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The Degradation Mechanisms Study of the Organoclay by Using the Nitrogen Absorption/Desorption and X-ray Diffraction

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Abstract

Surfactants modified organoclays are known to undergo degradation during the melt process. In this work nitrogen absorption/desorption and X-ray diffraction were applied to study the mechanic of the degradation by employing the thermal treated commercial organoclay 93A. The 93A powder samples were heated in the Muffle furnace for 2 minutes at temperature ranged from 200 Celsius from 600 Celsius (200°C, 250°C, 300°C, 350°C and 600°C). The N2 absorption/desorption results showed the BET surface area is 10.402 m2/g, 9.455 m2/g, 14.169 m2/g, 8.860 m2/g and 9.198 m2/g respectively. The XRD results showed the d-space [001] 2θ=3.8 for all the samples (200°C -350°C) which did not change compared with the original 93A while the 600°C this unique reflection disappeared. The results indicate that the silicate clay skeletons thermal resistant ability can protect the surfactant molecules from degradation in the test temperature range low 350°C and the surfactant (which intercalated in the galleries) at the edge part of the galleries is first to degrade. High heating temperature can accelerates the vapour of the surfactants in the degradation process.

Keywords: Organoclay; Degradation; Surface area; Clay porosity; X-Ray diffraction

Introduction

The exploration of layered materials such as clay related polymer nanocomposites are one of the most attractive research fields for the novel materials designers which merged with the development of nanoscience and nanotechnology during the recent decades [1-5]. And the organoclay based polymer fillers, which composed of sodium montmorillonite (MMT) cationically exchanged with alkyl ammonium surfactants which expand the interlayer distance of the clay, have attracted considerable interest in many properties, such as mechanic properties, gas barrier properties, fire retardancy, conductivity, thermal stability, and degradability [1-14]. And with the incorporation of nanofillers/nano-reinforcements into polymer matrices, the clay based nanofillers are considered to be the most promising area which could lead to a significant enhancement compared to conventional composites [1]. These improvements can be realized without significantly increasing the density of the polymer or changing its optical properties at very low loading level. All these advantages make this kind of materials loads of interesting prospects for a wide range of applications in microbiology, nanotechnology, electronics, food packaging and so on [2-4].

Generally, the clay surface is hydrophilic and the surfactants such as tertiary or quaternary alkyl ammonium salts are bipolar molecules with hydrophobic tails [1,3,7]. For the clay nanocomposites, the significant property enhancements are rely on the affinity which to some extent is determined by the polarity of the polymer matrix and the type of organic modifier. And the affinity of the polymer with the surface of the clay and organoclay is essential for the favorable interactions within these materials. And the intercalated surfactant in the organoclay galleries is the bridge for the affinity of the clay layers and the polymer matrix and in some cases it also provides the resultant materials additional property such as antibacterial ability [7]. And also research reports that the compatibility of the polymer matrix and the organoclays can be greatly improved by the modifying the surfactant alky tails (branched or chain) which can provide more or less coverage during the exfoliation [2-4,12]. Thus, to obtain high levels of exfoliation is the key approach to achieve the high aspect ratio and surface area which is essential for the affinity. Therefore, the dispersion, or exfoliation of the individual organoclay layers within the polymer matrix is very important in the significant property enhancements.

Even the raw clay such as montmorillonite is not thermally stable at high temperatures, the organoclays filled with the surfactants may undergo degradation reactions at temperatures below the typical melt processing temperatures for the matrix polymers [3-6]. The instability of the surfactants in the clay galleries might be the first to degradation during the melt exfoliation process which will be resulted in the failure of the effective affinity function for each individual layer in the polymer matrix [11-13]. And the lack of thermally stable organoclays is one of the difficulties in the clay/polymer nanocomposites development. Thus, organoclay degradation becomes an issue that must be considered when forming polymer nanocomposites by melt processing. Although there are loads of the reports about the organoclay degradations during the melt process [8-21], the details about the mechanic of degradation are still unclear which is of prime importance to the understanding of organoclay degradation.

Thus, this study is focused on the thermal process effects on the organoclays during the melt process by monitoring the external surface areas and the interlayer spaces. These results provide the insights into the understanding of the organoclay degradation and the direction for stable organoclay designing and also provide the clue to improve the quality of organoclay based polymer nanocomposites in the thermal process.

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Experimental

Materials

The 93A organoclay (Organic Modifier: methyl dihydrogenated tallow ammonium; X-Ray Diffraction d-Spacing (001)=2.36 nm) was purchased form Southern Clay Products (USA). All other chemicals used in this experiment were used as received and the water used in this work was distilled water.

Samples thermal degradation

The organoclay degradation process was carried out by heating the 93A in the Muffle furnace for 2 minutes at different temperature ranged from 200 Celsius from 600 Celsius (200°C, 250°C, 300°C, 350°C and 600°C). And during the experiment the sample weight was recorded before and after the heating at each temperature.

Absorption/Desorption

The surface area, isotherm, and pore size distribution were measured by nitrogen adsorption and desorption at liquid nitrogen temperature (77 K) on a Quantachrome Autoabsorb. The tubes used in this experiment were 9 mm and 12 mm in diameter which were completely cleaned before each measurement using acetone and water in turn and dried in the oven at 70°C over-night. Prior to the determination of the adsorption isotherm, the samples (approximately 0.45 g) were outgassed for 12 h at 25°C. The samples are in powder format and load as they are. The compressed sample was compressed by the FT-IR sample compressor.

X-Ray diffraction

All the samples for XRD were determined by powder X-ray diffraction (XRD) analyses with X-ray diffractometer (Cu Kα, λ=1.5418Å) and generated at 30 kV, 30 mA. Scattering angles were ranged from 1° to 50°.

Results and Discussion

Melt process is considered the most efficient and flexible way for the polymer/organoclay nanocomposites fabrication and the organoclay dispersion i.e. exfoliation is determined by several aspects such as the extruder and screw configurations and residence times during the process. The shortcoming of this process is the degradation of the organoclay which is mainly affected by the process temperature. The melt temperature for the polymer matrix can be as high as several hundred Celsius while the tolerant temperature for the organoclay surfactants normally much lower than that value. And thus the degradation happens. Though the whole degradation is much complicated in the real exfoliation melt process, here we used the commercial organoclay 93A as an example to simplify this process by heating the organoclay in the furnace at different temperature to module the melt exfoliation process and then characterise the surface area and gallery distance to see the mechanic of clay degradation. The 93A samples that heated under different temperatures for 2 minutes is showed in Figure 1 and from the picture we can see that organoclay colour changed from white to grey from the range of room temperature 25°C to 350°C (Figures 1a-1f) and the colour become darker when the temperature increase. The 93A sample treated with 600°C for 2 minutes became black (Figure 1g). And this colour change indicates the degradation occurred during this heating process.

Weight difference of the samples during this thermal heating process was also recorded and the result is showed in Figure 2. From the curve we can clearly see that the sample resident weight remained from 96% to 70% when heated from 200°C to 350°C and at the temperature 600°C only 61% left. And these results indicate that during this thermal degradation process, the surfactant in the organoclay was released which contributed to the weight loss of the clay samples. Though in the test condition, the situations that the organoclay undergo are different from the real melt extrusion where the organoclay is in the melt polymer and lack of oxygen environment, the thermal treatments are similar as far as the effects on the organoclay are concerned.

As we know 93A organoclay is made from the cations exchange and the inter-gallery surfactant is quaternary alkyl ammonium salts and the microstructure of the clay is showed in Figure 3a and we hypothesize there are four possibilities for the degradation of organoclay 93A which is showed in the Figure 3b (1-4). In the first situation (Figure 3b-1), the clay platelet breaks down into smaller ones while the gallery distance keeps the same. This process is associated with weight loss and surface area increase significantly; in the second situation (Figure 3b-2), the clay platelets change the arrangements and the inter platelet distances and angels changes, and there is slightly changes in surface area and the no change in gallery distance; in the third situation (Figure 3b-3), the platelet half break and the damaged layers form inter-platelet pores and this associated with the weight loss and surface area increase, while gallery distance keep the same; in the forth situation (Figure 3b-4), the platelets break down into smaller ones and the deformation occur at the edge part of the layers which is associated with weight loss. In order to further confirm these possibilities, the surface area and pore size distribution were calculated through nitrogen absorption/desorption and the gallery distances (d-space, [001]) were monitored by X-ray diffraction.

Nitrogen absorption/desorption tests were carried out for the above mentioned samples. And isotherm curves showed that all the samples have low BET surface areas which mean that the samples have the similar low microspore surface area (Table 1) but have large portion of macrospore and mesopore characteristic. And the results show these samples don't have too much different in the BET surface area which range from lower 8.860 to higher 14.169 m^2/g, as the N$_2$ cannot get into the galleries of the clay [15-18], this surface area is mainly contributed by the external platelet macrospores/mesopores. These results indicate during the degradation process the clay did not break down into smaller platelets.

In order to further characterise the heat treated samples of 93A, X-ray diffraction experiments were carried out and results are showed in Figure 4. From results we can see that the [001] reflection appeared at 2θ=3.8 for all the samples (200°C-350°C) and did not change in all these samples compared with the original 93A at 25°C (Figure 4), but for the sample treated at 600°C, the [001] reflection disappeared. All other peaks kept the same in all these samples include the 600°C treated. These results showed that during the degradation process, the gallery distance does not change when the heat temperature is lower than 350°C (for 2 minutes). However, if the temperature increased to 600°C, the organoclay is no longer in stacking order which characterises layered platelets and this structure is suppressed and replace by the edge to edge or edge to face assemblies (no 001 reflection). These results indicate that upon the thermal treatment, the interlayered surfactant is transformed into oxide pillars which stabilize the gallery spacing between the adjacent clay layers [16].

SEM observation in Figure 5 showed that the clay sample at room temperature has the typical flask layered structure (Figure 5A) but when the samples treated with high temperature from 250°C, the

Figure 1: The images of 93A organoclay heated at different temperature 25°C (a); 150°C (b); 200°C (c); 250°C (d); 300°C (e); 350°C (f) and 600°C (g).

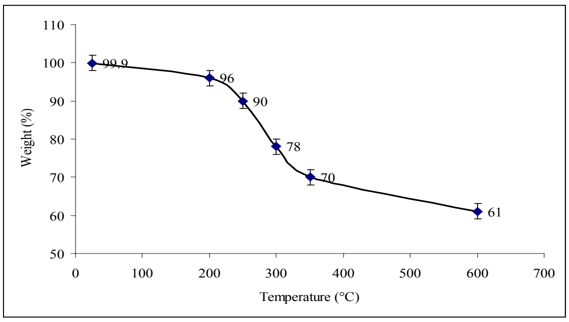

Figure 2: The sample resident weight curve in the thermal heating process.

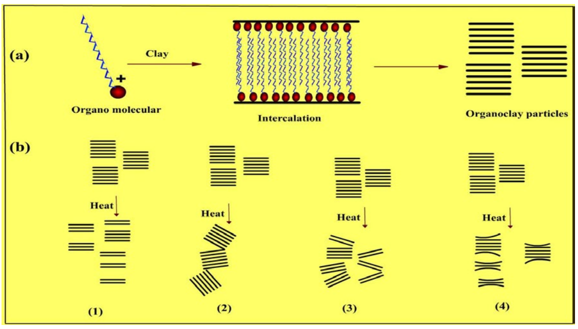

Figure 3: The illustration of organoclay microstructure (a) and the possibilities of the degradation process (b)

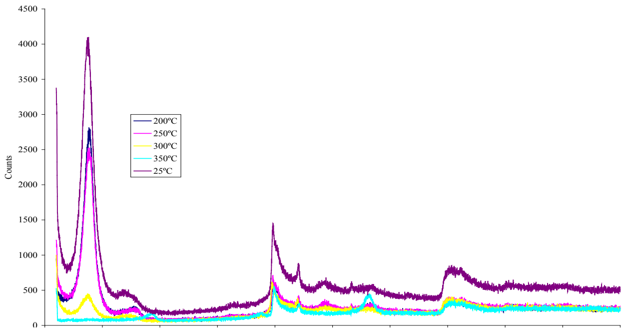

Figure 3: XRD spectra of the 93A organoclay 25°C (a); 200°C (b); 250°C (c); 300°C (d); 350°C (e) and 600°C (f).

structure began to change and the crashed surface morphology was observed (Figure 5B); and when the temperature continue to increase to 350°C and 600°C (Figures 5C and 5D), the clay particles completely lose their layered structure. SEM morphology showed that during the thermal degradation, the organic molecular inside the galleries is first undergoing the degradation and the surfactant molecules are the key issue when the orgnoclays are treated at high temperatures.

From the above analysis, it is clearly indicate that in these 4 hypothesis, only the second and the forth situation are possible. And one reasonable explanation for the degradation during the thermal treatment process is that at the relatively lower temperature, due to the silicate clay skeletons thermal resistant ability, the surfactant (which intercalated in the galleries) at the edge part of the galleries is first to degrade while the far deep into the galleries surfactant molecules can still hold in the position and this process is showed in the Figure 6. To this point, the higher heating temperature just accelerates the vapour of the surfactants in the degradation process.

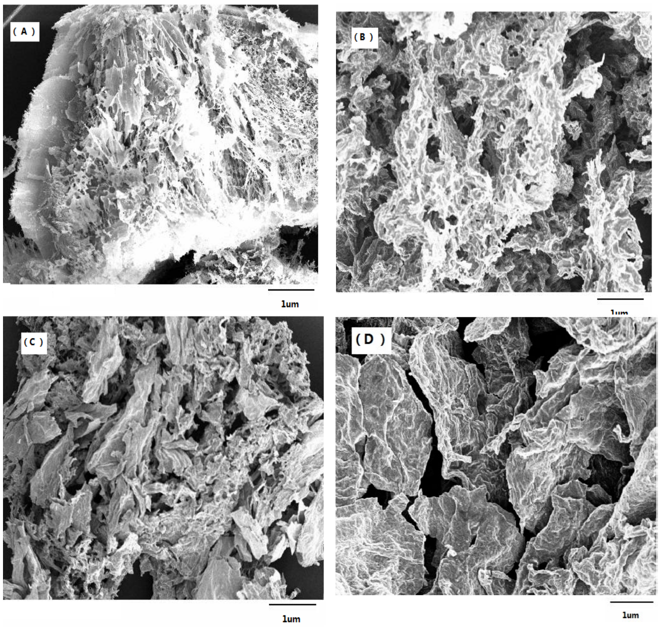

Figure 5: Typical morphology of clay samples in SEM. (A) 25°C; (B) 250°C; (C) 350°C; (D) 600°C.

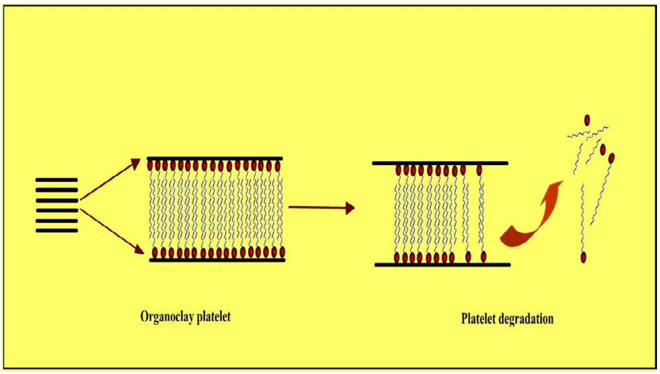

Figure 6: The illustration of organoclay platelet degradation process

Temperature (°C)	25	200	250	300	350	600
S_{BET} (m^2/g)	10.402	9.455	14.169	8.860	9.198	

Table 1: The BET surface area (S_{BET}) of the samples at different temperature

Conclusions

The organoclay degradation is not always associated with the surface area and interlayer distance changes. The nitrogen absorption/desorption surface area is mainly contributed by the inter-particle pores. The surface area and the gallery distance do not change during the degradation process. And the degradation process starts at the edge part of galleries in the organoclay platelets which is associated with the weight loss. This study might be useful for the guide of designing the target organoclay for the different purposes. And also it might be useful for the reference of the thermal based polymer process regarding the degradations.

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1. References

2. Khudyakov IV, Zopf RD, Turro NJ (2009) Polyurethane Nanocomposites. Designed Monomers and Polymers 12: 279-290.
3. Ray SS, Okamoto M (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. Progress in Polymer Science 28: 1539-1641.
4. Pavlidou S, Papaspyrides CD (2008) A review on polymer–layered silicate nanocomposites. Progress in Polymer Science 33: 1119-1198.
5. LeBaron PC, Wang Z, Pinnavaia TJ (1999) Polymer-layered silicate nanocomposites: an overview. Applied Clay Science 15: 11-29.
6. Paul DR, Robeson LM (2008) Polymer nanotechnology: nanocomposites. Polymer 49: 3187-3204.
7. Luo JJ, Daniel IM (2003) Characterization and modeling of mechanical behavior of polymer/clay nanocomposites. Composites Science and Technology 63: S1607-S1616.
8. Nigmatullin R, Gao F, Konovalova V (2008) Polymer-layered silicate nanocomposites in the design of antimicrobial materials. Journal of Materials Science 43: 5728-5733.
9. Cui L, Khramov DM, Bielawski CW, Hunter DL, Yoon PJ, et al. (2008) Effect of organoclay purity and degradation on nanocomposite performance, Part 1: Surfactant degradation. Polymer 49: 3751-3761.
10. Ratinac KR, Gilbert RG, Ye L, Jones AS, Ringer SP (2006) The effects of processing and organoclay properties on the structure of poly(methyl methacrylate)/clay nanocomposites. Polymer 47: 6337-6361.
11. Ryu JG, Park SW, Kim H, Lee JW (2004) Power ultrasound effects for in situ compatibilization of polymer–clay nanocomposites. Materials Science and Engineering: C 24: 285-288.
12. Zampori L, Stampino PG, Dotelli G (2009) Adsorption of nitrobenzene and orthochlorophenol on dimethyl ditallowyl montmorillonite: A microstructural and thermodynamic study. Applied Clay Science 42: 605-610.
13. Chavarria F, Paul DR (2006) Morphology and properties of thermoplastic polyurethane nanocomposites: Effect of organoclay structure. Polymer 47: 7760-7773.
14. Chow WS, Abu Bakar A, Mohd Ishak ZA, Karger-Kocsis J, Ishiaku US (2005) Effect of maleic anhydride-grafted ethylene–propylene rubber on the mechanical, rheological and morphological properties of organoclay reinforced polyamide 6/polypropylene nanocomposites. European Polymer Journal 41: 687-696.
15. Xu B, Zheng Q, Song Y, Shangguan Y (2006) Calculating barrier properties of polymer/clay nanocomposites: Effects of clay layers. Polymer 47: 2904-2910.
16. Nguetnkam JP, Kamgac R, Villiéras F, Ekodeck GE, Razafitianamaharavo A, et al. (2005) Assessment of the surface areas of silica and clay in acid-leached clay materials using concepts of adsorption on heterogeneous surfaces. Journal of Colloid and Interface Science 289: 104-115.
17. Remy MJ, Vieira Coelho AC, Poncelet G (1996) Surface area and microporosity of 1.8 nm pillared clays from the nitrogen adsorption isotherm. Microporous Materials 7: 287-297.
18. Lantenois S, Nedellec Y, Prélot B, Zajac J, Muller F, et al. (2007) Thermodynamic assessment of the variation of the surface areas of two synthetic swelling clays during adsorption of water. Journal of Colloid and Interface Science 316: 1003-1011.
19. Koo J, Park S, Satija S, Tikhonov A, Sokolov JC, et al. (2008) Characterization of Langmuir–Blodgett organoclay films using X-ray reflectivity and atomic force microscopy. Journal of Colloid and Interface Science 318: 103-109.
20. Mohino F, Martin AB, Salerno P, Bahamonde A, Mendioroz S (2005) High surface area monoliths based on pillared clay materials as carriers for catalytic processes. Applied Clay Science 29: 125-136.
21. Kawi S, Yao YZ (1999) Silica bonded K10 montmorillonite (SBM): a high surface area catalytic clay material. Microporous and Mesoporous Materials 28: 25-34.
22. Kawi S (1999) A high-surface-area silica–clay composite material. Materials Letters 38: 351-355.