Thermal stabilization ability of polyhedral oligomeric silsesquioxane nanofillers

Sin Vila and Miguel Sanchez-Soto

The polyhedral oligomeric silsesquioxane nanofillers examined in this study provided little or no improvement to the thermal properties of melt-blended acrylonitrile butadiene styrene polymer composites.

The recent developments in thermoplastic nanotechnology using nanofillers have opened up the possibilities of enhancing the mechanical, chemical, and thermal properties of polymers.[1–3] Within the broad range of nanoparticles available, polyhedral oligomeric silsesquioxanes (POSS) have become popular because of their organic-inorganic nature and easy incorporation into the polymer matrix.[2, 3] Compared with copolymerization methods, the use of melt-blending techniques to produce thermoplastic nanocomposites is an attractive approach because it is high yielding, simple, and inexpensive. The enhancement of properties with melt-blending is, however, not always effective owing to poor interactions between the POSS and matrix.[4, 5]

In this work,[6] we focused on creating new melt-blended nanocomposites with acrylonitrile butadiene styrene (ABS) grafted with maleic anhydride (ABS-g-Ma), with the attempt to enhance its thermal stability. We assessed the resulting nanocomposites with different analytical methods to understand the key factors playing a role in the overall effectiveness of the POSS incorporation.

We modified ABS-g-Ma with three different POSS nanofillers incorporated into its matrix, namely aminopropylisobutyl, glycidyl, and trisilanol, resulting in three nanocomposites: APOSS, GPOSS, and TPOSS, respectively. These composites were prepared using melt blending with a twin-screw compounder, and the degradation conditions consisted of submitting the nanocomposites and the standard ABS-g-Ma to oven-aging at different temperatures from 200–320°C in steps of 40°C and 0–75min periods of time in steps of 15min. We assessed the degree of dispersion of POSS molecules into the matrix prior to degradation by scanning electron microscopy (see Figure 1), and observed no relevant differences between samples. The nanocomposites showed no POSS aggregates or inhomogeneities,
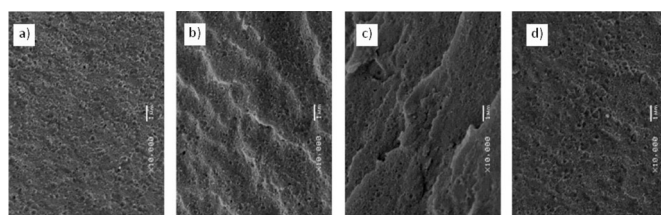

Figure 1. Scanning electron micrograph at 10,000x magnification of a) acrylonitrile butadiene styrene (ABS) grafted with maleic anhydride (ABS-g-Ma), and ABS-g-Ma composites with polyhedral oligomeric silsesquioxane (POSS): b) ABS-g-Ma/aminopropylisobutyl (APOSS), c) ABS-g-Ma/glycidyl (GPOSS) and d) ABS-g-Ma/trisilanol (TPOSS).
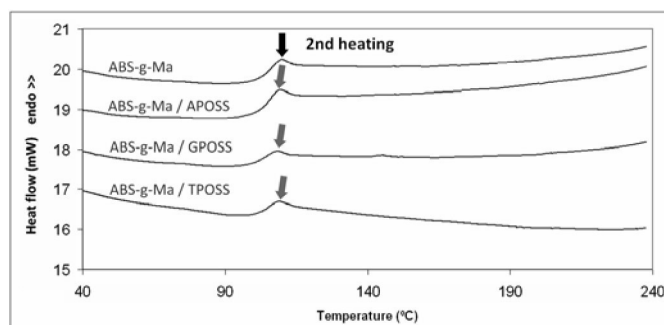

Figure 2. Differential scanning calorimetry heatflow plot during the second heating of ABS-g-Ma and its nanocomposites ABS-g-Ma/APOSS, ABS-g-Ma/GPOSS and ABS-g-Ma/TPOSS.

leading us to conclude good dispersion and miscibility between the nanofillers and matrix.

We used differential scanning calorimetry to identify the glass transition temperature (Tg) of each composite, and the possible effects of the nanofillers on the matrix prior to degradation. The heatflow plot depicted in Figure 2 shows that all nanocomposites have a small decay
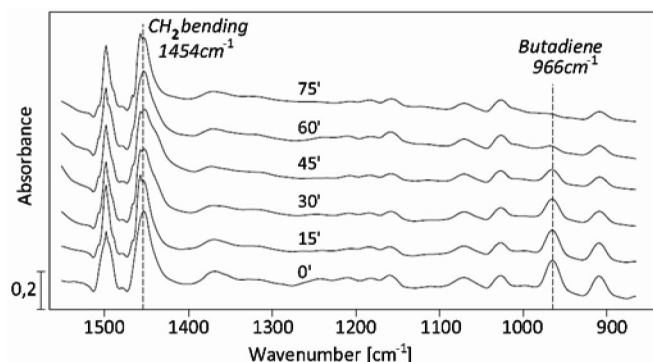
Figure 3. Fourier transform IR spectra of ABS-g-Ma undergoing thermo-oxidation at $320°C$ in 15min steps over the range 0–75min.

Table 1. Drop in butadiene/CH_2 ratio between the virgin material and the degraded sample at $280°C$ for 75min for each material.

Drop in butadiene/CH_2 bending ratio $[S_0\text{-}S_{280°\times75'}]$	
ABS-g-MA	48.21%
ABS-g-MA/APOSS	51.24%
ABS-g-MA/GPOSS	45.02%
ABS-g-MA/TPOSS	42.87%

of $\sim2°C$ in Tg, indicating that the different POSS nanofillers act as plasticizers. This behavior can be attributed to an increase of the free-volume at the ABS backbone caused by the local mobility of the bulky POSS structures, promoting molecular mobility.[1,4,5] Additionally, no further melting point (Tm) peaks were observed, indicating that the nanofillers are thoroughly blended and dispersed within the matrix.

During the aging process, we used attenuated total reflectance Fourier transform IR (ATR-FTIR) spectroscopy to follow the depletion progress of the most sensitive fraction of the ABS matrix, i.e., butadiene, in relation to the CH_2 bending group. Figure 3 shows the progress plot of ABS undergoing degradation at $320°C$ from 0min to 75min, clearly exhibiting a butadiene decay along with thermo-oxidation. This trend is summarized for each sample in Table 1, showing little or no benefit of the nanofillers on the overall thermo-oxidation resistance.

Alternatively, we carried out thermogravimetric analysis (TGA) to follow the weight decay progress as a function of temperature and subtract the onset temperatures at which 5% ($T_{5\%}$) and 50% ($T_{50\%}$) of weight loss occurred. The derivative function of the above thermograms provided the temperature of maximum weight loss (T_{max}) and the thermogravimetric traces led to the calculation of the activation energy (E_a) required to initiate the degradation process. Table 2 summarizes the

Table 2. Summary of thermogravimetric analysis (TGA) and kinetic degradation of ABS-g-Ma and its composites. $T_{5\%}$, $T_{50\%}$, T_{MAX}: temperature at which 5%, 50%, and maximum weight loss occurs, respectively. n: Order of reaction. E_a: Activation energy.

	TGA Parameters			Kinetic Parameters	
	$T_{5\%}$	$T_{50\%}$	T_{MAX}		E
Material	°C	°C	°C	n	[kJ/mol]
ABS	353	416	414	2.54	99.0
ABS-APOSS	351	418	416	2.45	98.8
ABS-GPOSS	357	419	416	2.46	106.5
ABS-TPOSS	361	421	416	2.46	106.9

most relevant results from the thermogravimetric and kinetic analysis, where TPOSS and GPOSS provided little improvements and APOSS had an almost negligible effect.

Although yellowing has been acknowledged as a physical manifestation of polymer degradation, limited research is available on quantifying this color variation. Accordingly, we also focused on assessing the appearance deterioration on the surface in terms of yellowing using CIELAB spectrophotometry, quantifying the variation in terms of color lightness (L*), green-magenta hue (a*) and blue-yellow hue (b*). Figure 4 shows our results, in which no relevant differences could be found in yellowing between the nanocomposites and base material.

In summary, despite the appropriate dispersion and miscibility of the nanofillers melt-blended in the ABS-g-Ma matrix, the GPOSS, TPOSS, and APOSS nanofillers provided little or no improvements to the matrix. These limited effects of the melt-blended nanoparticles on the overall polymer matrix, particularly on the thermal properties, are likely caused by the competing effects between the intermolecular constraints of the rigid POSS structures and the free volume increment promoted by the local mobility of the pendant moieties of the same dispersed nano-cages, yielding to a poor interaction between both phases and consequently voiding the potential POSS contribution. Moreover, the above competing inefficiencies became an additional drawback for the ABS-g-Ma/APOSS nano-hybrid as the unreacted APOSS fraction exhibited its lower degradation temperature in an isolated state, resulting in a slight decay of the overall TGA onset temperature. The findings from this paper have encouraged us to further study the theoretical compatibility between the matrix and the nanofiller in terms of solubility parameters to assist in the selection of materials for melt-blended nanocomposites prior to empirical testing.
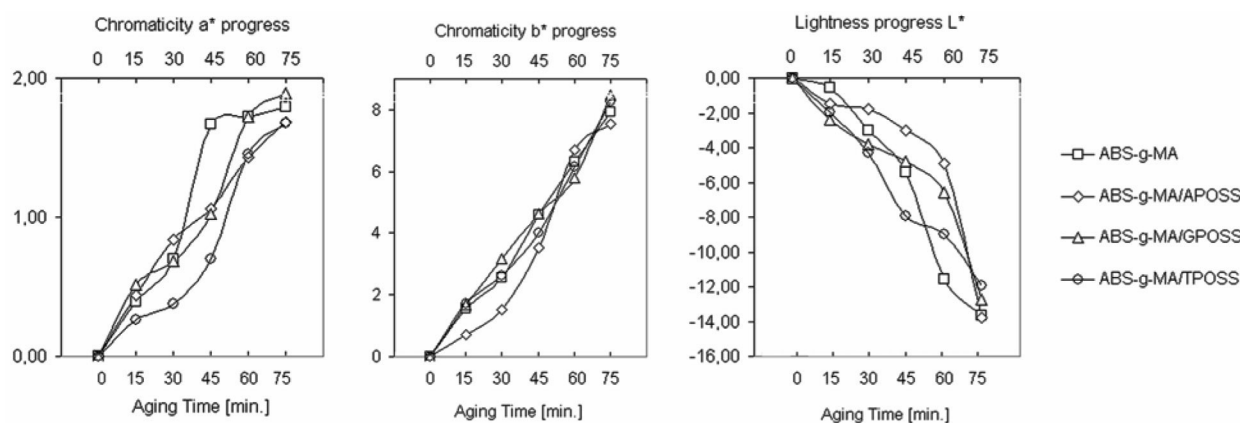
Figure 4. *Color variation of each sample aged at 240°C up to 75min expressed in chromaticity a* (green-magenta), b* (blue-yellow) and lightness L*.*

Author Information

Sin Vila and Miguel Sanchez-Soto
Catalan Center for Plastic
Polytechnic University of Catalonia (UPC)
Barcelona, Spain

Sin Vila is a final-year PhD student in nanocomposites degradation at UPC with a mechanical engineering diploma specializing in plastics (UPC, 1997) and a bachelors degree in mechanical engineering (Queensland University of Technology, Australia, 2000). Over the past decade he has held management roles in plastic design and manufacturing.

Miguel Sanchez-Soto is a professor at UPC and a researcher at the Catalan Center for Plastic. He has published 32 indexed articles on plastic materials. Additionally, he has been actively involved in various European Union programs and coordinates scientific projects funded by the Spanish government.

References

1. J. Wang, Z. Ye, and H. Joly, *Synthesis and characterization of hyperbranched polyethylenes tethered with polyhedral oligomeric silsesquioxane (POSS) nanoparticles by chain walking ethylene copolymerization with acryloisobutyl-POSS*, **Macromol. 40** (17), pp. 6150–6163, 2007. doi:10.1021/ma0706733
2. M. B. Nair and F. D. Blum, *Copolymers and blends of methyl acrylate and acrylic isobutyl poss nanomaterials*, **Polym. Prepr. 46** (1), pp. 367–368, 2005.
3. B. X. Fu, M. Y. Gelfer, B. S. Hsiao, S. Phillips, B. Viers, R. Blanski, and P. Ruth, *Physical gelation in ethylene-propylene copolymer melts induced by polyhedral oligomeric silsesquioxane (POSS) molecules*, **Polymer 44** (5), pp. 1499–1506, 2003. doi:10.1016/S0032-3861(03)00018-1
4. A. Fina, D. Tabuani, T. Peijs, and G. Camino, *POSS grafting on PPgMA by one-step reactive blending*, **Polymer 50** (1), pp. 218–226, 2009. doi:10.1016/j.polymer.2008.11.002
5. O. Monticelli, A. Fina, A. Ullah, and P. Waghmare, *Preparation, characterization, and properties of novel PSMA-POSS systems by reactive blending*, **Macromol. 42** (17), pp. 6614–6623, 2009. doi:10.1021/ma900969b
6. N. V. Ramírez and M. Sanchez-Soto, *Effects of POSS nanoparticles on ABS-g-Ma thermo oxidation resistance*, **Polym. Composites 33** (10), pp. 1707–1718, 2012. doi:10.1002/pc.22304