The kinetic of thermal degradation of poly styrene-co-acrylonitrile (SAN) /OMT nanocomposites using Flynn Wall Ozawa method

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Abstract
In this study the modified montmorillonite (OMT) was added to poly styrene-co-acrylonitrile (SAN) and the SAN/OMT nanocomposites were prepared in four compositions, by the melt mixing method. The situation of the layers inside the matrix of the nanocomposites was confirmed by XRD and TEM analysis.Then, the thermal degradation of SAN/OMT nanocomposites under nitrogen purge at different heating rates was investigated. In this study, the activation energies of SAN/OMT nanocomposites were calculated using Flynn Wall Ozawa method and it was concluded that with increasing of the OMT content in nanocomposite, the activation energy values were decreased. It was concluded that clay particles or layers take part in the thermal degradation mechanisms and they must not be regarded as inert materials.

Keywords: SAN, nanocomposites, XRD, TEM, kinetic study.

Introduction
Polymer nanocomposites are a class of composites in which the layered silicate, usually clay, is used as the filler with a capability of delivering one nanometer thickness layers inside the polymeric matrix [1, 2]. Using a minimal loading of the clay is enough to enhance most of the physical, mechanical and thermal properties of the nanocomposites significantly [3].

Experimental
The SAN/OMT nanocomposites were prepared in four compositions, by the melt mixing method using a twin-roll mill. Milling was performed at 140˚C (rolls temperature) for 35 min and 25 rpm revolution rate of the slower rotating roll. The amount of added OMT were 2, 5, 7, 10 wt%. The morphological study was investigated by XRD and TEM analysis.

Results and discussion
The XRD patterns was shown in Figure 1. However, due to the fact that only the intercalated state can be deduced directly from the XRD data and the so-called exfoliation state is usually judged when no diffraction peak appears in XRD patterns, it is necessary also to verify the nanocomposites by TEM. The well known salami morphology with the intercalated clay particles concentrated on the interphase area, was easily detectable in the micrograph in Figure 2. The thermal decomposition of SAN/OMT nanocomposites under nitrogen purge at different

heating rates was investigated (Figure 3). The effect of clay, and its content, on the thermal properties of the nanocomposites were studied in two thermal regions, 300–450 and 450–600˚C. In the first region, the onset temperature of decomposition decreases as clay content increases. This has been attributed to the thermal degradation of the modifying cations that occurs around 200˚C by a Hoffman degradation mechanism [1]. On the other hand, T_{10} also decreases with increasing clay content. However, the mass percent obtained at T_f increases and the vaule of W% decreases with increasing OMT content. Between 450 and 6 N 00˚C, nanocomposites did not show a significant mass loss; however, the residual mass percent at this region was higher for nanocomposite with higher OMT content. In this study, the activation energies of SAN/OMT nanocomposites were calculated using Flynn Wall Ozawa method (equation 1) in which with increasing of the OMT content in nanocomposite, the activation energy values were decreased (Figure 4).

$$\ln(\beta) = \ln\left(\frac{AE_a}{R}\right) - \ln G(\alpha) - 5.3305 - 1.052\left(\frac{E_a}{RT}\right) \quad (1)$$

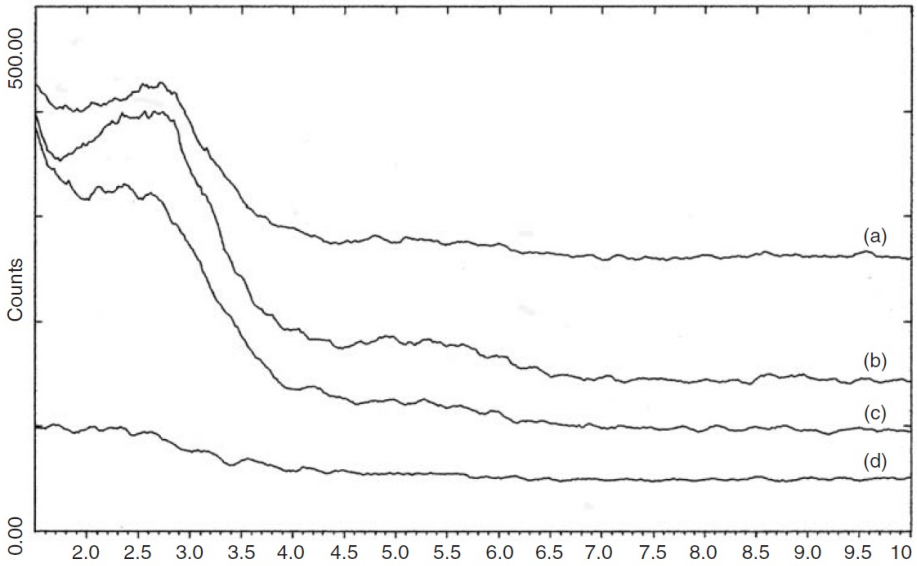

Fig. 1: XRD patterns for: (a) SAN/OMT 10%, (b) SAN/OMT 7 %, (c) SAN/OMT 5%, and (d) SAN/OMT 2%.

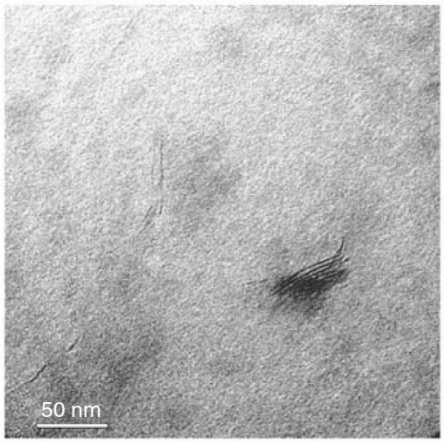

Fig. 2: TEM images for different nanocomposites SAN/OMT5.5%

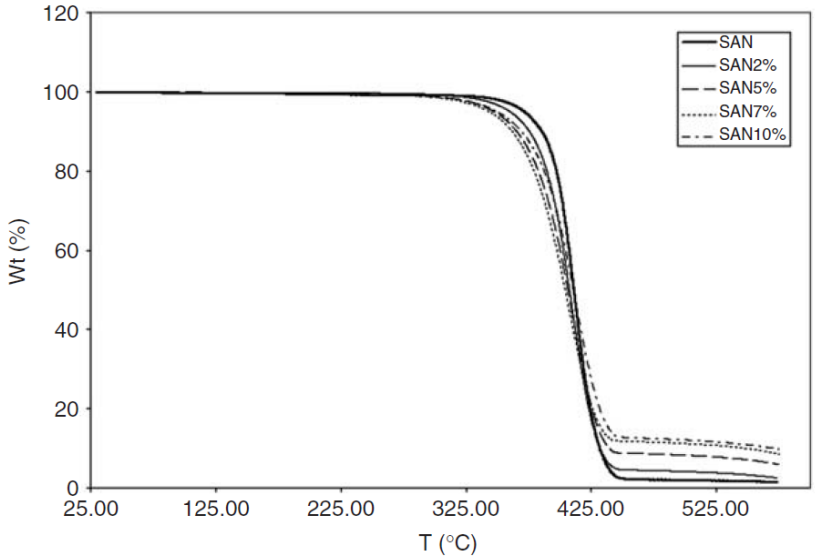

Fig. 3: The thermal degradation of SAN/OMT

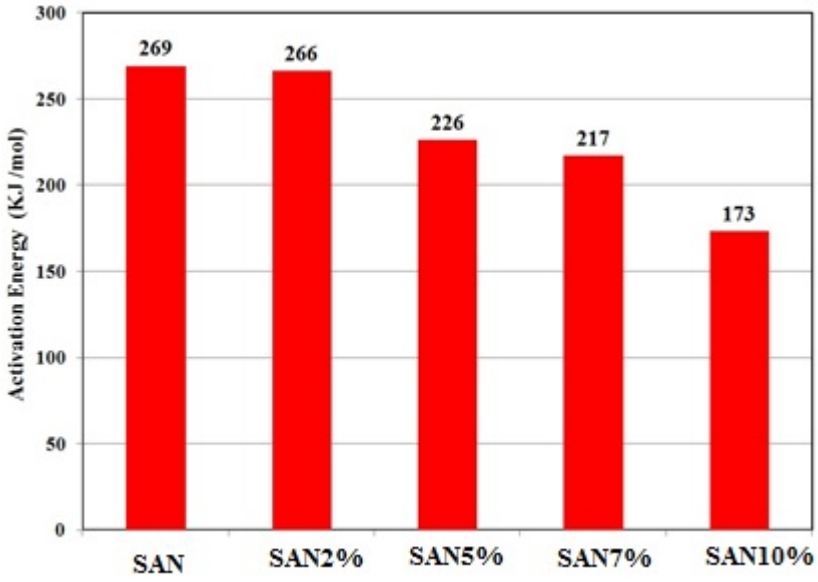

Fig. 4: Variation of Activation Energy values in SAN nanocomposites.

Conclusions

SAN nanocomposites were prepared by the melt mixing method. The nano structure was confirmed by XRD and TEM analysis. Thermal degradation of nanocomposites was investigated by TGA and the degradation kinetic was studied by Flynn Wall Ozawa method. The results show the relationship between degradation behavior and the activation energy value, in which reduction in activation energy values was observed by increasing the clay content in SAN nanocomposites. Even though the thermal property enhancement effect of clay nanofillers

observed in many of the polymeric nanocomposites has been attributed to the barrier property and char promoting effect of the clay, which protects the inner materials from further decomposition or combustion, the reduced activation energy values by increasing clay content showed their accelerating effect on thermal degradation reactions.

References

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