

RESEARCH ARTICLE

Heat treatment effect on the distribution of organic clay in polymer nanocomposites

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Abstract: In this paper, the effects of heat treatment temperature on the degree of exfoliation of organic clay under different compatibilizers were tested by using organic clay 93A, high density polyethylene (HDPE) and compatibilizer (PE-g-MA), polyethylene maleic anhydride copolymer (PEMA), maleic anhydride and polyethylene blend (MA/PE). The proportion of organic clay is 5 wt%, HDPE is 90 wt% and compatibilizer is 5 wt%. Temperature ranged from 210°C to 250°C, the position of [001] peak in the sample was determined, FESEM, TGA, FTIR and XRD was used to analyze the influence of temperature on the distribution behavior of clay in polymer system. The results are very significant for the industrial production of clay composite materials.

Keywords: organic clay, nanocomposites, compatibilizer, HDPE, XRD

1 Introduction

Clay is silicoaluminate with very small particles, its structure is composed of silica tetrahedron and alumina octahedron. Clay is an important mineral material, due to the large specific surface, perfect physical adsorption and surface chemical activity, it is widely used as polymer additives, which can facilitate intercalation and expansion^[1]. Clay/polymer nanocomposites are widely used in insulation materials, oxygen resistant sealing materials, drug slow-release carriers, organic-inorganic composite fluorescent materials and other fields with the characteristics of economy, simplicity and environmental friendliness^[2].

These excellent properties of clay materials are related to the degree of peeling and dispersion of clay in polymer^[3]. For example, the increase of the specific surface area of the clay after peeling can cause the increase of Young's modulus. In more cases, the ultimate goal of the material treatment process is to completely peel the clay into a single sheet, because the majority of properties can only be reflected in the case of full peeling, such as light transmittance, water oxygen barrier performance^[4,5].

However, this kind of ideal stripping is not easy to achieve. There are different degrees of clay particles dispersed in the polymer system as aggregation state. Therefore, in practical application, different strategies can be adopted according to the compatibility between clay and polymer. Due to the interaction between the hydrophilic polymer molecules and the silicate surface of clay, the bipolar polymer molecules are easy to adsorb and disperse the peeled clay flakes. However, a large proportion of polymers are hydrophobic polymer molecules, which are not compatible with the surface of clay^[6]. In this case, it is very necessary to pre-treat the clay or polymer system. The usual way is to add compatibilizer in the treatment. This method has a very good effect on polymers without any polar functional groups, such as PP, PE^[7].

Many methods can be used to prepare nanocomposites based on clay. In practical application, melting method is widely used to prepare clay composite because of its high efficiency, flexibility and mature technology. Because of the difference of thermal behavior and physical properties of different compatibilizers, the comparative test is very necessary. The melting temperature in the process of heat treatment, such as screw extrusion and casting grinding, is the main factor affecting the distribution of organic clay. Therefore, the common organic clay 93A and high-density polyethylene (HDPE) were used to study the effect of heat treatment temperature on the degree of stripping of organic clay under the action of different compatibilizers. The results have an important guiding role in the industrial production of clay composite materials^[8-10].

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2 Experimental

2.1 Materials

The 93A organoclay (Organic modifier: methyl dihydrogenated tallow ammonium; X-Ray Diffraction d-Spacing (001) = 2.36 nm), high density polyethylene (HDPE), compatibilizer polyethylene maleic anhydride copolymer (PEMA), maleic anhydride grafted polyethylene (PE-g-MA), MAH/PE copolymer.

2.2 Thermal treatment

The degradation process was carried out in the Muffle furnace for 2 minutes at different temperature (200°C, 250°C and 300°C).

2.3 Extrusion experiment

Samples for exfoliation were prepared by extrusion using a 16mm twin screw extruder (length/diameter = 24/1) with a screw speed of 200 r/min.

2.4 Characterizations

All the samples for XRD were determined by powder X-ray diffraction (XRD) analyses with X-ray diffractometer Philips X'Pert Pro (PANalytical, USA) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. Crystal structure and morphology were measured by scanning electron microscope (Hitachi). The infrared absorption characteristics of samples were investigated by MAGNA-IR750 infrared spectrometer. Thermogravimetric (TGA) experiment was conducted by using TGA-2950 thermal analyzer with a heating rate of 20°C/min.

3 Results and Discussion

The degradation results of organic clay in muffle furnace are shown in Figure 1. Temperature range from 200°C to 220°C, no obvious color change of the organic clay was observed in the treatment. However, from 250°C to 300°C, the color of the organic clay reflected darker, which indicated that the organic clay has degraded. These results showed that the temperature of screw extrusion and mold forming should not exceed 250°C when using organic clay to prepare composite materials. The results verified the organic clay start to degrade at high temperature, influence have an impact on physical and chemical properties of the final product^[11].

The processing is shown in Figure 2. HDPE, compatibilizer and organic clay were mixed before screw extrusion, with the proportion of 90%, 5% and 5%. The extrusion temperature of the twin-screw extruder is set at 220°C to facilitate the stripping and dispersion of clay. The



Figure 1. The degradation of the organoclay under different temperatures (a: 200°C; b: 210°C; c: 220°C; d: 250°C; e: 300°C)

material is granulated and dried after being extruded by twin-screw to reduce the moisture content. The temperature is set to 250°C or 210°C in the mold. The size of sample is 25mm \times 25mm \times 1mm, which is used for XRD testing^[12, 13].

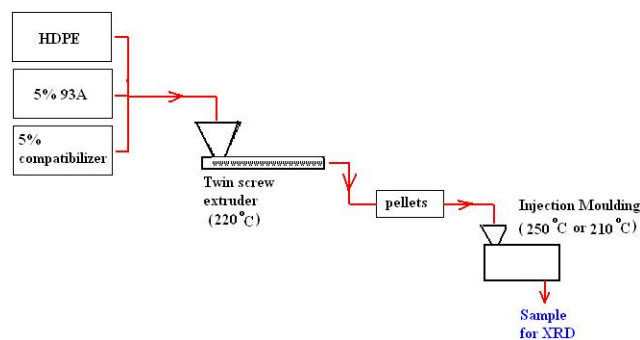


Figure 2. An illustration of the sample process

Figure 3 shows the IR spectra of 93A clay at different temperature. As we can see, The -OH expansion vibration peak at 3640-3600 cm^{-1} are the reflection of the crystal water in the montmorillonite lattice, indicating that water on the organic surface is basically lost, while the crystal water in the lattice remains. Peaks at 2920-2845 cm^{-1} attribute to -CH stretching vibration absorption peak (two kind of vibration of symmetric and asymmetric), it indicates organic quaternary loose salt on groups of absorption peak. The internal vibration of silicon-oxygen tetrahedron and aluminium-oxygen octahedron is between 400-800 cm^{-1} , and the strong absorption peak at 1050 cm^{-1} is skeleton vibration of Si-O-Si. No obvious differences in Figure 3 complains the suitable temperature of stripping ranges from 200°C to 300°C.

The SEM images of 93A clay at different temperature are shown in Figure 4. The results displays 93A clay is evenly dispersed and has the same particle size, which is associated with the result of IR spectra in Figure 3.

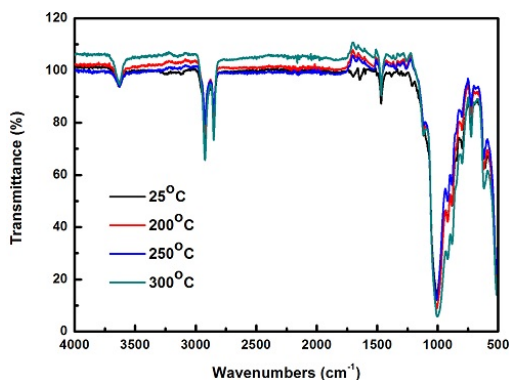


Figure 3. The IR spectra of 93A at different temperature

This result further illustrates the suitable temperature of stripping ranges from 200°C to 300°C.

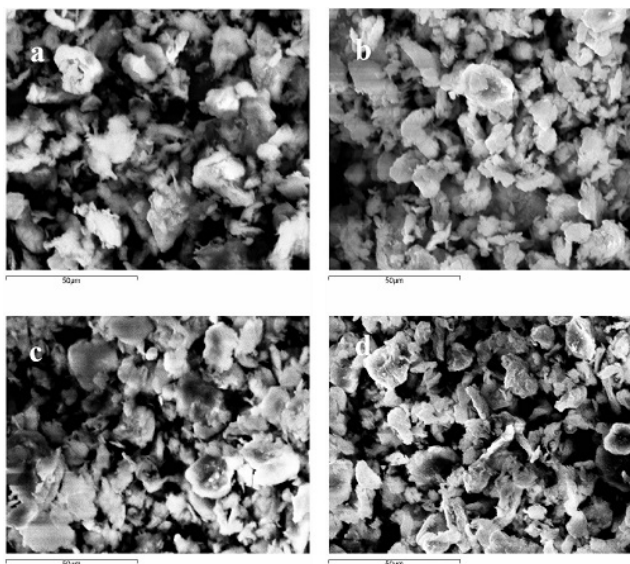


Figure 4. The SEM images of 93A clay at different temperature (a: 25°C; b: 200°C; c: 250°C; d: 300°C)

To illustrate the compatibilizer's decomposition temperature, TG analysis was conducted. The results in Figure 5 show the decomposition temperature of PE-g-MA is higher than PEMA and MA/PE, about 350°C. the decomposition temperature of PEMA and MA/PE is about 250°C.

The results of X-ray spectra of various clay composite samples at 250°C are shown in Figure 6. It can be concluded that no obvious characteristic in [001] peak of pristine material range from 1° to 9°, as well as HDPE (b), which did not add compatibilizer. However, obvious characteristic peak at the position of 3.5° occurred in HDPE+93A(5%) system, indicating that unavailable of distribution for clay. When 5% of compatibilizer PEMA (d) was added, there was an obvious characteristic peak

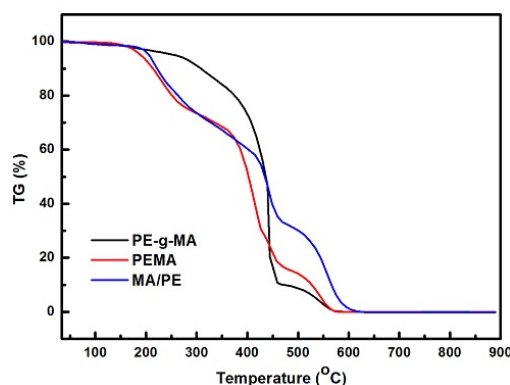


Figure 5. TGA curves of PE-g-MA, PEMA and MA/PE

at 3.3°, similarly, the compatibilizer was MA-g-PE (e) and MA/PE (f), an obvious characteristic peak appear at the position of 3.3°. These results implicated clay are partially degraded under condition of high temperature, which have an impact on layered structure of clay, as well as distribution in the polymer system^[14].

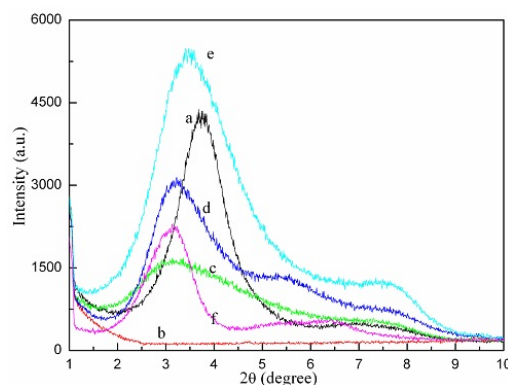


Figure 6. XRD curves for samples at 250°C. (a: 93A; b: Raw HDPE; c: HDPE + 93A(5%); d: HDPE + 93A(5%) + PEMA(5%); e: HDPE + 93A(5%) + PE-g-MA(5%); f: HDPE + 93A(5%) + MA/PE(5%) copolymer)

XRD curves of different clay composite samples at 210°C are shown in Figure 7. Seen from the figure that, the [001] peak of the pristine clay (a) was at 3.75°, no obvious characteristic peak of HDPE (b) sample can be found at the range of 0.9-10°, as well as HDPE+93A(5%), indicating that the perfect distribution of the organic clay. When adding 5% compatibilizer PEMA (d), obvious characteristic peak occurred at 3.3°, which certified that PEMA is not useful to the distribution of clay/HDPE system. When the compatibilizer is replaced by PE-g-MA (e) and MA/PE (f), no obvious peak can be observed, which illustrated that the clay can completely distribute in the polymer. These results verified that the appropriate treatment temperature is an important factor in the distribution of clay^[15,16].

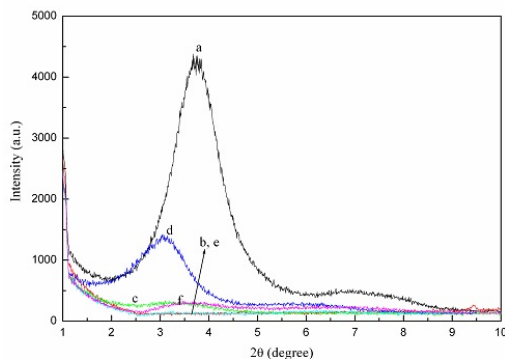


Figure 7. XRD curves for samples at 210°C. (a: 93A; b: Raw HDPE; c: HDPE + 93A(5%); d: HDPE + 93A(5%) + PEMA(5%); e: HDPE + 93A(5%) + PE-g-MA(5%); f: HDPE + 93A(5%) + MA/PE(5%) copolymer)

4 Conclusions

The temperature is very important to synthesis of organic clay composite. If temperature exceeds normal criterion, clay will begin to degrade in the process of treatment, affecting the physicochemical properties. At high temperature, the organic molecules in the clay partially degrade, which leads to side-effect in layer structure of the clay, influence have an impact on the distribution of clay in the polymer. However, at suitable temperature, clay can be completely distributed in the polymer system. Therefore, appropriate treatment temperature is an important factor in the research.

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References

- [1] Li MG, Zang HJ, Feng JX, *et al.* Efficient conversion of chitosan into 5-hydroxymethylfurfural via hydrothermal synthesis in ionic liquids aqueous solution. *Polymer Degradation and Stability*, 2015, **121**: 331-339. <https://doi.org/10.1016/j.polymdegradstab.2015.09.009>
- [2] Cha J, Jin S, Shim JH, *et al.* Functionalization of carbon nanotubes for fabrication of CNT/epoxy nanocomposites. *Materials & Design*, 2016, **95**: 1-8. <https://doi.org/10.1016/j.matdes.2016.01.077>
- [3] Vaganov G, Yudin V, Vuorinen J, *et al.* Influence of multiwalled carbon nanotubes on the processing behavior of epoxy powder compositions and on the mechanical properties of their fiber reinforced composites. *Polymer Composites*, 2017, **37**(8): 2377-2383. <https://doi.org/10.1002/pc.23419>
- [4] Zhou Y, Pervin F and Rangari V K. Influence of montmorillonite clay on the thermal and mechanical properties of conventional carbon fiber reinforced composites. *Journal of Materials Processing Technology*, 2017, **191**(3): 347-351. <https://doi.org/10.1016/j.jmatprotec.2007.03.059>
- [5] Pathak A, Borah M, Gupta A, *et al.* Improved mechanical properties of carbon fiber/graphene oxide-epoxy & brid composites. *Composites Science & Technology*, 2016, **135**: 28-38. <https://doi.org/10.1016/j.compscitech.2016.09.007>
- [6] Yuan W, Xiao Q, Li L, *et al.* Thermal conductivity of epoxy adhesive enhanced by hybrid graphene oxide/AlN particles. *Applied Thermal Engineering*, 2016, **106**: 1067-1074. <https://doi.org/10.1016/j.applthermaleng.2016.06.089>
- [7] Wu XP, Liu C, Qi H, *et al.* Synthesis and adsorption properties of halloysite/carbon nanocomposites and halloysite-derived carbon nanotubes. *Applied Clay Science*, 2016, **119**: 284-293. <https://dx.doi.org/10.1016/j.clay.2015.10.029>
- [8] Shu Z, Chen Y, Zhou J, *et al.* Nanoporous-walled silica and alumina nanotubes derived from halloysite: controllable preparation and their dye adsorption applications. *Applied Clay Science*, 2015, **112-113**: 17-24. <https://doi.org/10.1016/j.clay.2015.04.014>
- [9] Zhou Q, Gao Q, Luo WJ, *et al.* One-step synthesis of amino-functionalized attapulgite clay nanoparticles adsorbent by hydrothermal carbonization of chitosan for removal of methylene blue from wastewater. *Colloids and Surfaces A*, 2015, **470**: 248-257. <https://doi.org/10.1016/j.colsurfa.2015.01.092>
- [10] Wu XP, Gao P, Zhang XL, *et al.* Synthesis of clay/carbon adsorbent through hydrothermal carbonization of cellulose on palygorskite. *Applied Clay Science*, 2014, **95**: 60-66. <https://doi.org/10.1016/j.clay.2014.03.010>
- [11] Nigay P, Sani R and Cutard T. Modeling of the thermal and mechanical properties of clay ceramics incorporating organic additives. *Materials Science and Engineering: A*, 2017, **708**: 375-382. <https://doi.org/10.1016/j.msea.2017.09.131>
- [12] Wu XP, Xu YQ, Zhang XL, *et al.* Adsorption of low-concentration methylene blue onto a palygorskite/carbon composite. *New Carbon Materials*, 2015, **30**(1): 71-78. <https://doi.org/10.1016/j.carbon.2015.02.010>
- [13] Yuan X, Zhu B, Cai X, *et al.* Optimization of interfacial properties of carbon fiber/epoxy composites via a modified polyacrylate emulsion sizing. *Applied Surface Science*, 2017, **401**: 414-423. <https://doi.org/10.1016/j.apsusc.2016.12.234>
- [14] Lee S, Choi S, Kwon SH, *et al.* Modification of surface functionality of multi-walled carbon nanotubes on fracture toughness of basalt fiber-reinforced composites. *Composites Part B: Engineering*, 2015, **79**: 47-52. <https://doi.org/10.1016/j.compositesb.2015.03.077>
- [15] Laginhas C, Nabais J and Titirici M. Activated carbons with high nitrogen content by a combination of hydrothermal carbonization with activation. *Microporous and Mesoporous Materials*, 2016, **226**: 125-132. <http://qmro.qmul.ac.uk/xmlui/handle/123456789/15866>

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- [16] Sung D, Kim M and Park Y. Prediction of thermal conductivities of carbon-containing fiber-reinforced and multiscale hybrid composites. *Composites Part B: Engineering*, 2018, **133**: 232-239.
<https://doi.org/10.1016/j.compositesb.2017.09.032>