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THERMAL ANALYSIS OF POLYMER-SILICATE NANOCOMPOSITES

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Abstract

The thermal behavior of epoxy-smectite nanocomposites (hybrids) is examined by non-isothermal thermogravimetry (TG, DTG and DTA) in air atmosphere. It has been shown that the thermal stability of hybrids is much greater than that of epoxy resin and strongly depends on both the smectite loading and the type of the gallery cations of organically modified smectites. The kinetics of degradation of nanocomposites is significantly influenced by the presence of smectites and proceeds in three stages. Stage I is attributed to the effect of quaternized ammonium ion exchanged smectite, as stages II and III are associated with the decomposition of the bulk epoxy resin. Because of the interfacial interactions and the silicate-polymer multilayered nanoscale organization, the nanocomposites act as excellent heat insulator and mass transport barrier, which shift the thermal decomposition peaks towards much higher temperatures.

Keywords: DTA, DTG, interfacial effects, layered silicate-epoxy nanocomposites, multilayered structure, TG, thermal stability

Introduction

Concurrent with the recent stage in the preparation of nanoscale materials, nanostructured composites based on hybrids of polymers and smectic clay minerals are emerging with the prospect of solving recognized limitations of fiber composites and filled polymers. In the chemical intercalation approach the polymer is chemically bonded to the ionic sites at the internal surfaces of the lamellae through an ion exchange. That intercalation provides chemical continuity and morphological hierarchy, from which a higher level of stability may be derived. The exploitation of polymer-silicate nanocomposites requires the knowledge of their behavior under environmental conditions including their thermal stability and degradation. Thermal analysis

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Table 1 Characteristics of the thermal decomposition of epoxy resin, smectite clays and nanocomposites

	Degradation Stage I			Degradation Stage II			Degradation Stage III			
Sample	Temperature region I, ΔT_I/K	$T_{\text{peak I}}$/K	Mass loss I, W_I/ mass%	Temperature region II, ΔT_{II}/K	$T_{\text{peak II}}$/ K	Mass loss II, W_{II}/ mass%	Temperature region III, ΔT_{III}/K	$T_{\text{peak III}}$/ K	Mass loss III, W_{III}/ mass%	[*]Total mass loss, W_T/ mass%
Araldit	–	–	–	433–668	603	75.3	668–818	731	22.5	98.5
STN	423–651	463/553	15.7	813–903	853	4.2	953–1013	991	2.5	31.0
2.5 v% STN	–	–	–	551–763	663	67.6	763–893	823	11.4	82.5
5 v% STN	455–533	493	3.0	533–730	648	62.0	730–909	803	15.0	81.0
10 v% STN	563–663	638	5.0	663–745	713	54.0	745–909	833	20.0	82.5
SAN	483–691	500/603	17.1	691–993	813	32.4	993–1043	1023	2.2	54.5
2.5 v% SAN	403–591	527	18.3	591–698	641	50.5	698–853	785	20.0	89.5
5 v% SAN	423–557	503	4.4	557–728	649	59.6	728–868	793	18.0	83.0
10 v% SAN	551–649	643	8.2	649–733	683	48.7	733–883	811	18.0	77.0
SPN	443–573	513	52.5	–	–	–	968–1033	1003	2.0	64.5
2.5 v% SPN	393–523	463	17.0	523–613	548	52.5	613–783	709	19.5	89.5
5 v% SPN	393–611	503/593	14.5	611–716	655	52.1	716–893	813	21.2	89.0
10 v% SPN	348–523	463	3	523–723	643	57.8	723–878	815	28.3	90

[*]Total losses are a little bit higher than the simple sum of losses for the main 3 decomposition stages, mainly because of minor losses after stage III.
ΔT – temperature range of the degradation stages I, II and III, in the TG curves, in K;
T_{peak} – temperature of the DTG peak in the degradation stages I, II and III, in K;
W – mass loss of the corresponding degradation stages I, II and III, in mass%

methods are very useful in such investigation, as they permit the estimation of the temperature range of thermal stability and the changes undergone as a consequence of the accelerated aging. Recently, active studies are followed on flammability of polymer layered silicate nanocomposites in USA research groups [1].

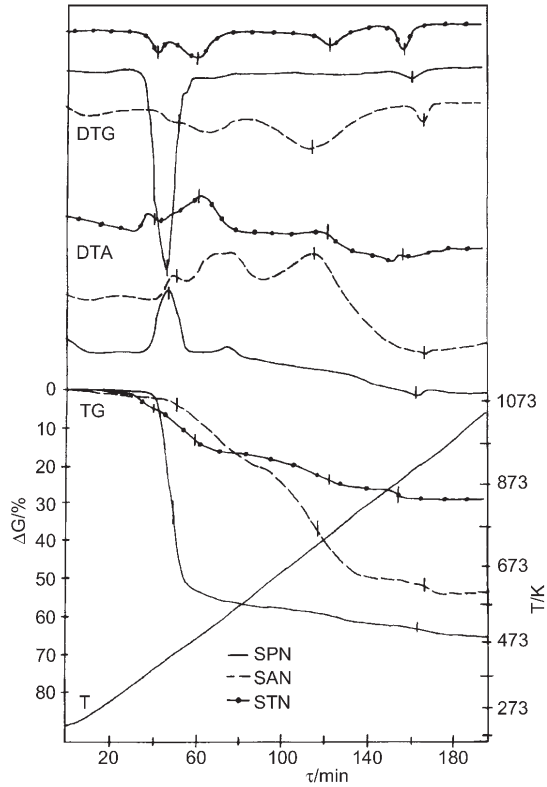

Fig. 1 Comparison of the thermal DTA, DTG and TG curves of smectic clays: SPN, SAN and STN

In our previous study on layered silicate-polymer nanocomposites, we have shown that clay exfoliation gives rise to greatly improved rheological and mechanical properties making possible new materials application of these polymers [2–4]. The aim of the present work is to estimate the thermal stability of epoxy-smectite nanocomposites, influenced by the smectite clay concentration and the chain length of the quaternized ammonium ion used in exchanged smectites.

Experimental

Nanocomposites have been prepared from smectic clay in an epoxy resin by chemical intercalation and *in situ* polymerization. Smectites used are SAN, STN and SPN, which are organically modified clays by the following quaternized ammonium (QA) ions: SAN – $[C_{16}H_{33})_x (C_{18}H_{37})_y N^+(CH_3)_2]$; STN – $[(C_8H_{17})_3 (CH_3)N^+]$ and SPN – $[(C_2H_5)_2 (CH_3)N^+ (O\text{-}iPr)_{25}]$. Epoxy resin Araldite LY556, anhydride curing agent HY917 and accelerator DY070 in proportions 100/90/2 are used as a basic matrix. The samples investigated are nanocomposites containing 2.5, 5 and 10 v% smectic clay in the epoxy resin. The synthesis method includes ultrasonic dispersing of the smectites in the epoxy resin, following by *in situ* polymerization in two stages of the temperature treatment – 348 K for 2 h and 403 K for 2 h. A simultaneous thermoanalytical method (TG, DTG and DTA) is applied to study the thermal decomposition process. The heating curves of samples have been recorded by help of MOM Budapest (Hungary) derivatograph in the temperature range 293–1273 K, at heating rate of 5 K min^{-1}. The composite degradation is investigated in air atmosphere without induced circulation.

In order to estimate thermal stability of samples studied, the following degradation stages, temperature peaks and mass losses of the smectic clays, the epoxy resin and the epoxy-smectite nanocomposites are determined and summarised in Table 1.

Results and discussions

Thermal analysis of smectite clays

Figure 1 shows the curves (TG, DTG, DTA) of STN, SAN and SPN smectic clays used as inorganic ingredients for nanocomposite preparation. Table 1 summarizes thermal analysis data for all samples. Inspecting the curves we noticed a significant difference between smectites, which is attributed to the complex degradation of the QA salt of different chain length. The SPN clay decomposes in two stages – low temperature stage I, and high temperature stage III. The main mass loss occurs in the low temperature stage I, at $T_{peak\ I}$=513K at the loss amounting to about 52.5 mass%. The process is highly exothermal and it is attributed to the desorption and fully dissociation of the paraffin-like SPN – $[(C_2H_5)_2 (CH_3)N^+(O\text{-}iPr)_{25}]$. An endothermal DTA effect and a very low mass loss (2 mass%) characterize the high temperature stage III, indicating the total degradation.

In contrast, kinetics of mass loss of both SAN and STN clays, proceed in three stages I, II and III. We noticed (Table 1 and Fig. 1), that the decomposition of SAN - $[C_{16}H_{33})_x (C_{18}H_{37})_y N^+(CH_3)_2]$ and STN – $[(C_8H_{17})_3 (CH_3)N^+]$ occurs mainly in stages I and II, wherein DTG peaks appear at higher temperatures, as follows: $T_{peak\ I}$=553 K (STN) and 603 K (SAN), and $T_{peak\ II}$=853 K (STN) and 813 K (SAN). Strong exothermal effects characterize stages I and II, which are attributed to dissociation of the corresponding QA ion. Specifically, stage I is separated in two peaks of both DTG and DTA curves, wherein the low temperature DTG peak (463 and 500 K for STN and SAN, respectively) is associated with desorption of the absorbed QA. Stage III is also characterized with the small mass losses (2–2.5 mass%) and the endothermic DTA peak of the total degradation.

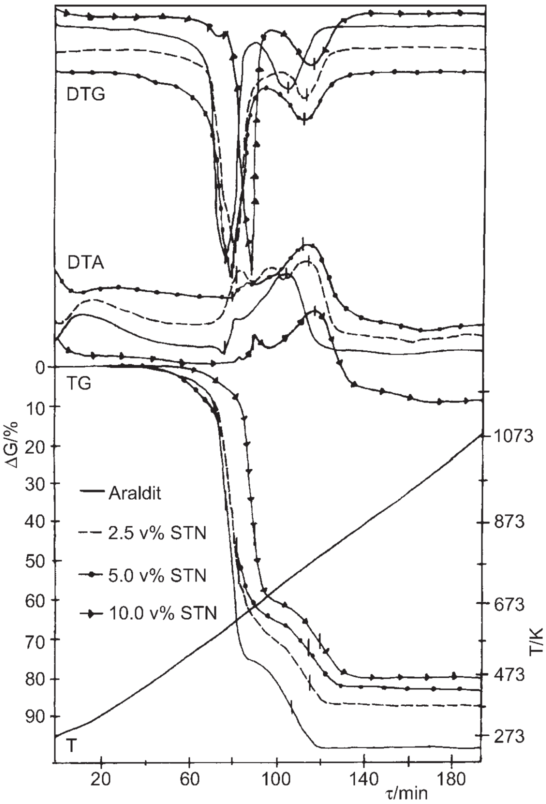

Fig. 2 The effect of the smectite loading on thermal DTA, DTG and TG curves of STN-epoxy nanocomposites: *Epoxy resin*, 2.5, 5 and 10 v%

In general, the temperature ranges of the degradation stages of STN, SAN and SPN smectite clays determine the different kinetics of decomposition of the corresponding QA salt. The paraffin-like SPN exchanged smectic clay shows the lowest thermal stability, and STN clay – the highest thermal stability. Total mass losses of 31 (STN), 54.5 (SAN) and 64.5 mass% (SPN) are calculated respectively, which give information about the total amount of the exhanged QA ion absorbed on the silicate surfaces of the smectite clays.

Thermal analysis of epoxy-smectite nanocomposites

The TG and DTG curves of epoxy-smectite nanocomposites are a mix of the equivalent curves of both the epoxy resin and the smectites. Figure 2 is an example, which compares the thermal curves (TG, DTG, DTA) of the epoxy resin and the STN-epoxy nanocomposites, containing 2.5, 5 and 10 v% STN respectively. As one can see from Fig. 2, the degradation of the epoxy resin proceeds in two stages II and III at 603 and 731 K, respectively. In contrast, stage I occurs in the degradation of nanocomposites and it is associated with the smectite clay loading. The kinetics of degradation in stage I of nanocomposites depends significantly on both the smectite concentration and the type of the QA exchanging ion. For example, DTG peaks of SAN nanocomposites (Table 1) are as follows: 527 K (2.5 v% SAN), 503 K (5 v% SAN) and 643 K (10 v% SAN), which are very near or coincide to the temperature interval of stage II of epoxy resin. Specifically, no thermal effects are associated with stage I for the nanocomposites, whenever two exothermal DTA peaks are found in stage I for STN clay (Figs 1 and 2). Obviously, the thermal behavior of nanocomposites in stage I is associated with diffusion processes. In general, the low heat and mass losses of nanocomposites in stage I are attributed to the multilayered polymer-silicate structure which strongly suppresses the heat and mass transport.

The shapes of TG and DTG curves of nanocomposites in stages II and III are similar to that of the epoxy resin, but DTG peaks of nanocomposites occur at much higher temperatures than the corresponding DTG peaks of the epoxy resin (Fig. 2 and Table 1). The mass loss of epoxy resin in stage II is attributed to decomposition of the

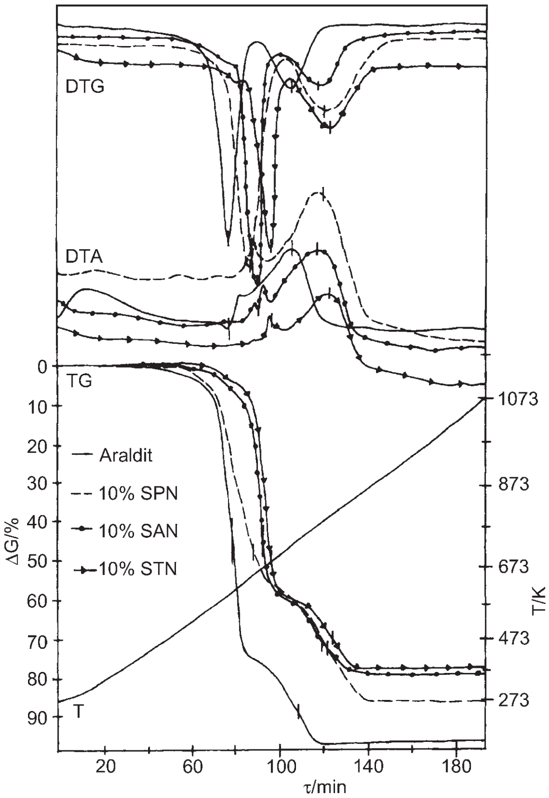

Fig. 3 The effect of the type of alkylammonium exchanged smectite on thermal DTA, DTG and TG curves of epoxy-smectite nanocomposites: *Epoxy resin*, 10 v% STN, 10 v% SAN and 10 v% SPN

ends of the epoxy network, because of the rapid decrease in mass (75.3 mass%) and it is accompanied by a small exothermal effect. Whenever, stage III is attributed to degradation of the main chain, and is characterized by very high exothermal effect and lower mass loss (22.5 mass%).

We notice, that smectite loading of 2.5 to 10 v%, improves significantly the thermal stability of nanocomposites. The DTG peaks of SAN nanocomposites are shifted towards higher temperatures with 55–110 K by increasing the smectite concentration. The total mass loss of nanocomposites decreases, which could be attributed not only to the presence of inorganic filler, but also with the strong barrier properties. As, for the example SAN-epoxy nanocomposites the total mass loss of epoxy resin is 98.5 mass%, compared with 89.5 mass% (2.5 v% SAN), 83 mass% (5 v% SAN) and 77 mass% (10 v% SAN). We propose that the increased thermal stability and the decreased mass loss of nanocomposites originate from the exfoliated polymer-silicate nanostructure, which act as an excellent insulator and mass transport barrier for the volatile products generated as the epoxy resin and QA ions decompose.

The thermal stability strongly depends not only on the smectite concentration, but also on the type of QA salt used to modify the smectites. Figure 3 compares the TG, DTG and DTA curves of smectite-epoxy nanocomposites, containing 10 v% of STN, SAN and SPN clays. By varying the nature of the exchanging QA ion one could successfully control the thermal stability of nanocomposites. We notice, that STN nanocomposites show the best thermal stability, following by SAN and SPN nanocomposites, respectively. The nanocomposite thermal stability, which is determined from the DTG peaks of the degradation stages I and II, significantly increase with 50–130 K by increasing the chain length of the QA ion. For example, stage II peak appears at the following temperatures: $T_{\text{peak II}}$=603 K (*epoxy resin*), 643 K (10 v% SPN), 683 K (10 v% SAN), and 713 K (10 v% STN). The DTG peak in stage III is also shifted with 80–102 K towards higher temperatures, in the upper mentioned order of samples.

Note, that the chain length of the QA ion greatly affects the extent of clay expansion upon epoxy solvation, resulting in a clay exfoliation. Therefore, the improved thermal stability of STN, SAN and SPN nanocomposites could be associated with the formation of the exfoliated nanocomposites. Better clay exfoliation is expected for longer chain modified STN and SAN nanocomposites, which gives rise to thermal stability. Exfoliated nanocomposites form two-dimensional (2–0) silicate sheets of great surfaces, which are separated from one another in a nanoscale distance and the polymer is confined in-between. Such structure strongly prevents any diffusion processes, which explains the exclusive properties, as thermal stability, flame retardation, water resistant. In case of the thermal stability, the silicate sheets act as a barrier for the heat transfer towards inside of the composite, and suppress mass transport of the volatile products generated as the confined polymer and QA ions decompose. Based on that structural peculiarity, the barrier properties of nanocomposites open great possibilities of the new materials application.

Conclusions

This paper reports effects of both the smectite loading and the chain length of the quternized ammonium (QA) ion on the thermal characteristics of epoxy-smectite nanocomposites. Some important conclusions may be mentioned:

1. Significant differences are determined in the thermal characteristics of STN, SAN and SPN smectic clays and are attributed to different kinetics of degradation of the exchanging QA ion, depending on the chain length.

2. The TG, DTG and DTA curves of nanocomposites represent a mix of the corresponding curves of smectite clay and epoxy resin. The low temperature degradation stage I of nanocomposites is associated with diffusion processes. In general, the thermal stability of nanocomposites increases with 50–130 K comparing to the epoxy resin. The mass losses in stages II and III are attributed to the decomposition of the ends of the epoxy network and to the degradation of the main chain, respectively. The effect originates from the exfoliated polymer-silicate nanostructure, which acts as an excellent heat insulator and mass transport barrier for the volatile products generated as the epoxy resin and QA ions decompose. Exfoliated nanocomposites form two-dimensional (2–0) silicate sheets of great surfaces, which are separated from one another in a nanoscale distance and the polymer is confined in-between. Such structure strongly prevents any diffusion processes.

3. The chain length of QA ions greatly affects the extent of clay expansion upon epoxy solvation, so it initiates clay exfoliation. Therefore, the improved thermal stability of STN, SAN and SPN nanocomposites could be associated with the formation of the exfoliated nanocomposites. By varying the nature of the exchanging QA ion one could successfully control the thermal stability of nanocomposites. Better clay exfoliation is expected for longer chain modified STN and SAN nanocomposites, which gives rise to thermal stability.

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