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AFFILIATIONS
1 Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology, Harbin 150080, People's Republic of China
2 College of Rongcheng, Harbin University of Science and Technology, Rongcheng 264300, People's Republic of China

ABSTRACT

We carried out molecular dynamics simulations to examine the structural, interfacial, and mechanical properties of amorphous polyethylene/montmorillonite (PE/MMT) nanocomposites loaded with 0 wt. %, 3.3 wt. %, 4.0 wt. %, and 5.1 wt. % of modified organic MMT (O-MMT). The MMT nanoparticles were simulated in two stages: first treated with octadecyl trimethyl ammonium chloride and then doped in amorphous PE. The effects of the O-MMT content on the microstructure parameters (interaction energy, free volume, and interfacial thickness) and macroscopic mechanical properties (Young's modulus, bulk modulus, and shear modulus) were analyzed. A strong correlation between mechanical properties and interfacial thickness was observed by analyzing the obtained data from simulation, and we verified them through experiments.

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I. INTRODUCTION

Polyethylene (PE) is one of the most common traditional polymers due to its good processability and low cost. However, its use is restricted because of lower strength and poor heat resistance. In recent years, to overcome these drawbacks, more and more nanoparticles have been widely used to modify the properties of polymers, which arise mainly from effective interfacial interaction between inorganic phase and organic phase.

In 2008, Wang et al. prepared single-walled carbon nanotubes/epoxy resin (SWNT/EP) composites with the solution casting method, and the mechanical properties were investigated. As a result, when SWNTs orientated in the stretching direction, the average tensile strength and Young's modulus of 3.0 wt. % SWNT composites increased by 164% and 103%, compared to pure EP. This is because the repeated stretching promotes dispersion of SWNTs, and then, there are good alignment and strong interfacial bonding in composites. In 2009, Hamming et al. prepared polymethylmethacrylate (PMMA) composites with 2.0 wt. % unmodified and modified titanium dioxide (TiO₂), and then, dynamic mechanical analysis (DMA) was tested. The results discovered that the polymer interphase region had decreased molecular mobility due to an attractive interaction between the modified nanoparticles and the surrounding polymer so that the normalized modulus value \( (E_c' / E_p') \) of the TiO₂-PMMA composite was improved by 43.75% after TiO₂ modification. Subsequently, Livi et al. modified montmorillonite (MMT) nanoparticles with different intercalation agents and prepared PE/MMT nanocomposites with the addition of 1 wt. % MMT. As a result, the tensile modulus of PE/MMT nanocomposites exhibited a maximum increase of 37.5% compared with pure PE; this result is in a certain correlation with the surface properties of intercalation agents as well as with the dispersed state of nanoparticles. In 2016, Majeed et al. prepared montmorillonite (MMT)/rice husk (RH) hybrid filler-filled low-density polyethylene (LDPE) nanocomposite film with the method of extrusion blown film. The addition of MMT can fill the gaps of
composites, and the interaction with the LDPE matrix and the RH fiber was increased, and then, interfacial adhesion between LDPE and RH was improved. Thus, tensile and tear properties improved in MMT/RH/LDPE nanocomposites, and the maximum improvement of 8% in tensile strength and that of 5% in tear strength are observed with the addition of 3 wt. % MMT. In 2017, Guz et al. prepared 1 wt. % thermoplastic starch/larger zinc oxide nanorod (TPS/ZnO NR-L) composites with the method of casting. There are glycerol and water as plasticizers in composites so that the strain at break $\varepsilon_b$ increased by 26% and Young’s modulus $E$ and stress at break $\sigma_b$ decreased by 37% and 22%, respectively. In 2018, Xu et al. prepared PE/MMT composites with maleic anhydride grafted PE as the compatibilizer in the extrusion process, and the mechanical properties were investigated. As PE molecules entered the nanocomposite layers, compact structures were formed and the crystallinity was improved in the PE/MMT composites so that the tensile strength and bending strength exhibited a maximum increase of 21% and 45%, respectively. Meanwhile, Yi et al. prepared hydro-terminated polybutadiene/montmorillonite/epoxy resin (HTPB/MMT/EP) nanocomposites by using the two-step method, and mechanical properties of nanostructured HTPB/MMT/EP were tested. As a result, when the contents of HTPB and MMT are 0.91% and 0.09%, the tensile strength, tensile modulus, and elongation at break of nanostructured HTPB/MMT/EP ternary composites were increased by 2%, 10%, and 8%, respectively, compared with HTPB/EP binary blend. This is owing to the HTPB/MMT interface structure, which generated the superposition effect and the toughening effect. On the basis of these experimental results, researchers agree that the interface structures have a great influence on the mechanical properties of nanocomposites. However, due to the complexity of interfacial microstructures in composites, the effect of microstructure on macroscopic properties needs to be further discussed.

In this study, we analyzed the interface structure of amorphous PE/MMT nanocomposites using the method of atomic simulation. We investigated the effect of organic MMT (O-MMT) on the structural properties and mechanical properties of PE and measured the interaction energy, fractional free volume (FFV), and thickness of the interfacial interaction zones.

II. SIMULATION AND OPTIMIZATION OF SYSTEMS

A. Systems of simulation

There are thousands of repeating units in the polymer, so the process of energy transformation is more complex, the simulation iteration time becomes extremely long, and the communication error rate increases. Thus, the difficulty of calculation grows geometrically. Furthermore, the studies found that the slippage phenomenon easily occurs in amorphous nanocomposite regions and that nanoparticles usually exist in amorphous regions. Therefore, amorphous regions of materials were determined as our research subject. In this paper, the amorphous PE and PE/MMT nanocomposite models were, respectively, established by Amorphous Cell module of Materials Studio (MS) software.

1. Amorphous PE modeling

Kang et al. showed that simulation accuracy is satisfactory when the number of repeating units is from 10 to 15 in polymer models. After considering the actual structure of PE and interaction between PE chains, two PE chains were loaded into the model, of which each PE chain was composed of 10 repeating units, and each repeating unit was composed of an alkane chain of 15 carbon atoms. The 3D triclinic PE model obtained is shown in Fig. 1; the density was set at 0.925 g/cm$^3$, the temperature was 423 K, and the corresponding initial lattice constant was $2.03 \times 2.01 \times 2.03$ nm$^3$.

2. MMT modeling

The MMT layer is in the form of a sandwich structure composed of two silicon-oxygen tetrahedrons separated by an aluminum-oxygen octahedron, between which there are six sodium ions (Na$^+$) in order to balance the interlayer charge. The MMT structure was constructed using the method of Boek et al.; the obtained 3D triclinic crystal model of MMT is shown in Fig. 2.
Notably, the 3D size of the MMT layer was \(a \times b \times c = 20.92 \times 18.12 \times 12.50 \, \text{Å}^3\), which is in the nanoscale range. In addition, its cation exchange capacity (CEC) was 93 mEq/100 g, which meets the requirements for preparing nanocomposites. Therefore, the PE/MMT nanocomposites can be easily formed during simulation.

### 3. PE/MMT nanocomposite modeling

In order to improve the compatibility of inorganic MMT nanoparticles and organic polymer matrices, MMT particles must be modified from hydrophilic to oleophilic. Therefore, octadecyl trimethyl ammonium chloride (18) was used as a modifier to complete the organic treatment of MMT. In this study, the modified MMT was called O-MMT, in which the interlayer charges were completely replaced by octadecyl trimethyl ammonium chloride cations (18\(^+\)). After that, O-MMT was mixed with PE to prepare PE/MMT nanocomposites with mass fractions of 0%, 3.3%, 3.7%, 4.0%, and 5.1%, which adopts the same method as PE modeling. A typical model of amorphous PE/MMT nanocomposites is shown in Fig. 3, and the sample names and characteristics of the PE/MMT nanocomposites are listed in Table I. According to previous research of our research group, the constructed models can reflect actual structures of PE/MMT nanocomposites and the simulation results are highly accurate.

### B. Simulation optimization

Because of the conformation differences between the original models and actual structures, the models of PE, MMT, O-MMT, and PE/MMT nanocomposites must be optimized by molecular dynamics equilibrium based on the periodic boundary condition and universal force field (UFF). In the process of optimization, the smart algorithm was adopted and van der Waals potential was described by the Lennard-Jones 12-6 formula for a temperature of 298 K and a pressure of 1 bar during 100 fs under the canonical ensemble (NVT) and constant-pressure, constant-temperature ensemble (NPT). In order to explore the stability of the statistical ensemble, the equilibrium states of models were estimated by the range

| Sample name  | PE (wt. %) | O-MMT (wt. %) |
|--------------|------------|---------------|
| PE           | 100        | ...           |
| PE-MMT-1     | 96.7       | 3.3           |
| PE-MMT-2     | 96.3       | 3.7           |
| PE-MMT-3     | 96.0       | 4.0           |
| PE-MMT-4     | 94.9       | 5.1           |

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TABLE II. Equilibration time and fluctuation ranges of temperature and total energy in PE/MMT nanocomposites.

| Sample name | Equilibrium time (ps) | Range of temperature fluctuation (%) | Range of total energy fluctuation (%) |
|-------------|-----------------------|--------------------------------------|---------------------------------------|
| YT-MMT      | 0                     | 3.61                                 | 1.56                                  |
| O-MMT       | 58                    | 4.87                                 | 1.11                                  |
| PE          | 96                    | 4.82                                 | 4.05                                  |
| PE-MMT-1    | 66                    | 3.37                                 | 3.54                                  |
| PE-MMT-2    | 58                    | 3.78                                 | 2.80                                  |
| PE-MMT-3    | 55                    | 2.92                                 | 1.41                                  |
| PE-MMT-4    | 68                    | 3.56                                 | 1.86                                  |

Then, carefully controlled experiments found that the equilibration time of different models was not all the same, as shown in Table II. The equilibrium time was always less than 100 ps during the process of molecular dynamics simulation. With increasing O-MMT content, the equilibration time and fluctuation ranges of temperature and total energy decreased first and then increased, exhibiting a minimum of 55 ps, 2.92%, and 1.41%, respectively, for PE-MMT-3. In PE/MMT nanocomposites, the interaction energy between MMT layers and PE molecular chains has a certain bound effect on the segment movement of PE. Thus, this result may be closely related to the changes in interaction energy and interface structures in PE/MMT nanocomposites.

III. SIMULATION RESULTS AND DISCUSSION

A. Analysis of interaction energy

The total energy $E_{\text{total}}$ of PE/MMT nanocomposites under UFF is given by

$$E_{\text{total}} (\text{kcal/mol}) = E_{\text{int}} + E_{\text{inn}}$$

$$= E_{\text{int(MMT-18)}} + E_{\text{int(MMT-PE)}} + E_{\text{int(PE-18)}}$$

$$+ E_{\text{MMT}} + E_{18} + E_{\text{PE}},$$  \hspace{1cm} (1)

where $E_{\text{int}}$ is the intermolecular interaction energy, $E_{\text{inn}}$ is the internal energy, $E_{\text{int(MMT-18)}}$ is the intermolecular interaction energy between MMT layers and 18° chains, $E_{\text{int(MMT-PE)}}$ is the intermolecular interaction energy between MMT layers and PE chains, $E_{\text{int(PE-18)}}$ is the intermolecular interaction energy between PE chains and 18° chains, $E_{\text{MMT}}$ is the internal energy of MMT layers, $E_{18}$ is the internal energy of 18° chains, and $E_{\text{PE}}$ is the internal energy of PE chains. The calculated results of energy are shown in Table III.

The intermolecular interaction $E_{\text{int}}$ in amorphous PE/MMT nanocomposites exhibits attraction, indicating that the molecules release energy in the binding process and exist in a state of mutual attraction, thus achieving a stable structure of molecular thermodynamic equilibrium. Moreover, with increasing O-MMT content, the maximum values of 452.22 kcal/mol and 64.06 kcal/mol, respectively, were obtained for PE-MMT-3. The same trend was observed for $E_{\text{inn}}$, and the maximum value of 944.12 kcal/mol was also obtained for PE-MMT-3. These results show that the mutual attraction between MMT layers and PE molecular chains or 18° is the strongest when the O-MMT content is 4.0%, and the corresponding structure is also the most stable. Under these conditions, the surface modification effect of MMT and the modification effect on PE are the best.

At the same time, the internal energy $E_{\text{PE}}$ of the PE molecules decreased first and then increased with increasing O-MMT content. The minimum value of 378 kcal/mol was obtained for PE-MMT-3, which is consistent with the trend of molecular dynamics equilibrium time for PE/MMT nanocomposites. This phenomenon occurred because when the content of MMT was 3.3% or 3.7%, the strong interaction between MMT layers and PE molecular chains or 18° was obtained for PE-MMT-3. The same trend was observed for PE-MMT-4, and the maximum value of 944.12 kcal/mol was also obtained for PE-MMT-3. These results show that the mutual attraction between MMT layers and PE molecular chains or 18° is the strongest when the O-MMT content is 4.0%, and the corresponding structure is also the most stable. Under these conditions, the surface modification effect of MMT and the modification effect on PE are the best.

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all above 500 kcal/mol, so that the molecular chains easily entangled each other. Under these conditions, the PE molecular chain had only a weak mutual attraction with the MMT layer or 18°. When the content of MMT was 5.1%, the repulsion energy between PE molecular chains was as high as 3107 kcal/mol so that the structure between PE molecular chains was mutually exclusive and unstable, that is, a stable structure between the PE chain and the MMT layer was not easily formed. Therefore, only when the O-MMT content was 4.0%, the cohesion energy of the PE molecular chains was the smallest. Under this condition, the PE chain can not only fully contact the MMT layer or 18° but also release significant energy during the molecular bonding process. In addition, the interface bonding was the closest, which made the molecular structure of PE/MMT composites more stable.

**B. Analysis of free volume**

In order to explore the free space of moving molecular segments, the free volume of polymers was calculated by the hard ball probe method. In the process of testing, probe atoms of 0.2 nm diameter roll on the van der Waals surface to generate Connolly surfaces, and a free volume is formed between the Connolly surfaces and probe atoms. Figure 5 shows the cross sections of free-volume structures in amorphous PE/MMT nanocomposites; the blue areas represent the cross sections of free-volume cavities, the gray closed contiguous areas are the free-volume spaces, and the maximum cross section of free-volume cavities is within the red frame. With increasing O-MMT content, the free-volume voids of PE/MMT nanocomposites tended to shrink first and then expand; PE-MMT-3 had small and scattered free volume cavities and the smallest maximum free volume cross section, but it is not accurate to assume that PE-MMT-3 had the smallest free volumes on the basis of the cross sections of cavities. Therefore, quantitative analysis was performed by means of the fractional free volume (FFV). The calculation formula of FFV is

\[
\text{FFV} \ (\%) = \frac{V_{\text{free}}}{V_{\text{total}}},
\]

where \( V_{\text{free}} \) is the free volume and \( V_{\text{total}} \) is the total volume. Figure 6 shows the FFV of the PE/MMT nanocomposites. With increasing O-MMT content, the FFV of the PE/MMT nanocomposites decreased first and then increased; the minimum value of 12.57% appeared at PE-MMT-3 and was 35.40% lower than that of pure PE. This result is consistent with the change trend of the largest cross sections of free-volume cavities shown in Fig. 5. The reason may be that when nano-MMT is doped into a PE matrix, the MMT layer itself is the crystal structure and occupies the free-volume micropores of the amorphous PE matrix, which reduces the FFV of the nanocomposites. Moreover, nano-MMT and PE chains form a large number of interfacial structures through hydrogen bonds or van der Waals bonds so that the alkane chains are arranged in a limited space around the heterogeneous nucleus and form new fine structures, which increases the number of reassembling crystalline structures and reduces the free volume per unit volume. In addition, the formation of interfacial interaction zones between nano-MMT and PE, to some extent,

![FIG. 5. Cross sections of free volume in amorphous PE/MMT nanocomposites: (a) pure PE, (b) PE-MMT-1, (c) PE-MMT-2, (d) PE-MMT-3, and (e) PE-MMT-4.](image)

![FIG. 6. Change in FFV in amorphous PE/MMT nanocomposites.](image)
increases the density of entanglement points, and the mobility of molecular chain segments is hindered, which also changes the FFV of the PE/MMT nanocomposites. As a whole, because of the disordered doping of O-MMT, there are organic-inorganic phase interfaces and the compactness of the molecular structures is reinforced so that it is possible to improve the mechanical properties of the nanocomposites.

C. Analysis of interfacial interaction zones

Structurally, the interfacial interaction zone is the region formed by the direct interaction between nanoparticles and matrix molecules. In this region, the bonding effect is stronger and the free volume space is smaller so that the structure is relatively compact and the corresponding density is larger. At the same time, the loose transfer layer is the epityax of the interaction zone, which is transferred outward from the interface interaction zone. In the loose transfer layer, the bonding interaction is weaker and the free volume space is larger so that the structure is relatively loose and the corresponding density is low. It can be seen from this analysis that the influence of the interface interaction zone on the macroscopic properties of nanocomposites is much greater than that of the loose transfer layer. Therefore, characteristics of the interfacial interaction zone were studied in this work.

In order to observe the change in interfacial interaction more intuitively, the thickness of the interface interaction zone in PE/MMT nanocomposites was studied. The typical structure of an amorphous PE/MMT nanocomposite is shown in Fig. 7, in which the pink chain is the main PE chain and the gray chain is the main 18\textsuperscript{t} chain. The corresponding thickness is shown in Fig. 8, where $d_{\text{MMT-PE}}$ is the minimum thickness between the MMT layer and the PE chain and $d_{\text{MMT-18}}$ is the minimum thickness between the MMT layer and 18\textsuperscript{t}. It can be seen from Fig. 8 that $d_{\text{MMT-PE}}$ and $d_{\text{MMT-18}}$ had the same trend of decreasing first and then increasing with the increase in O-MMT content and that the minimum values were obtained at PE-MMT-3, which were 2.25 Å and 2.26 Å, respectively. This result occurs because the thickness of the interfacial interaction zone largely depends on the interfacial bonding strength between nanoparticles and the surrounding medium. A larger interfacial bonding strength results in a stronger binding effect on the surrounding medium and thus a smaller free volume space and denser interfacial interaction zone. Under these conditions, because of the addition of O-MMT, the adhesion strength of the interface between MMT nanoparticles and alkane chains is improved, and the mechanical properties may be significantly improved.

D. Analysis of mechanical properties

Young’s modulus ($Y_m$), bulk modulus ($K_m$), and shear modulus ($G_m$) are generally used to characterize the mechanical properties of materials. $Y_m$ is a kind of physical quantity that represents the tensile or compressive strength of a material within the elastic limit. $K_m$ is the ratio of shear stress to shear strain. A greater $G_m$ indicates stronger rigidity. Assuming that the isotropic material is always in the state of equilibrium during loading stress, $Y_m$, $K_m$, and $G_m$ can be calculated by the Lame constant ($\lambda$, $\mu$),

$$Y_m(\text{Pa}) = \mu \left( \frac{3\lambda + 2\mu}{\lambda + 2\mu} \right),$$

$$K_m(\text{Pa}) = \lambda + \frac{2}{3}\mu,$$

$$G_m(\text{Pa}) = \mu.$$

On this basis, the Mechanical Properties program of Materials Studio (MS) was used to perform uniaxial tensile and pure shear deformation on the balance trajectory after molecular dynamics simulation. Then, the internal stress tensor is obtained based on the virial function at the atomic level, and its partial derivative is taken to get the elastic coefficient matrix. Therefore, the mechanical properties can be easily obtained. In the simulation process of mechanical properties, it is assumed that the MMT layers are rigid nanoparticles and the entropic effects and volumetric expansion properties are ignored. Moreover, PE/MMT nanocomposite systems are always in
a state of mechanical equilibrium after elastic deformation. Mechanical properties of amorphous PE/MMT nanocomposites are shown in Fig. 9. The figure shows that with increasing O-MMT content, \( Y_m \), \( K_m \), and \( G_m \) increased first and then decreased, reaching peak values of 8.37 GPa, 11.23 GPa, and 3.04 GPa, respectively, for PE-MMT-3. It is because there are a large number of interfaces in PE/MMT nanocomposites, which is conducive to improving the transfer efficiency of stress and reducing the ability of chain segment transition. Fig. 10(a) and 10(b) show the size scope of the MMT layers was about 0.2 \( \mu \text{m} \) in the PE/MMT composites (which is still considered nanoscale), as shown in Fig. 10(c). Then, the scope size of the MMT layers was about 0.2 \( \mu \text{m} \) in the PE/MMT composites (which is still considered nanoscale), as shown in Fig. 10(c) 21. 26. This has a good strengthening effect on mechanical properties of nanocomposites.

When the O-MMT content is relatively low, MMT nanoparticles are loosely distributed in the PE matrix so that the distance between MMT layers becomes large. Under these conditions, the distance between MMT layers becomes large. The free-volume space enlarges, and the mechanical properties of PE/MMT nanocomposites are slightly increased compared with those of pure PE. With increasing O-MMT content, the interfacial structure between organic and inorganic phases becomes compact, and the distance between MMT layers is reduced; thus, the thickness of the interfacial interaction zone decreases, which virtually reduces the free volume space and enhances the interaction energy between PE molecular chains and MMT layers. Based on the above microscopic structures, the strong hindering effect on the synergistic transition of PE chain segments is generated, which reduces the freedom degree of molecular chain segment transition to a certain extent so that mechanical properties can be improved rapidly. However, when the O-MMT content continues to rise, the interface between nanoparticles and alkane chains is liable to form physical defects. These defects become stress concentration points and facilitate slip because of the weaker intermolecular interaction energy under the action of external forces, thereby decreasing the mechanical properties of the nanocomposites.

Therefore, only when the mass fraction of nanoparticles is moderate, that is, an \( \omega \) (O-MMT) of 4.0\% in this study, the most stable interface structures were observed because of the interaction energy between MMT layers and alkane chains, in which the PE chains were bonded tightly around MMT layers so that the transition ability of the chain segments was weakened. Meanwhile, the distance between the organic phase and the inorganic phase in PE/MMT nanocomposites was the smallest, and the thickness of the interfacial interaction zones reached its minimum value so that the free space into which the molecular segments can jump reduced, and then, the transition ability of chain segments weakened, too. Thus, mechanical properties of PE/MMT nanocomposites were significantly improved compared to those of pure PE.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Nano-MMT was modified by octadecyl trimethyl ammonium chloride (18), which is called O-MMT, and then O-MMT of 0 wt. \%, 3.3 wt. \%, 3.7 wt. \%, 4.0 wt. \%, and 5.1 wt. \% were doped into PE using a melt blending method at 150 °C, respectively, which are named in turn as PE, PE-MMT-1, PE-MMT-2, PE-MMT-3, and PE-MMT-4.

A. Analysis of scanning electron microscopy (SEM)

It had been proved in the previous research work of this research team that, after MMT particle modification, the scale of MMT was significantly reduced and fewer stacking phenomena appeared, which significantly improved the nano effect, as shown in Figs. 10(a) and 10(b). Then, the size scope of the MMT layers was about 0.2 \( \mu \text{m} \) in the PE/MMT composites (which is still considered nanoscale), as shown in Fig. 10(c) 21. 26. The prepared PE/MMT composites can be considered as PE/MMT nanocomposites in this work. Thus, the experimental results of our micromorphology characterization agree with the simulated ones.

B. Analysis of mechanical properties

Mechanical properties of PE/MMT nanocomposites were tested with a dynamic mechanical analyzer (Q800, TA Corporation of the United States) with the fixed-frequency of 1 Hz. The calculation formulas of alternating stress \( \sigma \) and alternating strain \( \varepsilon \) are

\[
\varepsilon = \varepsilon_0 \exp(i\omega t), \\
\sigma = \sigma_0 \exp(i\omega t + \delta),
\]

where \( \varepsilon_0 \) and \( \sigma_0 \) are the strain and the stress with maximum amplitude, respectively, \( \omega \) is the angular frequency of alternating forces, and \( \delta \) is the lag phase angle. The calculation formula of complex modulus \( Y^i \) is

\[
Y^i = \frac{\sigma}{\varepsilon} = \frac{\sigma_0}{\varepsilon_0} \exp i\delta = \frac{\sigma_0}{\varepsilon_0} \cdot (\cos \delta + i\sin \delta) = Y^r + iY^i,
\]

where \( Y^r(\text{Pa}) = (\sigma_0 \cos \delta)/\varepsilon_0 \) is the real modulus, namely, Young’s modulus, and \( Y^i(\text{Pa}) = (\sigma_0 \sin \delta)/\varepsilon_0 \) is the imaginary modulus with a difference of \( \pi/2 \) from the strain, that is, loss modulus. Young’s modulus \( Y^r \) of PE/MMT nanocomposites are shown in Fig. 11.

As shown in Fig. 11, with the increase in O-MMT content, Young’s modulus \( Y^r \) of PE/MMT nanocomposites first increased and then decreased, which is consistent with the simulation results. When the O-MMT content was 4.0 wt. \%, the highest Young’s modulus was achieved at 333.40 MPa, an increase of 10.49\% compared to pure PE.
the value at 0 wt. %. It is because Young’s modulus is the measure of energy absorbed during elastic deformation. First of all, the MMT layer is a kind of inorganic rigid particle, which has a good aspect ratio and has a 2D reinforcing effect. After MMT nanoparticle modification, they exhibit a good surface effect, which increases the specific surface area per unit volume of PE/MMT nanocomposites so that MMT layers are more likely to form a large number of physical cross-linking points with alkane chains through van der Waals bonds or hydrogen bonds, which enhances the interface binding strength between inorganic phases and organic phases in nanocomposites. This undoubtedly enhances the transmission of internal stress. Second, the MMT layers have the function of heterogeneous nucleation, which can increase the number of nucleation centers in polymers. It enables PE chain segments to be arranged in a limited space, and then, the relatively compact microstructure is formed; thus, the free volume space becomes small. This strengthens the interaction between molecules to some extent. Based on the above analysis, when PE/MMT nanocomposites are subjected to external forces, the dispersion stress effect of the MMT layers and the absorption stress effect between molecular chains effectively hinder the slip of molecular chains so that Young’s modulus $Y'$ of PE/MMT nanocomposites was improved.

V. CONCLUSIONS

In this paper, the organic montmorillonite (O-MMT) was disorderly doped into polyethylene (PE), and then, the amorphous PE/MMT nanocomposites were prepared using Materials Studio (MS) software. We carried out molecular dynamics simulations to examine the structural, interfacial, and mechanical properties of nanocomposites. By analyzing the potential energy, free volume, interfacial interaction zone, and other parameters, the interfacial characterization was obtained between MMT layers and amorphous PE. The microstructures and mechanical properties of PE/MMT nanocomposites were simulated, and we verified them through experiments. The results are given as follows:

1. The microstructure analysis showed that the PE/MMT composite systems were the amorphous PE/MMT nanocomposite systems.
2. The microphysical property analysis showed that when the content of O-MMT was 4.0 wt. %, the interaction energies between MMT layers and PE molecules or octadecyl trimethyl ammonium chloride cations (18+) were the largest, up to 452.22 kcal/mol or 64.06 kcal/mol, respectively, while the fractional free volume reached the minimum value of 12.57%, and thus, the interfacial thicknesses between MMT layers and PE molecules or 18+ were the smallest, as low as 2.26 Å or 2.25 Å, respectively. At this point, the interface structure of PE/MMT nanocomposites reached the stable state.
3. The mechanical property analysis showed that due to the influence of interaction energy, free volume, and interfacial
structure, the mechanical properties increased first and then decreased with the increase of O-MMT content, and this is consistent with the experimental results. When the mass fraction of O-MMT was 4.0%, Young’s modulus, bulk modulus, and shear modulus emerged to the maximum value, up to 106.04%, 106.16%, and 107.52%, respectively.

(4) The correlation between interface thickness and mechanical properties was built, which provides the theoretical basis for the improvement of mechanical properties of nanocomposites.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support provided by the National Natural Science Foundation of China (Grant No. 51577045) and a project of the Shandong Province Higher Educational Science and Technology Program (Grant No. J17KB135).

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