMT layers is around 3.2 nm, which is in accordance with the XRD result. Figure 4(b,e,h) are the TEM graphs of sample which was mixed for 6 min at 40 rpm. In Figure 4(e, h), it is clearly visible that several MMT nanoplatelets are randomly dispersed in the matrix, indicating that the exfoliation of MMT layers had taken place. Besides the exfoliation state, TEM micrographs of sample A4 also show some ordered stacks of MMT sheets, which are corresponding to the intercalated nanostructures. In Figure 4(e), we can measure that the interlayer spacing of MMT layers is around 3.3 nm, which is in accordance with the XRD result. The TEM results of sample which was mixed for 1 min at 30 rpm are shown in Figure 4(c,f,i). In Figure 4(f,i), it is obviously shown that the intercalated nanostructure has occurred in the nanocomposites. In Figure 4(i), we can measure that the interlayer spacing of MMT layers is around 3.3 nm, which is in accordance with the XRD result.

For samples A3 and A4, the mixing time is 6 min, but the rotor speed is different. TEM results show that exfoliated nanostructure occurs in sample A4, while sample A3 only has intercalated nanostructures. This is a direct evidence of XRD results. For samples A3 and B1, the rotor speed is 30 rpm, but the mixing time is different. The TEM results show that the microstructures of both samples do not have so much difference, which means the mixing time has little effect on the microstructure of HDPE/MMT nanocomposites prepared by the novel vane mixer.

XRD and TEM analyses show that mixing time and rotor speed, which represents the elongation flow, have different effects on the exfoliation and intercalation of MMT layers in the nanocomposites. A short mixing time with a certain rotor speed can lead to intercalated nanostructures. But as the mixing time continues to increase, there is no any improvement in the intercalation of MMT layers. For the rotor speed, when the rotor speed is slow at first, intercalated structures occur in nanocomposites. When the rotor speed is fast enough, exfoliated nanostructures can be obtained in the nanocomposites.

The possible reason why MMT layers disperse under the steady or elongation flow field is shown in Figure 5. For the steady shear case, the velocity gradient is almost perpendicular to the flow direction. At first, the stacks of layers decreased in height by sliding layers apart from each other. Then the polymer chains entered the MMT layers pushing the end of the layers apart [as shown in Figure 5(a)]. Thus the MMT layers which aggregated in the steady shear flow were difficult to disperse if the compatibility between the polymer matrix and MMT layers is not sustainable. However, according to recent works, polymer melt drops are broken more efficiently under elongation flow than under shear flow.<sup>35–37</sup> Logically, we have experimental basis to determine that the MMT layers will be separated easily under a strong stretched force during the blend processing [as shown in Figure 5(b)]. In this work, the vane mixer has improved the



**Figure 4.** TEM graphs of A3 (a, d, g), A4 (b, e, h), and B1 (c, f, i).

elongation flow significantly during polymer processing. This is conducive to the uniform dispersion of MMT in HDPE matrix.

#### Thermal Properties

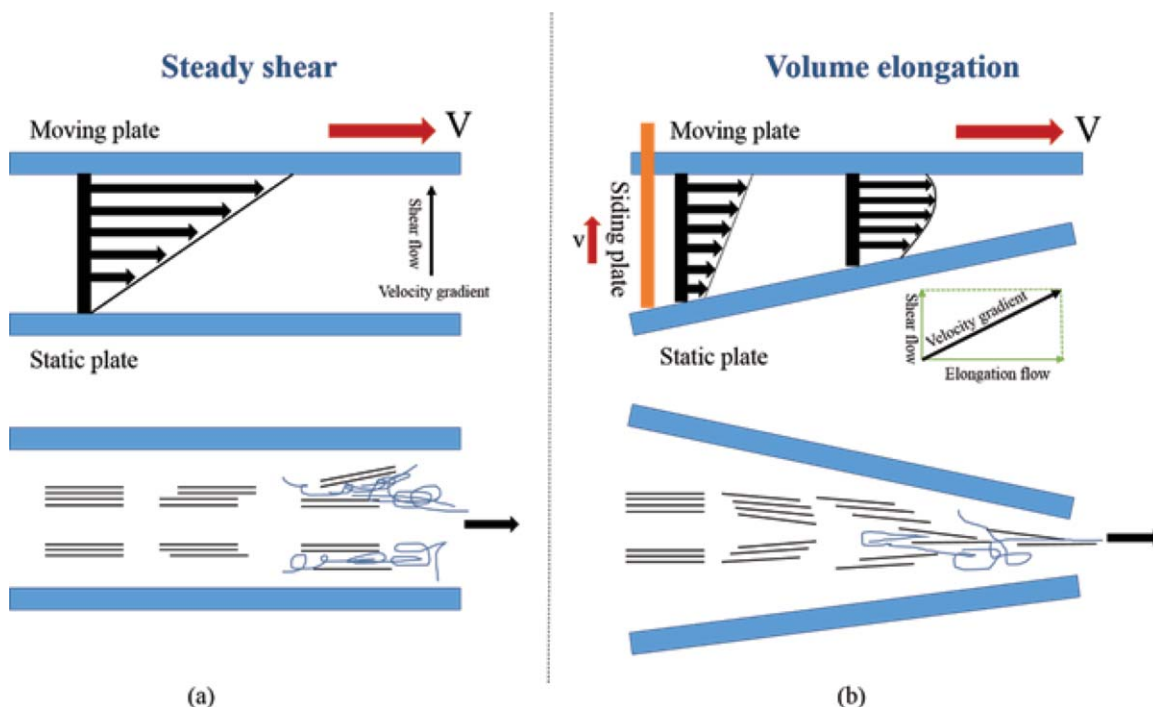
Figures 6 and 7 show the DSC cooling thermograms of the samples. The DSC data obtained from the thermograms are collected in Table III.

From Figure 6 and Table III, it demonstrates that when the rotor speed changes from 10 rpm to 50 rpm,  $T_c$  of the nanocomposites shows a slight increase from 106.9°C to 108.3°C. When the rotor speed is 10 rpm and mixing time is 6 min,  $T_c$  is 106.9°C.  $T_c$  changes to 108.3°C while the rotor speed increases to 50 rpm. One possible reason of the increase of  $T_c$  is the high rotor speed, which means higher strain rate (both shear rate and elongation rate), leads better intercalation of MMT layers, which can lead to more surface area available for the nucleation of crystals, and result in a higher  $T_c$ .

In Figure 7, it can be seen that all samples with respect to mixing time from 1 min to 10 min exhibited a strong crystallization peak at around 107°C, and the  $T_c$  of samples did not change considerably by changing mixing time. According to this case, this is mainly because the increase of mixing time has little influence on the intercalation of the MMT sheets, while the rotor speed is constant. The results also showed that the nanocomposites mixed for 1 min at 30 rpm is enough for basic intercalation of MMT layers into HDPE matrix.

These DSC results of samples with different rotor speed and mixing time are in agreement with the observations from XRD and TEM.

The thermal decomposition behavior of HDPE/MMT nanocomposites was investigated by TGA, as presented in Figures 8 and 9. The TGA data are collected in Table III. It is well known that polymer/clay nanocomposites have better thermal properties

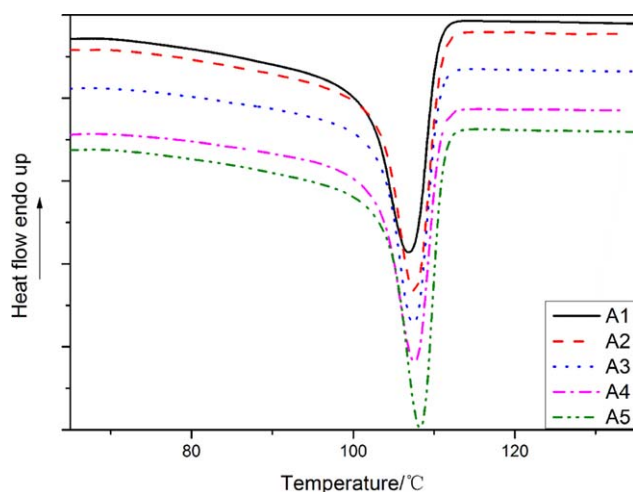


**Figure 5.** The schematic diagram of dispersing process for the layers in different flow field (a) steady shear flow; (b) volume elongation flow. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

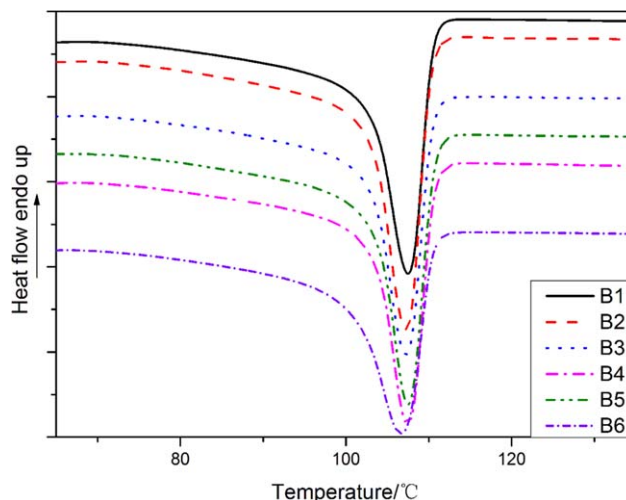
when comparing with the original matrix.<sup>6</sup> The enhancement of thermal stability observed in nanocomposites is recognized to be a consequence of fine intercalation of clay, which resulted in oxygen and heat permeability reductions in the polymer matrix during heating scans.<sup>45</sup>

From Figure 8 and Table III, thermal stability decrease when rotor speed increase from 10 rpm to 50 rpm. The thermal stability results of samples with different mixing time from 1 min to 10 min in Figure 9 and Table III are shown to be the same. The thermal stability reduces with the increasing of mixing time. Similar phenomenon was observed in previous paper.<sup>46</sup> Zheng *et al.*

prepared nanocomposites of high impact polystyrene (HIPS), polymethyl methacrylate (PMMA), acrylonitrile butadiene Styrene copolymers (ABS), polypropylene (PP) and polyethylene (PE) with a methyl methacrylate oligomerically modified clay by melt blending. By XRD and TEM analyses, they described the PS nanocomposite as a mixed intercalated/exfoliated nanocomposite, the HIPS nanocomposite as delaminated, ABS and PP as microcomposites, and PE as a mixed immiscible/delaminated system. The TGA test showed that neither the onset temperature nor the mid-point temperature of the nanocomposites is increased by nanocomposite formation, which is usual. They



**Figure 6.** DSC crystallization exotherms of the samples with different rotate speed. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

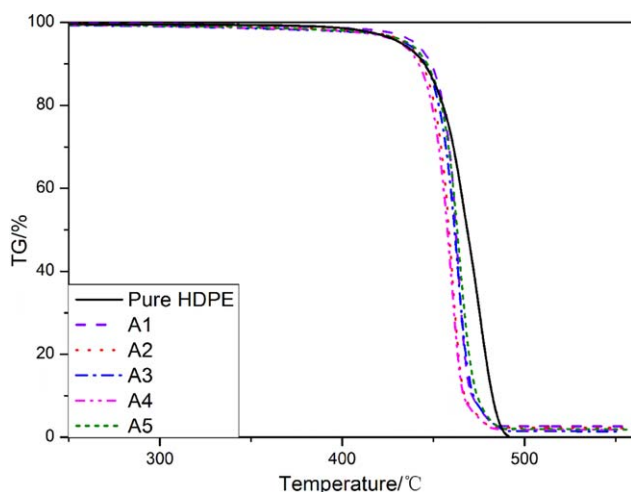


**Figure 7.** DSC crystallization exotherms of the samples with different mixing time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

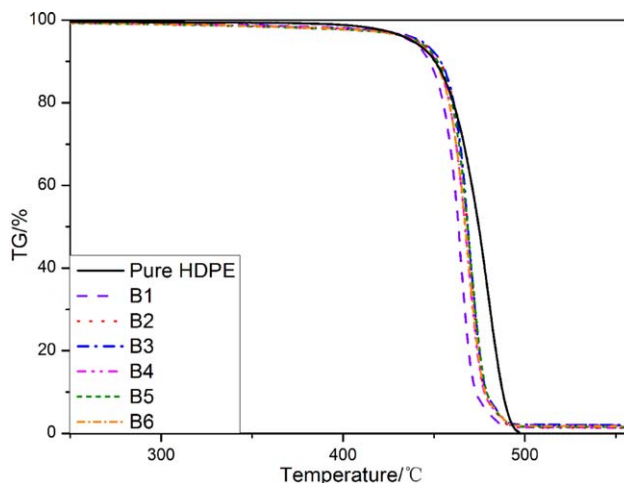
**Table III.** DSC Data for All HDPE/MMT Nanocomposite Samples

Samples	$T_c$ (°C)	$T_m$ (°C)
A1	106.9	124.1
A2	107.5	123.6
A3	107.4	123.4
A4	107.7	123.2
A5	108.3	122.8
B1	107.5	123.6
B2	107.2	123.5
B3	107.2	123.6
B4	107.4	123.4
B5	107.5	123.3
B6	106.9	124
Pure HDPE	432.7	469.3
A1	440.3	462.3
A2	438.5	461.8
A3	435.7	461.8
A4	435.8	461.6
A5	436.6	463.5
B1	437.2	463.5
B2	435.7	463
B3	437.3	463.1
B4	435.7	461.8
B5	434.9	463
B6	433.6	461.9

thought the possible reason was that the thermal stability of the methacrylate clay is not very good and thus it is unlikely that the thermal stability of the nanocomposite can be improved. Thus in this situation, the decline in thermal stability of nanocomposites may be attributed to that the thermal stability of MMT layers themselves is not very good.



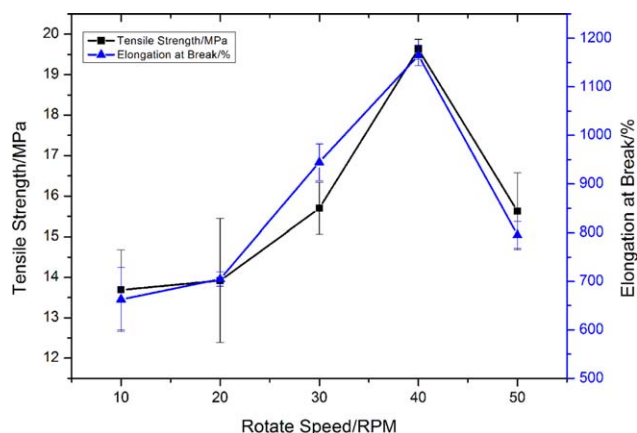
**Figure 8.** TGA curves of the samples with different rotate speed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



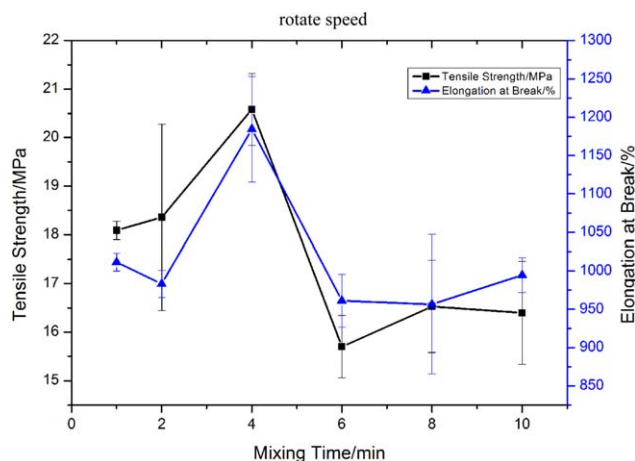
**Figure 9.** TGA curves of the samples with different mixing time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Mechanical Properties

Figure 10 shows tensile strength and elongation at break curves of the samples with different rotor speed. It can be seen that both tensile strength and elongation at break increase significantly at first and then decrease with rotor speed from 10 rpm to 50 rpm. The quality of tensile strength reveals a steady increase from 13.69 MPa at 10 rpm to 19.63 MPa at 40 rpm, which is 43.4% higher than the sample with rotor speed of 10 rpm. The elongation at break grows from 662.91% at 10 rpm to 1164.75% at 40 rpm, which shows the same trend with tensile strength. This is very similar to previous research.<sup>47</sup> The improvement in the tensile strength and elongation at break may be caused by stress transfer between HDPE matrix and MMT layers. XRD and TEM results have proved that the increasing rotor speed results in a good dispersion of MMT layers in HDPE matrix, which can improve the stress transfer between the HDPE matrix and the MMT layers. But with the sustained increasing of the rotor speed to 50 rpm, the tensile strength and elongation at break drops to 15.63 MPa and 795.2%.



**Figure 10.** Tensile strength and elongation at break curves of the samples with different rotate speed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 11.** Tensile strength and elongation at break curves of the samples with different mixing time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The tensile strength and elongation at break curves of the samples with different mixing time, while the rotor speed is 30 rpm, collected in Figure 11 show the similar changing trend. The tensile strength shows a steady increase from 18.09 MPa, when the mixing time is 1 min, to 20.58 MPa, when the mixing time is 4 min. The elongation at break rises from 1011.31%, when the mixing time is 1 min, to 1184.46%, when the mixing time is 4 min. After that, a longer mixing time, which is more than 4 min, leads to a decrease in both tensile strength and elongation at break. At last the tensile strength and elongation at break are steady about 16.5 MPa and 975%, while the mixing time is 10 min. The tensile properties increase at first may be because the intercalated nanostructures can be obtained even when the mixing time is 1 min, which is determined by XRD analyses. In previous work,<sup>34</sup> it is shown that the longer mixing time decreases tensile properties. Delva *et al.* studied the effect of multiple extrusions on the properties of PP/MMT nanocomposites prepared by a twin-screw extruder. In their work, the processing cycles which increase the distance between MMT layers was prolonged. But in the mechanical test, they found the mechanical properties decrease while the processing cycles were high (nine or more).

The decrease in tensile properties, when the rotor speed or mixing time is too high or too long, may be because of the loss of organic cations between MMT platelets. These organic cations work as surfactants between the surfaces of the MMT layers and make it possible for the HDPE to diffuse between the MMT layers. The lack of organic cations will reduce the stress transfer between the HDPE and the MMT layers and decrease the tensile properties.

## CONCLUSION

In summary, HDPE/MMT nanocomposites were prepared by vane mixer which is based on elongation flow. The effect of elongation flow on the properties of the nanocomposites was studied by changing the rotor speed and mixing time independently. DSC and TG results showed that the addition of MMT can improve crystallization of the HDPE. The XRD and TEM analyses showed that the best exfoliation and/or intercalation of

MMT layers occurs both at 40 and 50 rpm of rotor speeds when the mixing time is fixed at 6 min. For all samples prepared by vane mixer, the XRD results show that intercalated nanostructures occur in the nanocomposites. From the XRD results, we can determine the rotor speed which means the strain rate, has greater effect in the exfoliation and/or intercalation of MMT layers in nanocomposites than the mixing time. Meanwhile, the improvement of tensile strength and elongation at break show about 43.4% and 75.7% increase, when the rotor speed increases from 10 rpm to 40 rpm, and the mixing time is 6 min. The tensile strength and elongation at break show about 13.8% and 17.1% increase, when the mixing time increases from 1 min to 10 min, and the rotor speed is 30 rpm. The results of this study indicate that commercial MMT can be exfoliated and intercalated in HDPE/MMT nanocomposites without any additive, when prepared under elongation flow.

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## REFERENCES

- LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl. Clay Sci.* **1999**, *15*, 11.
- Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
- Morlat, S.; Mailhot, B.; Gonzalez, D.; Gardette, J. *Chem. Mater.* **2004**, *16*, 377.
- Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R. *Polymer* **2001**, *42*, 9929.
- Hambir, S.; Bulakh, N.; Kodgire, P.; Kalgaonkar, R.; Jog, J. P. *J. Polym. Sci. Polym. Phys.* **2001**, *39*, 446.
- Gilman, J. W. *Appl. Clay Sci.* **1999**, *15*, 31.
- Osman, M. A.; Rupp, J.; Suter, U. W. *Polymer* **2005**, *46*, 1653.
- Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* **1997**, *30*, 6333.
- Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. *J. Appl. Polym. Sci.* **1998**, *67*, 87.
- Reichert, P.; Nitz, H.; Klinke, S.; Brandsch, R.; Thomann, R.; Mulhaupt, R. *Macromol. Mater. Eng.* **2000**, *275*, 8.
- Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Kato, M.; Tsukigase, A.; Usuki, A. *Macromol. Mater. Eng.* **2000**, *280*, 76.
- Galgali, G.; Ramesh, C.; Lele, A. *Macromolecules* **2001**, *34*, 852.
- Hotta, S.; Paul, D. R. *Polymer* **2004**, *45*, 7639.
- Lertwilmolnun, W.; Vergnes, B. *Polymer* **2005**, *46*, 3462.
- Lee, H. S.; Fasulo, P. D.; Rodgers, W. R.; Paul, D. R. *Polymer* **2005**, *46*, 11673.
- Varela, C.; Rosales, C.; Perera, R.; Matos, M.; Poirier, T.; Blunda, J.; Rojas, H. *Polym. Compos.* **2006**, *27*, 451.



17. Morales-Teyssier, O.; Sanchez-Valdes, S.; Ramos-de Valle, L. F. *Macromol. Mater. Eng.* **2006**, *291*, 1547.
18. Cui, L.; Paul, D. R. *Polymer* **2007**, *48*, 1632.
19. Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
20. Morlat-Therias, S.; Mailhot, B.; Gonzalez, D.; Gardette, J. *Chem. Mater.* **2005**, *17*, 1072.
21. Ferreira, J.; Reis, P.; Costa, J.; Richardson, M. J. *Thermoplast. Compos.* **2013**, *26*, 721.
22. Ferreira, J. A. M.; Reis, P. N. B.; Costa, J. D. M.; Richardson, B. C. H.; Richardson, M. O. W. *Compos. Part B: Eng.* **2011**, *42*, 1366.
23. Vaia, R. A.; Giannelis, E. P. *Macromolecules* **1997**, *30*(25), 7990.
24. Vaia, R. A.; Jandt, K. D.; Kramer, J. E. *Macromolecules* **1995**, *28*, 8080.
25. Manias, E.; Chen, H.; Krishnamoorti, R.; Genzer, J.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* **2000**, *33*, 7955.
26. Chen, G. M.; Liu, S. H.; Zhang, S. F.; Qi, Z. N. *Macromol. Rapid Commun.* **2000**, *21*, 746.
27. Kim, G. M.; Lee, D. H.; Hoffmann, B.; Kressler, J.; Stoppelman, G. *Polymer* **2001**, *42*, 1095.
28. Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R. *Polymer* **2001**, *42*, 9513.
29. Schön, F.; Thomann, R.; Gronski, W. *Macromol. Symp.* **2002**, *189*, 105.
30. Yalcin, B.; Valladares, D.; Cakmak, M. *Polymer* **2003**, *44*, 6913.
31. Wang, K.; Liang, S.; Du, R. N.; Zhang, Q.; Fu, Q. *Polymer* **2004**, *45*, 7953.
32. Sharma, S. K.; Nema, A. K.; Nayak, S. K. *J. Appl. Polym. Sci.* **2010**, *115*, 3463.
33. Touati, N.; Kaci, M.; Bruzaud, S.; Grohens, Y. *Polym. Degrad. Stab.* **2011**, *96*, 1064.
34. Delva, L.; Ragaert, K.; Degrieck, J.; Cardon, L. *Polymers* **2014**, *6*(12), 2912.
35. Grace, H. P. *Chem. Eng. Commun.* **1982**, *14*, 225.
36. Scott, C. E.; Macosko, C. W. *Polym. Bull.* **1991**, *26*, 341.
37. Utracki, L. A.; Shi, Z. H. *Polym. Eng. Sci.* **1992**, *32*, 1824.
38. Xiaochun, Y.; Zhongwei, Y.; Zengwenbing, Y.; Guangjian, H.; Zhitao, Y.; Baiping, X. *J. Appl. Polym. Sci.* **2015**, 132.
39. Qu, J.; Zhang, G.; Chen, H.; Yin, X.; He, H. *Polym. Eng. Sci.* **2012**, *52*, 2147.
40. Wu, Z.; Zhao, Y.; Zhang, G.; Yang, Z.; Qu, J. *J. Appl. Polym. Sci.* **2013**, *130*, 2328.
41. Chen, F.; Jiang, X. P.; Kuang, T. R.; Chang, L. Q.; Fu, D. J.; Yang, J. T.; Fan, P.; Zhong, M. Q. *POLYM CHEM-UK* **6**, 3529 **2015**.
42. Kuang, T.; Mi, H.; Fu, D.; Jing, X.; Chen, B.; Mou, W.; Peng, X. *Ind. Eng. Chem. Res.* **2015**, *54*, 758.
43. Chen, B. Y.; Wang, Y. S.; Mi, H. Y.; Yu, P.; Kuang, T. R.; Peng, X. F. *J. Appl. Polym. Sci.* **2014**, *131*, 10.
44. I-Ta, C.; Sancaktar, E. *J. Appl. Polym. Sci.* **2013**, *130*, 2336.
45. Chiu, F.; Yen, H.; Chen, C. *Polym. Test.* **2010**, *29*, 706.
46. Zheng, X.; Jiang, D. D.; Wang, D.; Wilkie, C. A. *Polym. Degrad. Stab.* **2006**, *91*, 289.
47. Wang, N.; Zhao, C.; Shi, Z.; Shao, Y.; Li, H.; Gao, N. *Mater. Sci. Eng. B* **2009**, *157*, 44.