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Polynaphthoxazines-Montmorillonite Nanocomposites: Synthesis and Characterization

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Abstract: Polynaphthoxazines-clay nanocomposites were prepared from 1, 5-dihydroxynaphthalene, aniline, formaldehyde and different proportion montmorillonite(MMT) by *in-situ* reaction in ethanol. Dynamic TGA showed that nanocomposites have delayed decomposition temperatures when compared with pristine polynaphthoxazine indicating the enhancement in the thermal stability.

Keyword: Nanocomposites, polynaphthoxazine, montmorillonite.

Thermally resistant structural materials play a key role in the progress of the electronics and aerospace industries. Polybenzoxazine, a novel ring-opening phenolic resin, with superior properties such as no volatile emission when curing, near zero shrinkage and high mechanical performance, can be deemed as alternatives of traditional phenolics. Layered clays dispersed in a polymer matrix on nanoscale reinforced the thermal resistance and mechanical performance of the composite. The preparation of polybenzoxazine-clay nanocomposites with properties superior to that of pristine polybenzoxazine by melt and/or solvent blending has been reported[1,2]. In this study, a new class of polynaphthoxazines/montmorillonite (MMT) nanocomposites was synthesized by *in-situ* polymerization, characterized with x-ray diffraction (XRD) and evaluated on thermal resistance by thermal gravity analysis (TGA).

The general procedure for preparing the polynaphthoxazines/montmorillonite nanocomposites was carried out as follows: Na-MMT with cationic exchange capacity (CEC) about 100 meq/100 g was mechanically stirred to achieve a well dispersion in methanol, aniline and 37% formaldehyde were added to the dispersion and mechanically stirred for 2 h. To this mixture the required ratio of 1, 5-dihydroxynaphthalene was added. The mixture reacted under refluxing for 4 h, and the naphthoxazine/MMT nanocomposites precipitated from the reaction solution with yield over 95%. ^{1}HNMR spectrum of naphthoxazine from the nanocomposites was same to that of the pristine naphthoxazine, indicating the presence of MMT did not change the chemical structure of the product. In this process, aniline, formaldehyde and 1, 5-dihydroxynaphthalene were intercalated into the space between MMT layers and polymerized *in situ* to form

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nanocomposites.

X-ray diffraction analysis showed that the space of the adjacent silicate layers was 1.26 nm and the layered silicates in the nanocomposites made by *in-situ* polymerization were exfoliated under 5%, 7%, 10% MMT content (**Figure 1**). As can be seen from **Figure 2**, the thermal stability of the nanocomposites was improved by the presence of exfoliated MMT layers in comparison with the pristine polynaphthoxazines. The char yield at 700°C increased by *ca*. 14% with 5% MMT content in the nanocomposite and reached 65%. However, further increase in the amount of clay was less effective to improve the weight residues for nanocomposites.

Figure 1 XRD of pattens: MMT and poly-naphthoxazine-MMT (5%, 7%, 10%)

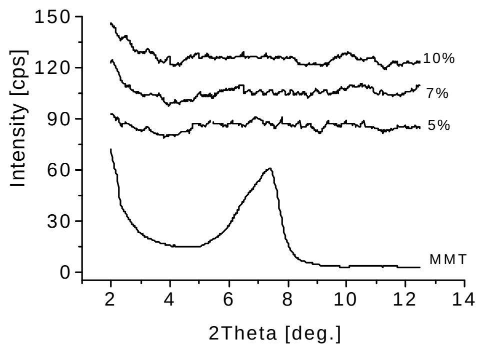
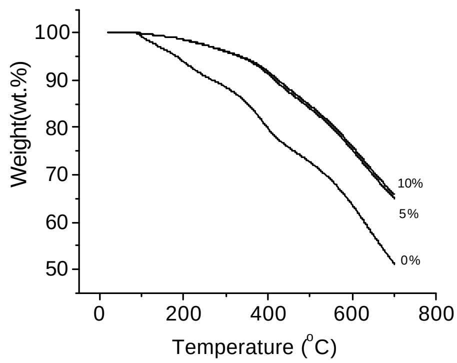


Figure 2 TGA of polynaphthoxazine-MMT nanocomposites with various MMT content after thermal treatment at 260℃/1 h: (a) 0%; (b) 5%; (c) 10%.



References

1. T. Agag, T. Takeichi, *Polymer*, 2000, *41*, 7083.
2. I. Hatsuo, *WO 00/29474*.

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