

PP-Clay Nanocomposites: Degradation and Stabilisation

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Abstract.

The work presented in this paper outlines the effect of processing on the oxidative stability of PP-clay-nanocomposites (PPNC) and discusses the effect of both clay type and the compatibiliser on the melt and long term thermal stability of PPNC. The challenges for stabilization of these materials will be highlighted giving examples of newly developed stabilization systems that results in significant improvements to the thermal stability of PPNCs

Introduction

Clay-reinforced polymer nanocomposites (PNC) have attracted great interest in the recent past due to the low nanofiller concentration typically required (1-5%) and the abundance and low cost of the nanoclay fillers combined with significant benefits in terms of the performance properties of the resultant nanocomposites, and especially fire retardancy, thermal and barrier properties [1]. To achieve PNCs with good performance properties, the clay platelets (e.g. montmorillonite, MT) must be sufficiently dispersed in the matrix, thus the clays are normally organically modified, typically with quaternary ammonium salts (quat), giving rise to organophilic clays (OMT). In the case of polyolefins, e.g. polypropylene, PP, the process of dispersion of OMT in the polymer is further improved by the addition of a compatibilising agent, typically graft copolymer containing maleic anhydride (MA) to produce a PP-nanocomposite (PPNC) [3]. However, although both quat and the compatibiliser are known to enhance the dispersion of the clays in PE and PP matrices, they are also known to affect both processing and long-term stability of these nanocomposites [4]. Much of the literature on processing of polyolefin nanocomposites tends to focus mainly on the clay morphology and final properties of the nanocomposites and not on their long term thermal stability [5,6]. This talk will highlight the effects of the nanofiller and the compatibiliser on the oxidative stability of PP-clay nanocomposites during melt processing and under thermal ageing conditions, along with the effect of antioxidants on the long term stability and performance of the PPNCs.

Effect of Processing on Morphology and Thermal Stability of PPNCs

A good clay dispersion and good thermal stability during processing are vital for achieving good performance properties for polyolefin-based nanocomposite products. The effect of OMT clays (Cloisite C20 and Dellite D67G) and the compatibiliser (PP-g-MA containing 1% MA) on the microstructure of the nanocomposite was examined using both transmission electron microscopy (TEM) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The latter has been shown to be a good method capable of determining OMT delamination in polymer-organoclay nanocomposites. The focus here is on measurements in reflectance mode of the clay silicon-oxygen (Si-O) infrared absorptions with the extent of resolution of the Si-O in- and out- of plane absorption bands indicating the state of dispersion of the layered silicate clays [7]. **Figure 1**, which compares the ATR (in the Si-O region) of a PP-D67G (without a compatibiliser) with that of a compatibilised PPNC analogue, shows clearly a striking difference in the Si-O absorption peaks of the two samples. In the absence of the compatibiliser PP-g-MA, the Si-O bands (out-of-plane and in-plane absorptions) are overlapped resulting in only one broad peak in this region, whereas in the compatibilised PPNC sample, a more resolved and separated absorptions of the clay Si-O bonds is clearly seen reflecting a more delaminated and better dispersed clay platelets in the PP matrix. This is further supported by results from TEM micrographs of the same samples which show clearly that the compatibilised PPNC sample has a

structure having clay particles that are well dispersed and is characteristic of a hybrid morphology containing both intercalated and some exfoliated (some single clay platelets) clay structures with increased contact surfaces between the delaminated clay platelets and the matrix (figure not shown here).

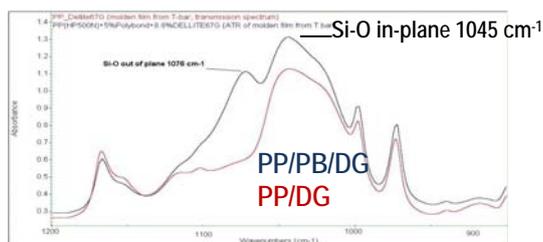


Fig. 1: ATR for thin films of PPNC with and without compatibiliser

Interactions between polymer matrices and the surface of clay layers has been shown to be among the most important parameters that influences the thermal stability of clay-polymer nanocomposites [7]. One of the main problems here is that OMT modified with a quat is known to decompose at high temperatures, giving rise to α -olefins and amines by a Hoffmann Elimination mechanism [4], which contributes to polymer's (PE or PP) degradation by a number of known reactions [8].

In view of the thermal instability of the quat in OMT at temperatures close to those typically used for PP processing, the effect of extrusion at 200 °C on the thermal oxidative stability of PPNC was compared with that of a corresponding sample but containing the natural unmodified clay, NaMT (Na-PPNC), by examining the changes in their apparent viscosity with processing time using a closed loop multi-extrusion test. We have shown that the viscosity of OMT-containing PP sample (PPNC) drops with time much more rapidly compared to that of the NaMT-containing sample (Na-PPNC) confirming the thermal instability of the OMT at the extrusion temperature used. The thermal instability of PPNCs is further demonstrated from the observed striking difference in the length of the measured DSC-oxidative induction time (OIT at 190 °C) of the two samples giving rise to an OIT of 350 min. for the Na-PPNC compared to only 50 min for the PPNC. Long term thermal ageing results measured in a Wallace air-flow oven at 125 °C have also

shown that PPNC samples (containing OMT) give much shorter lifetime than PP itself or Na-PPNC, corroborating further the detrimental effect of the OMT on the thermal stability of PP-based nanocomposites.

Effect of Antioxidants on the Stability of PPNCs

It is clear from the results above that stabilisation of PPNCs is essential if the full benefits of these materials are to be realized when used in-service. Overall, the poor thermo- as well as photo-oxidative stability of PPNCs is due to a complex combination of factors including the instability and degradation of the clay-organic modifier, the thermal and photo-instability of the MA-containing compatibiliser, the presence of catalytic metal ion, e.g. iron, impurities in the clay, and possible adverse interactions between the various components and their thermal- and photo-oxidative products. A further complication is that the performance of conventional antioxidants is typically compromised in the presence of both the OMT and the compatibiliser, hence generally stabilised polyolefin (PP and PE) nanocomposites have lower overall stability than their unfilled polyolefin polymer counterparts [7]. We have developed a number of antioxidant systems that have been shown to give rise to a significant improvement in the stability of PPNCs. Examples of PPNC stabilisation will be highlighted in this presentation.

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