

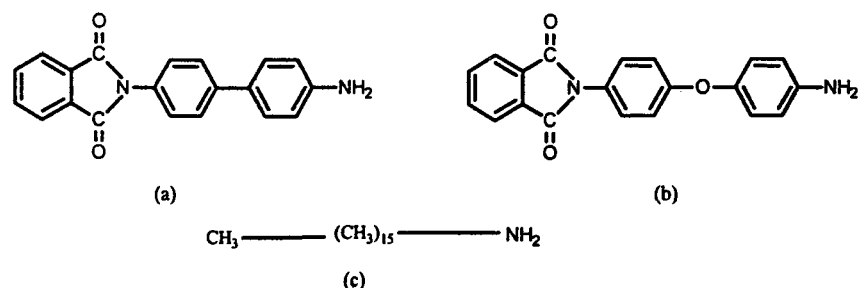
Morphological studies on Polyimide/Clay Nanocomposites Based on Thermally Stable Rigid-Rod Aromatic Amine Modifiers

Liang Zhumei, Yin Jie *

Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, National Lab of Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Introduction

The preparation and processing of most of polymer/clay nanocomposites need high temperature. This limited the application of commonly used organic modifiers of long alkyl chain containing ammonium salts because of their low thermal stability. Xie et al[1,2] have studied the thermal stability of the MMT modified by long chain alkyl quaternary ammonium ions using TGA-MS analyzer and found that the on-set temperature of decomposition of the resultant OLSs was approximately 180 °C. During this study, we synthesized two novel clay organic modifiers (OM-*l* and OM-*m*, Scheme 1). They were used to treat montmorillonite (MMT-*l* and MMT-*m*), which were applied to synthesize a series of PI/MMT nanocomposites by in-situ polymerization. FTIR, XRD, TEM, and TGA were used to obtain the information on the efficiency and thermal stability of the novel organo-modifiers and corresponding PI/MMT nanocomposites compared with commonly used 1-hexadecylamine (OM-16C).



Scheme 1 Chemical structure of organo-modifiers (a) OM-*l*, (b) OM-*m* and (c) OM-16C.

Experimental

Synthesis of OM-*l* and OM-*m*.

To the 250ml of four-necked flask fitted with a condenser, a stirrer, a nitrogen inlet tube and a dropping funnel were added 7.396g (0.04mol) 4,4'-diaminodiphenyl ether and 50ml dry N,N-dimethyl acetamide (DMA). After 4,4'-diaminodiphenyl ether was dissolved completely, a DMA solution (50ml) of 5.924g (0.04mol) phthalic anhydride was added drop wise. The reaction mixture was then maintained for 5 hours at room temperature, and heated to reflux and stirred for 5 hours. The reaction mixture was filtrated at reflux temperature. After cooling to room temperature, the product was precipitated from the reaction mixture. 7.05g green powdery primary product was obtained by filtration and after drying overnight at 70 °C under vacuum. The primary product was

purified by recrystallization with mixed solvent of ethanol and N-methyl-2-pyrrolidone (NMP) to obtain light green needle crystals. The synthesis of OM-*m* was followed by the procedure similar to that of OM-*l*. They were characterized through FTIR, ¹H NMR, MS and elemental analysis.

Preparation of organically modified MMT

MMT organo-modified with OM-*l* (MMT-*l*): 1.08g OM-*l* was mixed with 1ml concentrated hydrochloric acid (37%) and 15ml distilled water and heated at 80°C for a few minutes, and to it was added a dispersion of 2.5g Na-MMT in 100ml distilled water. The mixture was stirred vigorously for 1 hour at 80°C. The white precipitate was filtered and washed repeatedly by hot water (80°C) to remove the superfluous ammonium salts and make it free from chloride ions. The sample was subsequently collected and dried in vacuum oven at 80°C for 24 hours. The preparation of MMT modified with OM-*m* (MMT-*m*) and OM-16C (MMT-16C) was followed by the procedure similar to that of MMT-*l*.

Preparation of polyimide/MMT nanocomposites

To a 100ml three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and condensation equipment were added the modified MMT dispersion in *m*-cresol, 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA, 1.130g, 0.005mol). The solution was stirred until the diamine was completely dissolved (1.5hour). Diphenylether-3,3',4,4'-tetracarboxylic dianhydride (OPDA, 1.550g, 0.005mol) was subsequently added. The mixture was stirred vigorously at room temperature for 2 hours. The resulting red solution was clear and viscous. It was then heated to 180°C and stirred for 3 hours to obtain a yellow, transparent, highly viscous PI/MMT nanocomposite solution. It was used to cast thin films. The films were placed in the vacuum oven at room temperature to render the air-bubble remove from PI/MMT nanocomposite solutions, and then were thermally treated consecutively at 70°C for 12 hours, 120°C for 4 hours, 200°C for 4 hours, 260°C for 2 hours and 280°C for 2 hours to completely remove the solvent and achieve fully imidization, brown and transparent PI/MMT nanocomposite films were obtained.

Results and discussion

Table 1 listed the basal spacing of the organically treated MMT calculated from the Bragg Equation. The interlayer spacing of MMT was obviously increased after the treatment with ammonium chloride salt of OM-*m* and OM-*l* from $d=1.24\text{nm}$ for pure MMT to $d=2.34\text{nm}$ for MMT-*m* and $d=2.90\text{nm}$ for MMT-*l*, respectively. This suggested that organo-modifiers synthesized by us successfully intercalated between sheets of MMT. More importantly, it has been widely accepted that the basal spacing of MMT treated by long-chain aliphatic amine (or quaternary ammonium salt) is decided largely by the chain length and long chain length leads to high d -value. Although OM-*m* and OM-*l* have much smaller long axis length than OM-16C, the MMTs treated by them exhibited higher d -values than that treated by OM-16C. This might be contributed to the larger space volume of benzene and imide rings and highly rigid structure of molecules of OM-*m* and OM-*l*. This may also suggests that the d -value depends not only on the length of main chain but also on the main chain rigidity of organic modifiers.

Table 1 *d*-Value of MMT modified with various modifiers

Sample	2θ (o)	<i>d</i> (nm)	Peak intensity
Na-MMT	7.12	1.24	S
MMT-16C	4.28	2.06	S
MMT- <i>m</i>	3.78	2.34	S
MMT- <i>l</i>	3.04	2.90	S
	6.30	—	W

(S: strong; W: weak)

Fig. 1 showed the TGA analysis results of organo-modified MMTs. The initial thermal decomposition temperature (onset temperature) of MMT-16C, MMT-*m* and MMT-*l* was 252.1°C, 320.3°C and 344.8°C, respectively. MMT-*m* and MMT-*l* clearly showed higher onset decomposition compared to MMT-16C. This is clearly caused by the higher thermal stability of OM-*m* and OM-*l*. MMT-*m* showed slightly lower thermal stability because of the relatively poor thermal stability of ether linkage in OM-*m*.

XRD patterns were used to examine the morphology of the PI/MMT-*l* nanocomposite films with various MMT contents (Fig. 2). The 001 diffraction peak of the MMT disappeared completely in the nanocomposites when the MMT content was below 3 wt%. This indicated an exfoliated dispersion of MMT in PI. The diffraction peak of MMT was visible as the MMT content was above 4 wt% but the nanocomposite solution was clear and no obvious aggregation was observed even when the solvent was removed, also indicating that the MMT was well dispersed.

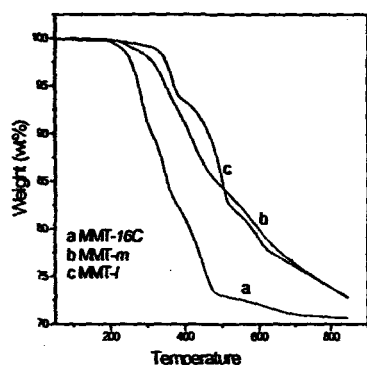


Figure 1 TGA curves of MMT-*l*, MMT-*m* and MMT-16C

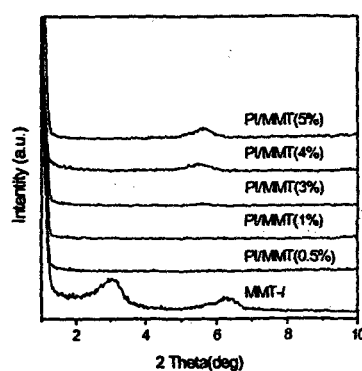


Figure 2 XRD patterns of MMT-*l* and PI/MMT-*l* nanocomposites with various MMT contents.

The exfoliation of MMT in the nanocomposites could be further confirmed by TEM analysis (Fig. 3). In the TEM photograph, the black lines represented the intersection of the MMT layer of about 1 nm thickness while the white part represented the PI matrix. It showed that MMT existed in exfoliated morphology and was almost orderlessly dispersed in the PI matrix. The results apparently demonstrated the good dispersibility of the OM-*l* modified MMT in the nanocomposites. The properties of the nanocomposites are under investigation.



Figure 3 TEM micrograph of the ultrathin-section of PI/MMT-1 nanocomposite film containing 3 wt% MMT.

References

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基于热稳定刚棒状芳香胺类有机改性剂的 聚酰亚胺/粘土纳米复合材料

梁竹梅 印杰*

高分子材料研究所, 化学化工学院, 复合材料国家重点实验室,
上海交通大学, 上海 200240

聚合物/粘土纳米复合材料在制备和加工过程中往往需要较高的温度, 因而使热稳定性较差的长碳链烷基铵盐类粘土有机改性剂的应用受到一定限制。本文从分子结构设计出发, 合成出两种新型热稳定刚棒状芳香胺类粘土有机改性剂 OM-1 和 OM-m。应用此改性剂制备出两种有机化蒙脱土 MMT-1 和 MMT-m 并用原位聚合法合成出一系列聚酰亚胺/蒙脱土纳米复合材料。文章通过红外, X 射线衍射和热失重等分析手段对所合成的有机改性剂的插层效果和所得有机化蒙脱土的热稳定性同常用的十六烷基铵盐粘土有机改性剂 (OM-16C) 进行了对比分析, 并通过透射电子显微镜进一步研究了蒙脱土在聚酰亚胺/蒙脱土纳米复合材料中的分散效果。研究发现, MMT-1 和 MMT-m 较 OM-16C 有机化蒙脱土 MMT-16C 的初始分解温度高出大约 50°C。对于 MMT-1 和 MMT-m, 当蒙脱土重量百分含量低于 3% 时, 可以得到剥离型聚酰亚胺/蒙脱土纳米复合材料。

关键词: 聚合物/粘土纳米复合材料 粘土有机改性剂 刚棒状 原位聚合