**Abstract:** Polymer blending has been widely used to fabricate polymeric films in the last decade due to its superior properties to a single component. In this study, an aluminum phosphate-coated halloysite nanotube (HNTs@AlPO$_4$) was fabricated using a one-pot heterogeneous precipitation method, organically modified HNTs@AlPO$_4$ (o-HNTs@AlPO$_4$) was used to improve the performance of polyethylene oxide/poly(butylene adipate-co-terephthalate) (PEO/PBAT) blends, and the mechanical and rheological properties of the PEO/PBAT/o-HNTs@AlPO$_4$ films were systematically discussed. According to our results, there is an optimal addition for adequate AlPO$_4$ nanoparticle dispersion and coating on the surface of HNTs, and organic modification could improve the interfacial compatibility of HNTs@AlPO$_4$ and the polymeric matrix. Moreover, o-HNTs@AlPO$_4$ may serve as a compatibilizer between PEO and PBAT, and PEO/PBAT/o-HNTs@AlPO$_4$ films have better mechanical and rheological properties than the PEO/PBAT blends without the o-HNTs@AlPO$_4$ component.

**Keywords:** polymer blends; inorganic particles; mechanical property; rheology

1. **Introduction**

Polymeric films have been widely used in heavy and light industries, dentistry, petrochemical, and several other fields due to their unique optical, mechanical, electromagnetic, and gas-sensing properties [1–4]. However, the pollution of refractory polymeric films has become a pressing issue that must be addressed immediately. Recently, because of their sustainable, renewable, and biodegradable properties, research on biopolymer films has become a hotspot for addressing the environmental pollution caused by polymeric films [5,6]. Moreover, blending two polymers has become a strategy for fabricating polymeric films with better properties than single component films [7–9].

Polyethylene oxide (PEO) can be used to synthesize water-soluble films and textile pulp due to its low toxicity, bioadhesion, good water solubility, and easy processing and molding. In addition, PEO can form complexes with several organic low molecular compounds and inorganic electrolytes and can be used as a polymer solid electrolyte film for lithium-ion transfer [10–13]. However, pure PEO is a flexible chain and uncharged semicrystalline polymer with poor mechanical and rheological properties. Therefore, blending PEO with other polymers is one method to solve this problem. Poly(butylene adipate-co-terephthalate) (PBAT) has been frequently blended with other polymers because of its biodegradability, rubber-like behavior, deformability, and toughness [14–20]. PBAT can improve the comprehensive performance of the blend system. However, polymer compatibility is a major challenge in polymer blending, and further interfacial compatibility improvement is necessary. Currently, one of the main strategies to minimize the interfacial tension of polymeric blends is to use a compatibilizer.

Inorganic particles have been widely used as fillers to improve the interfacial compatibility of polymeric blends due to their strong interfacial interactions and good dispersion [21–25]. Among the various inorganic particles, nanoparticles are the most widely used
because of their large specific surface area and unique nanoscale effects. In previous studies, numerous nanoparticles such as carbon-based nanoparticles, montmorillonite, halloysite nanotubes (HNTs), SiO$_2$, and Al$_2$O$_3$ have been introduced into polymeric blends [26–30]. Dil et al. achieved a balance between toughness and stiffness by adding spherical nanoSiO$_2$ particles into poly(lactic acid) (PLA)/PBAT blends, and discussed the effect of the interfacial assembly of nanosilica on the morphology, rheology, and mechanical properties of the polymeric blends [18]. Urquijo et al. blended PLA/PBAT with different carbon nanotube (CNT) contents and demonstrated that CNTs selectively located in the PBAT phase induced the coalescence of PBAT spherical particles [19]. Our previous work demonstrated that sepiolite (Sep) improved the toughness of PP/ABS, enhanced both the mechanical and thermal properties of PP/PA6, and functions as a nucleating agent and compatibilizer between polymers [31,32].

In this study, we designed and fabricated aluminum phosphate-coated halloysite nanotube (HNTs@AlPO$_4$) composite first time by a simple one-pot heterogeneous precipitation strategy. The influence of the AlPO$_4$ contents on the morphology of HNTs@AlPO$_4$ was discussed to adjusting the dispersion of AlPO$_4$ nanoparticles on the HNTs. Furthermore, in order to improve the poor mechanical and rheological properties of PEO, PBAT was blended into PEO given its good physicochemical properties as described above, and a silane coupling agent was used to modify HNTs@AlPO$_4$ to improve the compatibility with the polymeric matrix, and its potential applications as fillers in PEO/PBAT were discussed. Scanning electron microscopy (SEM) was used to investigate the morphology of the HNTs@AlPO$_4$ and PEO/PBAT/HNTs@AlPO$_4$ films. X-ray powder diffraction (XRD) was used to determine the crystallinity of HNTs@AlPO$_4$. Fourier transform infrared spectroscopy (FTIR) was used to investigate the modification of HNTs@AlPO$_4$ by the silane coupling agent, CG-570. Thermogravimetric/derivative thermogravimetric analysis (TG/DTG) was used to investigate the thermal performance of the PEO/PBAT/HNTs@AlPO$_4$ films. Differential scanning calorimetry (DSC) was used to investigate the crystallization behavior of the PEO/PBAT/HNTs@AlPO$_4$ films. The rheological analysis was performed to investigate the dynamic rheological performance of the PEO/PBAT/HNTs@AlPO$_4$ films.

2. Materials and Methods

2.1. Materials

PEO ($M_w$ = 100,000 Da) was purchased from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. PBAT ($M_n = 20,000$ Da) was purchased from Shanxi Jinhui Zhaolong High-Tech Co., Ltd., Shanxi, China. Its mass density is 1.24 g/cm$^3$ and its melt flow rate (MFR) at 190 ºC is about 5 g/10 min with 2.16 kg. H$_3$PO$_4$ ($\geq 85\%$) and Al(OH)$_3$ ($\geq 99\%$) were purchased from Sigma Aldrich. HNTs (Al$_2$Si$_2$O$_5$(OH)$_4\cdot nH_2O$) was obtained from Xi’an Mingchuangda Biotechnology Co., Ltd., Xi’an, China. The HNTs length was 0.2–2 µm, and the inner and outer diameters were 10–40 nm and 40–70 nm, respectively. Silane coupler γ-methacryloxypropyltrimethoxysilane (CG-570, 99.8%) with density of about 1.070 g/cm$^3$ and refractive index of around 1.425 at 25 ºC was purchased from Nanjing Chengong Silicone Material Co., Ltd., Nanjing, China. Dichloromethane (CH$_2$Cl$_2$, AR), ethanol (AR), hydrochloric acid (HCl, AR), and NH$_3$·H$_2$O (AR) were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were used as received without any further purification.

2.2. Fabrication and Modification of HNTs@AlPO$_4$

HNTs@AlPO$_4$ was fabricated using a previously reported one-pot heterogeneous precipitation strategy [33]. First, we prepared 160-mL HNT aqueous dispersion (6 wt.%), adjusted the pH of the mixture to 2 using HCl, and labelled this dispersion as A. Second, we prepared a mixed aqueous solution of H$_3$PO$_4$ and Al(OH)$_3$, and labelled this solution as B. For B solution, Al(OH)$_3$ was mixed with H$_3$PO$_4$ in 10 mL deionized water, and stirred to obtain a homogeneous solution at room temperature. Then, we added B dropwise to A, and stirred the mixture at room temperature for 30 min. Afterward, we adjusted
the pH of the reaction mixture to 4.8 using NH$_3$·H$_2$O (27%). Finally, HNTs@AlPO$_4$ was obtained after centrifugation, washing, and drying. To improve the interfacial compatibility between inorganic particles and organic polymers, HNTs@AlPO$_4$ was modified by a silane coupling agent, CG-570, to obtain organically modified HNTs@AlPO$_4$ (o-HNTs@AlPO$_4$) using our previously modified method [31]. The detailed procedure is as follows: 0.5 g silane coupling agent CG-570 was added into 60 mL ethanol/H$_2$O (v/v 18:1) and the pH of the mixed solution was adjusted to 4–6 with formic acid. Then, the above CG-570 solution was added into 6.25 g HNTs@AlPO$_4$ and stirred at 80 °C for 3 h. The final product was precipitated in ethanol by centrifugation at 5000 rpm for 3 min and dried at 60 °C for 24 h.

Table 1 shows the sample designation (I–IV) and HNTs@AlPO$_4$ and corresponding content of each component, Figure 1 shows the preparation and modification progress, and all samples were synthesized via the same procedure.

**Table 1. The details of the sample designations for the HNTs@AlPO$_4$ nanocomposites.**

| Sample Designation | HNTs (g) | Al(OH)$_3$ (g) | H$_3$PO$_4$ (g) |
|--------------------|----------|----------------|-----------------|
| HNTs@AlPO$_4$I     | 10       | 0.58           | 4.33            |
| HNTs@AlPO$_4$II    | 10       | 1.17           | 8.67            |
| HNTs@AlPO$_4$III   | 10       | 1.75           | 13.00           |
| HNTs@AlPO$_4$IV    | 10       | 2.33           | 17.33           |

**Figure 1.** A schematic diagram of the preparation and modification of HNTs@AlPO$_4$.

2.3. Preparation of PEO/PBAT/o-HNTs@AlPO$_4$ Films

The PEO/PBAT/o-HNTs@AlPO$_4$ films were prepared using a traditional solution casting method. The detailed procedure is as follows: 2.8-g PEO and 1.2-g PBAT (PEO/PBAT: 70/30) were dissolved in 80 mL CH$_2$Cl$_2$ and stirred at room temperature until a homogeneous solution was obtained. Then, o-HNTs@AlPO$_4$ was added with 1%, 3%, 5%, and 7%, respectively. The o-HNTs@AlPO$_4$ was stirred vigorously until the inorganic particles were completely dispersed in the polymeric matrix. Afterward, the film-forming solutions were poured into a polytetrafluoroethylene (PTFE) dish, the solvent was evaporated completely at room temperature for 4 h, and the final dried films were kept in a desiccator at room temperature. Table 2 shows the sample designation and corresponding content of each component, and PEO/PBAT/o-HNTs@AlPO$_4$x (x is the percentage of o-HNTs@AlPO$_4$) was prepared via the same procedure.

2.4. Characterization

An FEI Quanta 250 FEG field-emission SEM (FEI Inc., Valley City, ND, USA) was conducted under high vacuum at a voltage of 20 kV to observe the morphologies of the HNTs@AlPO$_4$ nanocomposites and PEO/PBAT films. XRD (D/MAX2500, Rigaku Corporation, Tokyo, Japan) was conducted with Cu K$_\alpha$ radiation (λ = 1.54 Å) over the range of 5°–45° with a scanning rate of 2°/min to investigate the structural characteristics of HNTs@AlPO$_4$. FTIR spectroscopy (Nicolet i550, Thermo Fisher Scientific Inc., Waltham,
MA, USA) was conducted to characterize the HNTs and HNTs@AlPO₄, with a resolution of 4 cm⁻¹, range of 400–4000 cm⁻¹, and scan number of 32. A TG 219 F3 thermal analyzer (Netzsch Instruments Co., Ltd., Selb, Germany) was conducted in a nitrogen atmosphere at a flow rate of 60 mL/min, and the PEO/PBAT films (approximately 5–10 mg) were heated from 50 to 700 °C at a scanning rate of 20 °C/min to evaluate the thermal stability. DSC 214 (Netzsch Instruments Co., Ltd., Hanau, Germany) was conducted at a heating rate of 10 °C/min to investigate the crystallization of the PEO/PBAT films. Under N₂ protection, the temperature was increased from 25 °C to 230 °C for 2 min at a ramp rate of 10 °C/min, then lowered to 25 °C for 2 min heated to 230 °C. Model 3365 (Instron Corporation, Boston, MA, USA) was used to determine the tensile performance of the PEO/PBAT films (sample size: 120 × 10 × 0.1 mm). The stretching rate was 5 mm/min. HAAKE MARS III (PolyLab OS., Thermo Fisher Scientific Inc., Waltham, MA, USA) was used to investigate the dynamic rheological properties of the PEO/PBAT films. The size of the film was 20 × 20 × 0.1 mm and the test gap of 1 mm at a temperature of 190 °C. During the test, the strain was 0.5% and the range of frequency was 0.01–100 Hz.

### Table 2. Formulations of the PEO/PBAT/o-HNTs@AlPO₄ films.

| Sample Designation          | PEO (g) | PBAT (g) | HNTs@AlPO₄ (g) |
|-----------------------------|---------|----------|----------------|
| PEO/PBAT                    | 2.8     | 1.2      | 0              |
| PEO/PBAT/o-HNTs@AlPO₄1      | 2.8     | 1.2      | 0.04           |
| PEO/PBAT/o-HNTs@AlPO₄3      | 2.8     | 1.2      | 0.12           |
| PEO/PBAT/o-HNTs@AlPO₄5      | 2.8     | 1.2      | 0.20           |
| PEO/PBAT/o-HNTs@AlPO₄7      | 2.8     | 1.2      | 0.28           |

### 3. Results and Discussions

#### 3.1. Structural and Morphological Characterization of HNTs@AlPO₄

In this section, AlPO₄ was coated on the HNT surfaces to fabricate HNTs@AlPO₄ using the heterogeneous precipitation method. We investigated the effect of the AlPO₄ content on the morphology of HNTs@AlPO₄ to obtain HNTs@AlPO₄ with a sufficient coating amount and uniform aluminum phosphate dispersion. Figure 2 shows the SEM images of the pure HNTs and HNTs@AlPO₄ nanocomposites. Figure 2a shows that the pure HNTs had a substantial amount of bulk structure in addition to the tubular structure, and the HNT surfaces were smooth and free of impurities. The HNT surfaces became rough after reacting with AlPO₄, and the AlPO₄ nanoparticles were uniformly precipitated on the HNT surfaces (Figure 2b,c). The amount of precipitation gradually increased as the addition of AlPO₄ content increased, and Figure 2d shows the optimum encapsulation before agglomeration. Figure 2e shows the self-aggregation of the AlPO₄ nanoparticles due to the limited surface area of the HNTs. In summary, these SEM results showed that AlPO₄ precipitated on the surface of HNTs in the form of sphere-like nanoparticles and there is an optimal ratio for the reacting raw materials.

The XRD measurements were conducted to further investigate the morphological and structural information of the HNTs@AlPO₄ composites, and Figure 3a shows the XRD curves of the pure HNTs and HNTs@AlPO₄ composites. The XRD curves revealed that pure HNTs had peaks at 2θ = 12.06, 19.96, 21.90, and 26.58. A new peak appeared at 2θ = 18.34 after coating with AlPO₄; as the molarity of AlPO₄ increased, this peak became more obvious, and HNTs@AlPO₄III had the highest peak, implying that HNTs@AlPO₄III was the best sample. The HNTs@AlPO₄ composite of HNTs is a silicate mineral with the corresponding molecular formula of Al₂O₃·2SiO₂·4H₂O [34,35]. We selected HNTs@AlPO₄III for further experiments according to the SEM and XRD results, and still named it after HNTs@AlPO₄.

To improve the compatibility of HNTs@AlPO₄ with the polymeric matrix, an organic
modification was conducted using a silane coupling agent to obtain o-HNTs@AlPO₄, and Figure 3b shows the IR curves of HNTs, HNTs@AlPO₄, and o-HNTs@AlPO₄. The absorption peaks at 3690 and 3620 cm⁻¹ were attributed to the stretching vibrations of –OH in the HNTs, and the absorption bands in the range of 950–1093 cm⁻¹ were attributed to the stretching vibrations of the Si–O groups in HNTs [36,37]. The absorption peaks at 2960 and 2855 cm⁻¹ were attributed to the stretching vibrations of –CH₃ and –CH₂– in the silane coupling agent, CG-570, after organic modification.

Figure 2. The SEM images of the pure HNTs and the HNTs@AlPO₄ nanocomposites as synthesized. (a) HNTs, (b) HNTs@AlPO₄I, (c) HNTs@AlPO₄II, (d) HNTs@AlPO₄III, and (e) HNTs@AlPO₄IV. The scale bar in the last image can be applied to the other images.

Figure 3. (a) The XRD curves of the pure HNTs and HNTs@AlPO₄ composites and (b) IR curves of HNTs, HNTs@AlPO₄, and o-HNTs@AlPO₄.
3.2. Thermal Properties of PEO/PBAT/o-HNTs@AlPO4 Films

The TGA and DSC measurements are widely used to investigate the thermal stability and crystallization behavior of various materials, respectively. Figure 4 shows the TGA and DSC curves of the PEO/PBAT and PEO/PBAT/o-HNTs@AlPO4 films, and Table 3 lists the corresponding data. The TG and DTG curves showed that the samples had only one weight-loss stage, and their thermal degradation behavior mainly occurred between 350 °C and 450 °C. The corresponding data revealed that the initial decomposition temperature ($T_0$) of PEO/PBAT was 307.59 °C, and as the o-HNTs@AlPO4 content increased, $T_0$ increased first and then decreased, and the $T_0$ of all of the PEO/PBAT/o-HNTs@AlPO4 films were higher than those of PEO/PBAT. Moreover, the carbon residue of PEO/PBAT was 6.18 wt.%, and as the o-HNTs@AlPO4 content increased, the carbon residue of the PEO/PBAT/o-HNTs@AlPO4 film became 9.45, 10.18, 11.80, and 13.07 wt.%, with only a minor change in the maximum decomposition temperature ($T_{\text{max}}$). In summary, adding the appropriate o-HNTs@AlPO4 content could improve the thermal stability of the PEO/PBAT blends. The DSC results show that the melting temperature ($T_m$) and crystallization temperature ($T_c$) of PEO/PBAT were 61.29 °C and 36.24 °C, respectively; the addition of o-HNTs@AlPO4 had little effect and only marginally increased the $T_m$ and $T_c$. When the o-HNTs@AlPO4 content was 7 wt.%, the $T_c$ suddenly decreased to 34.32 °C. This phenomenon may be due to excess o-HNTs@AlPO4 in PEO/PBAT/o-HNTs@AlPO4, making o-HNTs@AlPO4 difficult to disperse and resulting in localized agglomeration. Thus, the corresponding thermal stability and crystallization performance decline. $\Delta H_m$ in Table 3 represents the enthalpy of the melting process, and the corresponding values of PEO/PBAT/o-HNTs@AlPO4 films are listed. In conclusion, the TG and DSC results revealed that the o-HNTs@AlPO4 particles are compatible with PEO/PBAT, that the addition of o-HNTs@AlPO4 to polymeric blends increases the stability and crystallinity, and that there is an optimum o-HNTs@AlPO4 content.

![Figure 4](image-url) (a) The TG, (b) DTG, and (c,d) DSC curves of the PEO/PBAT and PEO/PBAT/o-HNTs@AlPO4 films, where (c,d) represent the heating and cooling processes, respectively.
Table 3. Data of the TG and DSC of the PEO/PBAT/o-HNTs@AlPO_{4} films.

| Sample Designation | $T_0$ (°C) | $T_{\text{max}}$ (°C) | Carbon Residue (wt.%) | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J/g) |
|-------------------|-------------|-----------------|----------------------|------------|----------|-------------------|
| PEO/PBAT          | 307.59      | 401.40          | 6.18                 | 61.29      | 36.24    | 86.62             |
| PEO/PBAT/o-HNTs@AlPO_{4}1 | 309.09 | 401.67          | 9.45                 | 61.72      | 36.45    | 88.74             |
| PEO/PBAT/o-HNTs@AlPO_{4}3 | 310.59 | 401.78          | 10.18                | 61.89      | 36.52    | 86.20             |
| PEO/PBAT/o-HNTs@AlPO_{4}5 | 309.83 | 401.86          | 11.80                | 61.98      | 36.98    | 88.44             |
| PEO/PBAT/o-HNTs@AlPO_{4}7 | 308.42 | 401.37          | 13.07                | 61.97      | 34.32    | 89.07             |

3.3. Mechanical Properties of PEO/PBAT/o-HNTs@AlPO_{4} Films

Model 3365 (Instron Corporation, Boston, USA) was used to conduct the tensile performance measurements to investigate the effects of o-HNTs@AlPO_{4} on the mechanical properties of PEO/PBAT, and Table 4 lists the results of the tensile strength (MPa), flexural strength (MPa), and elongation at break (%) for the PEO/PBAT films with various o-HNTs@AlPO_{4} contents. The tensile strength, flexural strength, and elongation at break of pure PEO/PBAT films were $3.59 \pm 0.08$ MPa, $202.72 \pm 6.81$ MPa, and $49.23 \pm 3.85\%$, respectively. When o-HNTs@AlPO_{4} was added to the blend, the strength and elongation both increased first and then decreased, and a certain o-HNTs@AlPO_{4} content could simultaneously improve the strength and toughness of the PEO/PBAT films. The tensile strength of the PEO/PBAT films improved by 25.91% when 3 wt.% o-HNTs@AlPO_{4} was added. The flexural strength and elongation at break were improved by 24.56% and 44.87%, respectively, when 5 wt.% o-HNTs@AlPO_{4} was added. However, the strength and toughness were simultaneously reduced when 7 wt.% o-HNTs@AlPO_{4} was added. In summary, the o-HNTs@AlPO_{4} particles are compatible with the PEO/PBAT blend and can improve the interfacial compatibility of PEO and PBAT. Moreover, excessive o-HNTs@AlPO_{4} particles prevent dispersion in the polymeric matrix, lowering the mechanical properties of the films [38]. This mechanical property result is consistent with the above TG and DSC results.

Table 4. The mechanical properties of the PEO/PBAT/o-HNTs@AlPO_{4} films.

| Sample Designation | Tensile Strength (MPa) | Flexural Strength (MPa) | Elongation at Break (%) |
|-------------------|--------------------------|--------------------------|--------------------------|
| PEO/PBAT          | $3.59 \pm 0.08$          | $202.72 \pm 6.81$        | $49.23 \pm 3.85$         |
| PEO/PBAT/o-HNTs@AlPO_{4}1 | $3.82 \pm 0.12$    | $238.82 \pm 7.35$        | $54.32 \pm 3.61$         |
| PEO/PBAT/o-HNTs@AlPO_{4}3 | $4.52 \pm 0.09$    | $241.03 \pm 8.18$        | $66.20 \pm 4.23$         |
| PEO/PBAT/o-HNTs@AlPO_{4}5 | $3.68 \pm 0.15$    | $252.51 \pm 7.64$        | $71.32 \pm 4.57$         |
| PEO/PBAT/o-HNTs@AlPO_{4}7 | $2.52 \pm 0.21$    | $187.57 \pm 8.56$        | $47.22 \pm 4.73$         |

3.4. Cryofractured Surfaces of PEO/PBAT/o-HNTs@AlPO_{4} Films

Figure 5 shows the SEM results of the cryofractured surfaces of the PEO/PBAT blends with various o-HNTs@AlPO_{4} contents, and the inserted white dotted ellipses represent PBAT, and the inserted red dotted rectangles represent o-HNTs@AlPO_{4}. The PEO/PBAT blends mainly displayed a matrix-dispersed phase morphology with PEO continuous and irregular or spherical PBAT-dispersed phases, and the short axis of the dispersed phase was almost less than 1 μm.
When o-HNTs@AlPO4 was added to PEO/PBAT, the irregular PBAT decreased and some spherical PBAT appeared, and the cross-section of PEO/PBAT/o-HNTs@AlPO4 became smooth (Figure 5b–d). Furthermore, the spherical-dispersed phase gradually merged with the continuous phase, and the rod-like o-HNTs@AlPO4 was primarily observed in the PEO continuous phase, with an almost aligned orientation. This arrangement may be due to the rapid volatilization of CH2Cl2 during the solution pouring process as well as the uniform distribution of o-HNTs@AlPO4 in the PEO matrix. The cryofractured surfaces became smoother and denser as the o-HNTs@AlPO4 content increased, and the spherical PBAT-dispersed phase gradually merged with the PEO continuous phase, resulting in the spherical structure decreasing or even disappearing in Figure 5c,d. Figure 5e shows the self-aggregation of o-HNTs@AlPO4, and the macroscopic phase separation between the inorganic particles and the polymeric matrix occurred due to the excessive addition of o-HNTs@AlPO4. In summary, the appropriate o-HNTs@AlPO4 content has good compatibility with the PEO/PBAT blend, and could further reduce the surface tension and improve the compatibility between PEO and PBAT, where o-HNTs@AlPO4 may serve as a compatibilizer in this blending system.

3.5. Rheological Properties of PEO/PBAT/o-HNTs@AlPO4 Films

The rheological behavior of polymeric blends is not only related to their microstructure and processability, but also plays a vital role in their interfacial interactions [39,40]. In this study, the localization of o-HNTs@AlPO4 particles with rough surfaces was observed to have good interfacial compatibility with PEO and PBAT. Figure 6 shows the effect of o-HNTs@AlPO4 on the storage and loss moduli of the PEO/PBAT blends. PEO/PBAT/o-HNTs@AlPO4 had a higher storage and loss moduli in both the low- and high-frequency regions than PEO/PBAT, demonstrating the melt reinforcement effect of inorganic particles. Moreover, with an increase in the o-HNTs@AlPO4 content, both the storage and loss moduli first increased and then decreased, and PEO/PBAT/o-HNTs@AlPO45 reached the
maximum. The changes in $G'$ were more than $G''$, indicating that the elasticity was greater than the viscosity of PEO/PBAT/o-HNTs@AlPO$_4$. These results revealed that with the increase in frequency, the viscoelastic behavior became better for all samples, and after the addition of o-HNTs@AlPO$_4$, the viscoelastic behavior of PEO/PBAT/o-HNTs@AlPO$_4$ were even better than that of the pure PEO/PBAT. It may be that the excessive content of o-HNTs@AlPO$_4$ reduces the cross-linking reaction between PBAT and PEO and enhances the disentanglement ability between molecular chains. Inorganic particles with good dispersibility could improve the rheological properties of the polymer blends [41,42]. In this study, o-HNTs@AlPO$_4$ was dispersed in the PEO/PBAT matrix in an oriented arrangement, increasing the interfacial area due to the good compatibility between o-HNTs@AlPO$_4$ and PEO and PBAT, and this result is similar to the trend in the thermal and mechanical properties discussed above.

Figure 6. (a) The storage modulus and (b) loss modulus versus angular frequency for the PEO/PBAT and PEO/PBAT/o-HNTs@AlPO$_4$ films at 190 °C.

Figure 7 shows the relationship between the complex viscosity and angular frequency of the PEO/PBAT blends. The addition of o-HNTs@AlPO$_4$ can increase the complex viscosity in all frequency regions compared with pure PEO/PBAT blends. PEO/PBAT/o-HNTs@AlPO$_4$ also reached the maximum, and the excessive addition of o-HNTs@AlPO$_4$ resulted in decreased compatibility and macroscopic phase separation. Furthermore, the complex viscosity curves of the PEO/PBAT/o-HNTs@AlPO$_4$ films merged into one in the high-frequency region (~100 rad/s) because the higher shear rate destroyed the interfacial interaction force between o-HNTs@AlPO$_4$, PEO, and PBAT.

Figure 7. Plots of the complex viscosity versus angular frequency for the PEO/PBAT and PEO/PBAT/o-HNTs@AlPO$_4$ films at 190 °C.
4. Conclusions

In summary, aluminum phosphate-coated halloysite nanotubes (HNTs@AlPO4) were fabricated using a modified one-pot heterogeneous precipitation method, and the influence of various AlPO4 contents on the morphology of HNTs@AlPO4 was investigated. Furthermore, organically modified HNTs@AlPO4 (o-HNTs@AlPO4) was introduced into the PEO/PBAT blends, and the influence of o-HNTs@AlPO4 on the morphological, mechanical, and rheological properties of the PEO/PBAT/o-HNTs@AlPO4 films was systematically investigated. Our results indicate that o-HNTs@AlPO4 fillers act as a compatibilizer, improving not only the mechanical properties but also the rheological properties of PEO/PBAT. This study provides a new route for mechanically well-balanced PEO blends and promotes the application of PEO films.

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