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Abstract: In this study, epoxy nanocomposites containing different fractions of n-phenylaminopropyl (POSS) were prepared. The nanocomposites were studied by transmission electron microscopy (TEM), gel content, dynamic-mechanical analysis (DMA) and thermogravimetric analysis (TGA). The parameters for Avrami's equation were calculated from the degradation curves. The dispersions used to form the nanocomposites were effective above 5 wt % of POSS, and the gel content increased with the addition of POSS. The DMA analysis exhibited an increase in the storage modulus (E') and a shifting of T_g to higher temperatures upon POSS incorporation. The weight loss indicated that the POSS promoted an increase in thermal stability of the epoxy resin. The Avrami parameters demonstrated that the addition of POSS decreased the Avrami constant (k'), increased the half-life ($t_{1/2}$) of degradation and promoted changes in the Avrami exponent (n). These results suggest that the increase in the glass transition temperature and thermal stability depend on the reactive groups in the POSS nanoparticles.

Keywords: *Epoxy, POSS, nanocomposites, thermal stability, glass transition.*

Introduction

Hybrid materials have received significant attention due to the ability to combine the properties of traditional polymers (processability and mechanical strength) with the properties of inorganic compounds (thermal and oxidative stability)[1]. In 1946, Scott[2] introduced the POSS monomers in the scientific field. Initially, POSS monomers were composed of aliphatic chain substituent groups of silicon (Si) atoms. After the discovery of hybrid POSS monomers, several modifications were performed[3]. Currently, these monomers are structurally well-defined molecules that have the form of a cage with typical size of approximately 1.5 nm[4,5]. These compounds exhibit a hybrid inorganic core containing silicon atoms and are surrounded by organic groups represented by $(RSiO_{1.5})_x$ (where R represents organic groups positioned at the vertices of the cages and x = 6-12). Because the monofunctional POSS monomer allows the incorporation of silsesquioxane units within the main chain of the polymers, bi-functional POSS can be incorporated by graftization through copolymerization or reactive processing. POSS monomers with functionalities higher than two can be used for the preparation of thermosetting nanocomposites[6]. Among the thermoset polymers, nanocomposites of epoxy/POSS have been studied[6,7-11].

Some studies with the addition of the octa nitrophenyl (OnpPOSS), octa aminophenyl (OapPOSS)[8], (propyletherglycidyl – POSS)[9], octavinyl – POSS (OVPOSS)[10] and ether dimethylsiloxypropylglycidyl (OG)[11] in epoxy resin demonstrated an increase in the thermal stability. Other studies demonstrated that the addition of POSS can increase[7] and decrease[8] the glass transition temperature (T_g) and also may promote improvements in the mechanical properties, such as impact and flexural resistances[10]. These improvements of the thermal and mechanical properties are attributed to the good dispersion on the nanometer scale[8,10], the interconnection formed between the polyhedral cages and the structure of the epoxy resin[9], the hybrid characteristics of POSS[10] and an increase in the crosslinking density of the cured resin[11,12]. Whereas the nanocomposite properties depend on the dispersion, the dispersion depends on the functionality of the POSS. Strachota et al.[3] demonstrated that the POSS monomers with different concentrations of epoxy groups can agglomerate due to the intra-and inter-molecular reactions between the cages. By forming nanocomposites of epoxy and POSS that also contain epoxy groups[13], we demonstrated that the degradation mechanism of the epoxy (random nucleation with one nucleus of an individual particle) was changed to D_n (diffusion model). The mechanism of diffusion was associated with the increase in the average distance between the chains. The increase in free volume promotes a reduction of the T_g[14,15]. On the other hand, the addition of POSS can also promote an increase in T_g[7]. The higher or lower T_g, in such cases, may not correlate with the dimension of the cages; as a result, the purpose of this study is to evaluate whether the

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addition of octafunctional POSS containing amine groups can modify the T_g and the thermal stability[13-15].

Materials

The following materials were utilized in this study (Figure 1). The epoxy resin diglycidyl ether of bisphenol-A (DGEBA) (Araldite GY-251) and the curing agent triethylenetetramine (TETA) (Ren Lan M1/HY956) were supplied by Huntsman Advanced Materials. Polyhedral oligomeric silsesquioxane N-phenylaminopropyl–POSS (AM0281) (($C_8H_{13}O)_y(SiO_{1.5})_x$; (x = 8, 10 and 12)) was obtained from Hybrid Plastics™. The POSS is a mixture of oligomers of x = 8, 10 and 12.

Methods

Nanocomposite preparation

The epoxy resin (DGEBA) was prepared based on the equivalents of reactive groups (g/eq) using triethylenetetramine (TETA) as a curing agent. An equivalent weight of 1/1 (g/eq) between the epoxy and amine groups was maintained. To obtain the nanocomposites, a pre-mix between the N-phenylaminopropyl–POSS and the curing agent TETA was performed at 50 °C and 400 rpm for 20 minutes to ensure the homogeneity of the system. Subsequently, 1, 2, 5 and 10 wt% of POSS was added to the resin. The incorporation of TETA/POSS in DGEBA was realized by maintaining the ratio of the epoxy and amine groups at 1/1 (g/eq). The curing of the resin was performed at a temperature of 25 ± 3 °C for 24 hours. After curing, the samples were post-cured in an oven under vacuum (–300 mm Hg) for 24 hours at 100 °C.

Transmission Electron Microscopy (TEM)

The morphologies of the specimens were examined by TEM (JEOL JEM-120 Ex II), which operated at an accelerating voltage of 80 kV. Sections of 50-nm thickness

were cut at a speed of 0.3 mm/s at room temperature using an ultramicrotome RMC Power Tome XL equipped with a diamond knife. The sections were collected on copper grids (300 mesh) and submitted for analysis by transmission electron microscopy (TEM).

Gel content (Gc)

The determination of gel content was performed using approximately 2 g of sample in a wire cage (120 mesh) suspended in a flask containing 250 mL of ketone at 80 °C. Extraction occurred for 6 hours as described in ASTM D 2765-01. After extraction, the samples were dried in a vacuum oven at 100 °C for 24 hours. The gel content of the samples was calculated as described in Equation 1:

$$Gc(\%) = \frac{m_i}{m_s} \times 100 \qquad (1)$$

where m_i is the insoluble mass, and m_s is the soluble mass of the sample contained in the cage.

Thermogravimetry (TGA)

The TGA analyses were performed on a Q50 (TA Instruments) under N_2 atmosphere (40 mL.min⁻¹) from ≈ 23 °C to 750 °C at a heating rate of 10 °C.min⁻¹. The mass utilized for the analyses was approximately 10 mg. The results obtained were used to estimate the kinetic parameters of degradation by the Avrami method[16-22].

Avrami method

The theory developed by Avrami during the years of 1939-1940[16-18] was based on the kinetics of the phase changes. Over the years, the Avrami derivations have been simplified by Evans[19] and placed in the context of polymers by Meares[20] and Hay[21]. According to the original Avrami's theory, the degree of conversion ($\alpha(t)$),
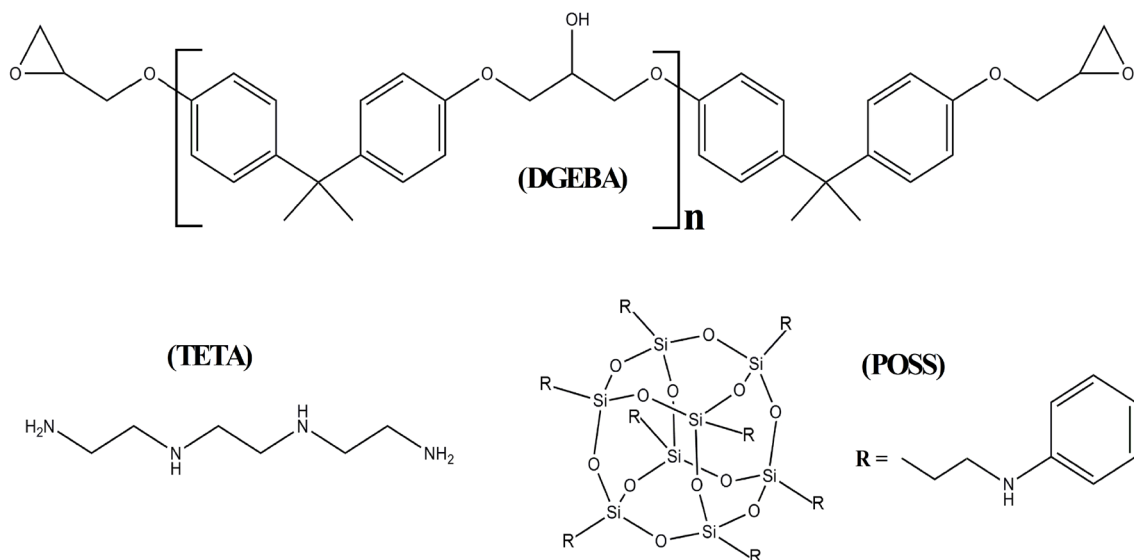

Figure 1. Schematic drawing of chemical structures used in the development of nanocomposites studied in this work. The molecular structure of POSS present n = 8 and substituent (R) is N-phenylaminopropyl group.

under isothermal conditions, can be obtained using the following relation:

$$\alpha(t) = 1 - e^{-kt^n} \qquad (2)$$

where k and n are the Avrami constant and Avrami exponent, respectively, being both dependent on the physical process.

Applying the double logarithm in Equation 2 (resulting in Equation 3), it is possible to observe a linear relationship between the terms $\ln[-\ln(1-\alpha(t)]$ vs. $\ln t$. Thus, the values of n and k can be obtained using the obtained angular and linear coefficients, respectively.

$$\ln\left[-\ln(1-\alpha)\right] = \ln k + n\ln t \qquad (3)$$

Jeziorny[22] modified the Avrami equation and noted that the constant k can be determined under non-isothermal conditions. However, in this case, the kinetic constant is determined as a function of the temperature ($\alpha(T)$). Thus, the corrected constant k' becomes:

$$\ln k' = \left(\frac{\ln k}{\beta}\right) \qquad (4)$$

where β is the heating rate. In this case, α is a function of temperature ($\alpha(T)$). In this work, the Avrami method is used to evaluate the kinetic degradation parameters[13,23]. The values of k and n were correlated with the velocity constant of degradation and the order of the degradation process occurring due to the microstructure, respectively, to the cured epoxy resin and the nanocomposites.

Dynamic-Mechanical Thermal Analysis (DMTA)

The viscoelastic properties were characterized by a Q800 AT DMA apparatus with a single-cantilever clamp using rectangular specimens of size $35 \times 10 \times 2$ mm³. The characterization of the specimens was performed under the following conditions: heated from room temperature (≈ 23°C) to 160 °C at a heating rate of 3 °C.min⁻¹, data sampling at 1 Hz frequency and strain amplitude of 0.08%.

Results and Discussion

Dispersion of the nanocomposites

Figure 2 shows the nanometric dispersion of POSS. The addition of 1 and 2 wt% of POSS resulted in the formation of clusters with poor dispersion along the matrix. The sample containing 5 wt% of POSS exhibited regions of random clusters along the sample. The sample containing 10 wt% POSS is homogeneously dispersed in the layers formed.

The POSS monomers can be considered as a spherical compact hexagonal structure that is able to crystallize and agglomerate. The crystallization of the nanocages depends on the type of the organic substituent present at the vertices of the polyhedral that represent the nanocages[24]. The POSS frequently crystallizes in the form of layers when the POSS incorporation is higher, due to the efficient dispersion of these particles in the matrix[25].

Gel content (Gc)

The gel content (Gc) analysis is presented in Figure 3. The extraction process was performed to evaluate the influence of POSS in the crosslinking bond formation.

The soluble fraction of the cured epoxy resin was 4.33%. This soluble fraction is associated with the unreacted low-molecular-weight fractions[26]. The nanocomposites exhibited a soluble fraction of 3% for 1, 2 and 5 wt% of POSS and 2.33% for 10 wt% of POSS. These results suggest that the less reactivity difference of the aromatic amines of POSS comparing with the TETA not hindered the cure of the epoxy resin and indicates a slight increase in crosslink density (correlated with the insoluble fraction).

Viscoelastic properties

Figure 4 shows the storage modulus as a function of temperature for the neat epoxy and the nanocomposites containing 1, 2, 5 and 10 wt% of POSS. In the glassy region, the modulus depends on the intermolecular forces, the cohesive energy density, the packing density and the molecular mobility[15]. The addition of POSS promotes an increase in the glassy region that indicates a reinforcement effect may be associated with the values of gel content.

The incorporation of POSS shifted the glass transition to higher temperatures. This shift is expected because the glass transition is a cooperative phenomenon of molecular vibration[27,28] and because the octafunctional POSS is able to increase the percolation of the crosslinked network, as suggested by gel content analysis.

Above T_g, network chains have sufficient thermal energy to overtake the potential barriers linked to van der Waals interactions. They undergo fast conformational
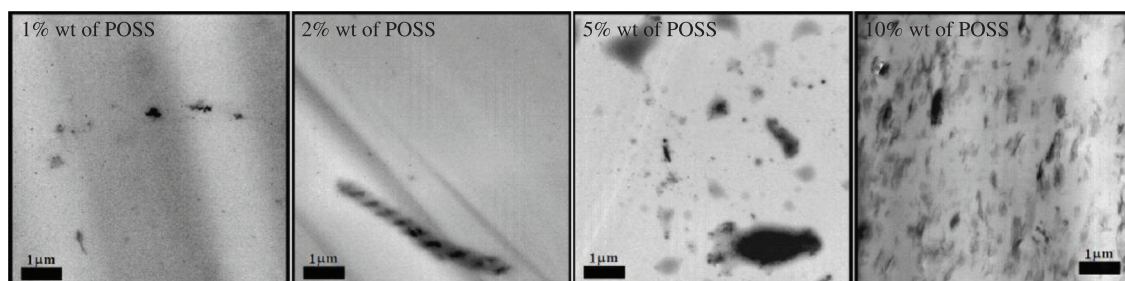

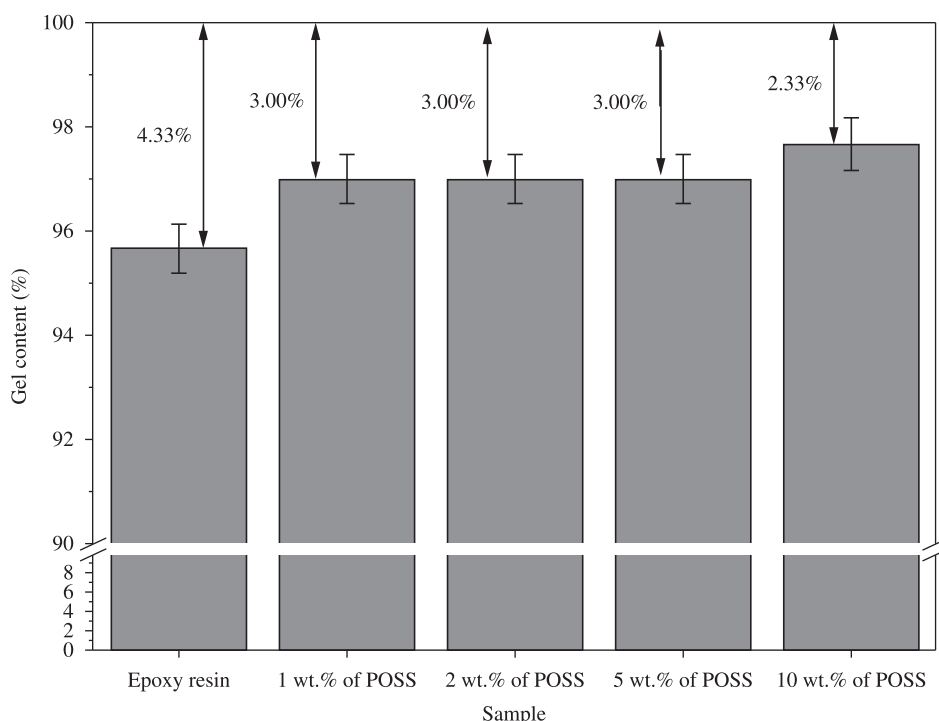**Figure 2.** TEM analysis shows the dispersion of the POSS nanocages in the cured epoxy resin.

Figure 3. Gel content analysis of the samples studied.
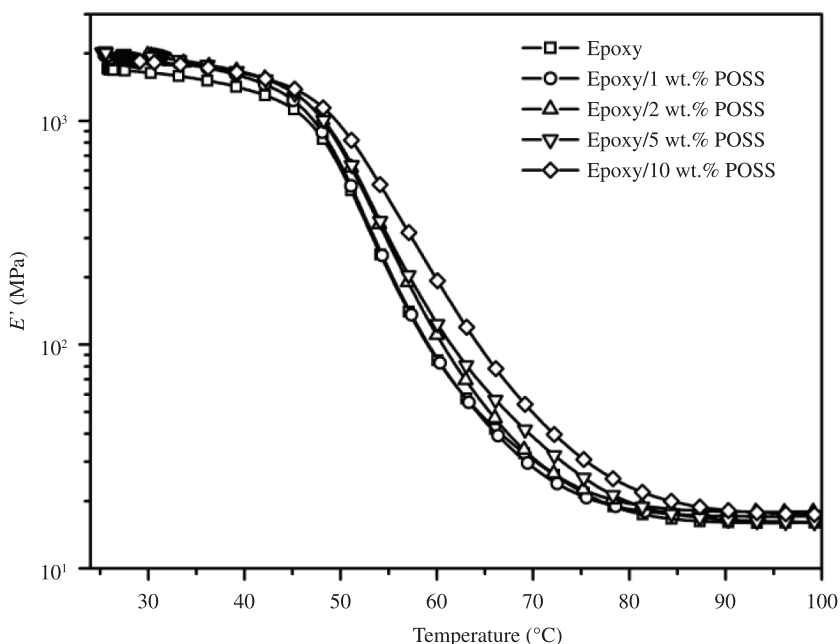

Figure 4. Curves of storage modulus (*E'*) obtained by analysis of DMTA.

changes by cooperative segmental motions, but crosslinking prevents any liquid flow[15,28]. In theory, incorporation of reinforcements should result in higher modulus values. As the temperature increases, the samples pass through a glass transition region and reach the elastomeric region, where more segments in the chain are moving in a cooperative way[15]. The elastomeric region not shows significantly variations with the presence of POSS.

Figure 5 and Table 1 shows the tan δ values and the parameters obtained from the tan δ curves. The samples containing 1, 2, 5 and 10 wt% POSS exhibited a shift to higher T_g, as shown in Figure 4.

In Table 1, the peak height and peak width at half-height are associated with the homogeneity, *i.e.*, a broader curve can be associated with a greater distribution of relaxation times[15,29]. According to the results, no
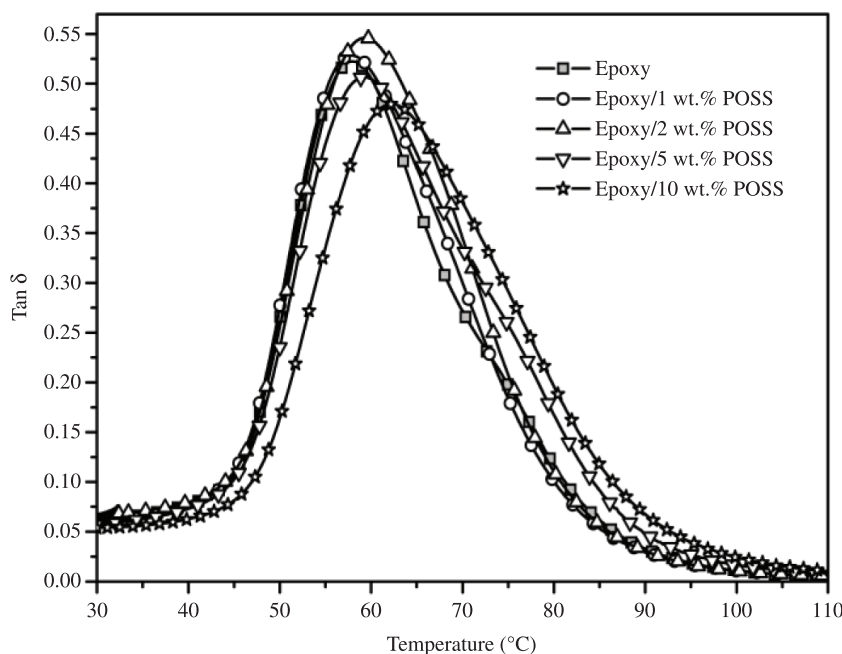
Figure 5. Tan δ curves (loss factor) for the nanocomposites.

Table 1. Parameters obtained by Tan δ curves in non-isothermal analysis.

Sample	T_g (°C)	Peak Height	Peak width at half-height
Epoxy	58.0	0.48	0.47
Epoxy 1 wt.% POSS	58.0	0.49	0.49
Epoxy 2 wt.% POSS	59.4	0.50	0.52
Epoxy 5 wt.% POSS	59.5	0.46	0.47
Epoxy 10 wt.% POSS	62.3	0.44	0.45

significant discrepancies among the results were obtained; however, the sample containing 10 wt% of POSS exhibits a reduction of the peak height and the half-height. This suggests more homogeneity of the 10 wt% of dispersed POSS (in accordance with the image of Figure 2) and the interaction between the nanocages and the epoxy matrix (in accordance with Figure 3). These results suggest that the POSS (even less reactive with amines than TETA reticulation agent) is able to increase the glass transition by the cooperative motion.

Thermal stability

Figure 6 shows the thermogravimetric analysis results for the epoxy/POSS nanocomposites as a function of the POSS content. The pure epoxy resin exhibited two stages of weight loss. The first stage (150-320 °C) is related to the presence of low molecular weight fractions that do not participate in the curing process[26], as seen in the *Gc* analysis.

The second stage of weight loss (320-550 °C), according to Levchik et al.[30] is related to the presence of allylic ethers formed by the amine or ester bonds from the dehydration of the secondary alcohol present in the structure of the epoxy. Because the degradation phenomena occur in a heterogeneous manner and simultaneously form, the chain scission gives rise to

several products, such as combustible gases, allylic alcohol, acetone and various hydrocarbons[31,32].

The incorporation of POSS monomer has not caused significant changes related to the first stage of weight loss. However, for samples containing 5 and 10 wt% of POSS showed a shift degradation curve in the range of 400-600 °C for higher temperatures. This shift is associated with the inorganic POSS inclusion that hinders the degradation of the epoxy resin at elevated temperatures.

Wang et al.[10] studied the thermal degradation of epoxy/POSS nanocomposites and indicated that over 50% of the degradation occurs in the silica layers and that the degradation of the material can be prevented. Liu et al.[6] suggest that the interconnections of the POSS monomer with the epoxy matrix promote the formation of a structure that is more dimensionally stable, leading to an increase in the thermal stability. Other factors that improve the thermal stability are:

- Good dispersion on the nanometer scale[8,10], which, as shown in Figure 2, occurs primarily for the sample containing 10 wt.% of POSS;
- The interconnection formed between the polyhedral cages with the structure of the epoxy resin[9] and an increase in the crosslinking density of the cured epoxy resin[11,12] associated with the gel content, as observed in Figure 3; and
- The hybrid characteristics of POSS[10].

Kinetic parameters (Avrami Method)

The Avrami method was previously created to evaluate the growth and formation of crystals[16-18]. However, it is possible to use this method for nanocomposites by making an analogy with the Avrami exponent of the heat transfer along the sample in the degradation process[13,23]. Figure 7 shows the curves determined from the Avrami equation. To achieve the most appropriate linear fit (analogous to crystallization), the analysis of the kinetic parameters being more representative at the beginning of the second stage of weight loss (320-550 °C) was taken into account. The prediction of these phenomena tends to be more important for the breaking of a three-dimensional network because it becomes more heterogeneous as the degradation progresses. In other words, the degradation becomes more apparent by combining the values of physical and chemical phenomena that occur simultaneously at higher temperatures.
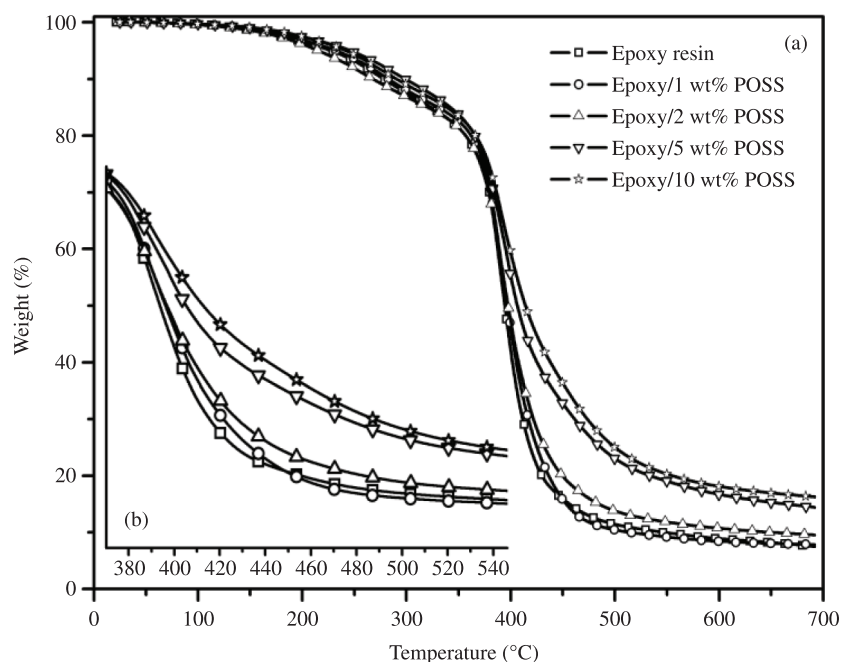

Figure 6. (a) Thermogravimetric curves and (b) amplification of the curves in the range of 370-540 °C.
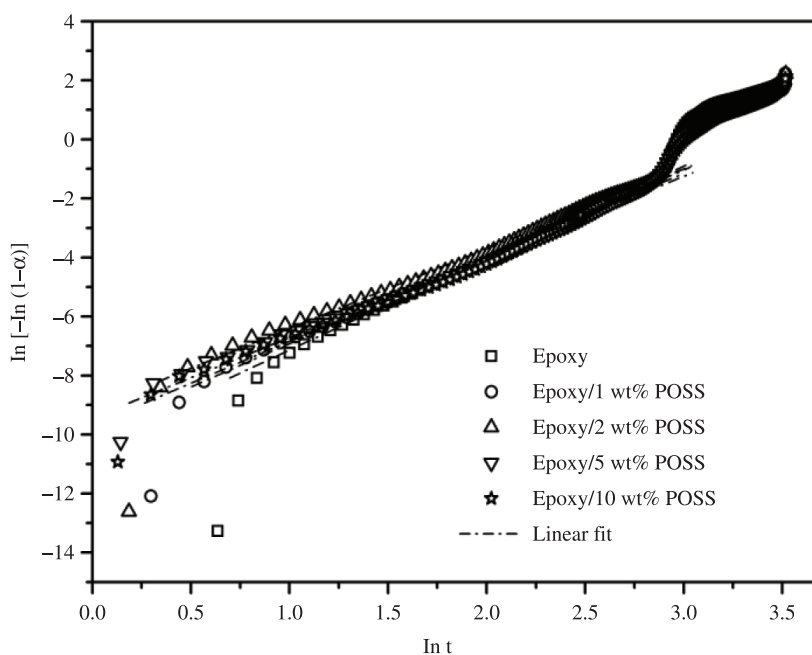

Figure 7. Linear fit plotted for the logarithmic form of the Avrami`s equation.

Table 2. Kinetic parameters of degradation obtained by the Avrami equation.

Sample	K' (min^{-1})	n	$t_{1/2}$ (min)
Epoxy	0.0067	2.70	5.58
Epoxy 1 wt.% POSS	0.0048	2.73	6.20
Epoxy 2 wt.% POSS	0.0037	2.84	6.28
Epoxy 5 wt.% POSS	0.0031	2.94	6.28
Epoxy 10 wt.% POSS	0.0021	3.12	6.42

The correlation coefficients (r) of the linear fits for all samples in a confidence interval of 95% were between 0.9988-1.0000. The results obtained are listed in Table 2. The incorporation of POSS monomer reduced the Avrami constant (k') and consequently increased the half-life ($t_{1/2}$) of the degradation reaction. The reduction of the k' means that the velocity of the degradation process tends to decrease due to the fact that POSS difficult to break chemical bonds. This observation can be directly observed by the displacement of degradation curves in Figure 6. This suggests that the presence of POSS may be hindering the degradation of the epoxy resin, thereby increasing the thermal stability.

In addition, an increase of the POSS content resulted in an increase in the Avrami exponent (n). For n values between 2 and 3, the degradation process propagates in two and three dimensions, respectively. The increase in the Avrami exponent demonstrated that the incorporation of POSS facilitated heat diffusion in three dimensions. The inclusion of POSS can increase the space between the polymeric chains, leading to a low thermal conductivity[9]. The decrease in thermal conductivity can be associated with the Avrami exponent, and thus, the three-dimensional diffusion suggests that there is greater free volume between the chains, which facilitates the dispersion of heat and increases the E_a of degradation. These results are corroborated by observation of the increase in the average distance between chains that facilitates the diffusive process on the degradation[33].

The change of T_g is not associated with the increased free volume, *i.e.*, T_g depends mainly on the type of the reactive groups present in POSS. In the case of a decrease in T_g, a POSS with epoxy reactive groups was used[15], whereas, as indicated in Figure 5 and Table 1, an increase in T_g is related to the influence of the amine reactive groups present in the nanocages. Therefore, the increase in T_g occurs because the reinforcement effect of POSS containing amine groups[34]. The increased thermal stability is observed for the different POSS monomers used[8-11,13] and is due to the hybrid characteristic and the ability to change the degradation mechanism by changing the volume of the cage.

Conclusions

The dispersions of POSS are effective above 5 wt % of POSS and exhibit an increase in the gel fraction with increasing POSS incorporation, indicating that the incorporation maintains the crosslink regions of the epoxy resin.

The addition of POSS shifted the T_g of the epoxy resin to higher temperatures because the POSS act as reinforcements and the higher concentration of amine groups probably can promotes the increase in the crosslink density.

The addition of POSS promotes the increase in the thermal stability because the hybrid characteristics of the nanocages and the formation of inert silica layers at high temperatures. The increase of the half-life ($t_{1/2}$) and the decrease of the Avrami constant (k') occurs because the POSS restricts the breaking of chemical bonds in the nanocomposites. The Avrami exponent (n) changed from 2 to 3 with the addition of POSS. For $n = 3$, the degradation reaction occurs in three dimensions, indicating higher volume between the tridimensional network of the epoxy resin.

The increase of T_g and the change in n values suggest that the molecular mobility is more dependent on the dispersion and the reactive groups present in the POSS nanocages than on the free volume between the chains; however, the large volume is the cause of the increased thermal stability.

References

1. Schwab, J. J. & Lichtenhan, J. D. – Appl. Organomet. Chem., **12**, p.707 (1998). http://dx.doi.org/10.1002/(SICI)1099-0739(199810/11)12:10/11<707::AID-AOC776>3.0.CO;2-1

2. Scott, D. W. – J. Am. Chem. Soc., **68**, p.1877 (1946). http://dx.doi.org/10.1021/ja01214a002

3. Strachota, A.; Whelan, P.; Kriz, J.; Brus, J.; Urbanová, M.; Slouf, M. & Matejka, L. – Polymer, **48**, p.3041 (2007). http://dx.doi.org/10.1016/j.polymer.2007.03.052

4. Liu, L.; Tian, M.; Zhang, W.; Zhang, L. & Mark, J. E. – Polymer, **48**, p.3201(2007). http://dx.doi.org/10.1016/j.polymer.2007.03.067

5. Bizet, S.; Galy, J. & Gerard, J-F. – Polymer, **47**, p.8219 (2006). http://dx.doi.org/10.1016/j.polymer.2006.09.040

6. Liu, Y.; Zheng, S. & Nie, K. – Polymer, **46**, p.12016 (2005). http://dx.doi.org/10.1016/j.polymer.2005.09.056

7. Fu, B. X.; Namani, M. & Lee, A. – Polymer, **44**, p.7739 (2003). http://dx.doi.org/10.1016/j.polymer.2003.09.033

8. Ni, Y.; Zhenga, S. & Nie, K. – Polymer, **45**, p.5557 (2004). http://dx.doi.org/10.1016/j.polymer.2004.06.008

9. Liu, H.; Zheng, S. & Nie, K. – Macromolecules, **38**, p.5088 (2005). http://dx.doi.org/10.1021/ma0504318

10. Wang, X.; Hu, Y.; Song, L.; Xing, W. & Lu, H. – J. Polym. Sci. Part B, Polym. Phys., **48**, p.693 (2010). http://dx.doi.org/10.1002/polb.21939

11. Huang, J-M.; Huang, H-J.; Wang, Y-X.; Chen, W-Y. & Chang, F-C. – J. Polym. Sci. Part B, Polym. Phys., **47**, p.1927 (2009). http://dx.doi.org/10.1002/polb.21788

12. Ni, Y. & Zheng, S. – Macromol. Chem. Physic., **206**, p.2075 (2005). http://dx.doi.org/10.1002/macp.200500267

13. Pistor, V.; Ornaghi, F. G.; Ornaghi, H. L. & Zattera, A.J. – Polym. Compos., **33**, p.1224 (2012). http://dx.doi.org/10.1002/pc.22181

14. Ornaghi, H. L.; Pistor, V. & Zattera, A.J. – Journal of Non-Crystalline Solids, **358**, p.427 (2012). http://dx.doi.org/10.1016/j.jnoncrysol.2011.10.014

15. Pistor, V.; Ornaghi, F. G.; Ornaghi, H. L. & Zattera, A.J. – Mater. Sci. Eng.: A, **532**, p.339 (2012). http://dx.doi.org/10.1016/j.msea.2011.10.100

16. Avrami, M. – J. Chem. Phys., **7**, p.1103 (1939).

17. Avrami, M. – J. Chem. Phys., **8**, p.212 (1940).

18. Avrami, M. – J. Chem. Phys., **9**, p.177 (1941).

19. Evans, U R. – Trans. Faraday Soc., **41**, p.365 (1945). http://dx.doi.org/10.1039/tf9454100365

20. Meares, P. – "Polymers: Structure and Bulk Properties", Van Nostrand, New York, chap. 5 (1965).

21. Hay J. N. – Br. Polym. J., **3**, p.74 (1971). http://dx.doi.org/10.1002/pi.4980030205

22. Jeziorny, A. – Polymer, **19**, p.1142 (1978). http://dx.doi.org/10.1016/0032-3861(78)90060-5

23. Poletto, M.; Pistor, V.; Zeni, M. & Zattera, A. J. – Polym. Degrad. Stabil., **96**, p.679 (2011). http://dx.doi.org/10.1016/j.polymdegradstab.2010.12.007

24. Waddon, A. J. & Coughlin, E. B. – Chem. Mater., **15**, p.4555 (2003). http://dx.doi.org/10.1021/cm034308b

25. Zeng, K. & Zheng, S. – J. Phys. Chem. B, **111**, p.13919 (2007). PMid:18031030. http://dx.doi.org/10.1021/jp075891c

26. Loos, M. R.; Coelho, L. A. F.; Pezzin, S. H. & Amico, S. C. – Polímeros, **18**, p.76 (2008).

27. Ferry, J. D. – "Viscoelastic Properties of Polymers", New York, John Wiley & Sons (1980).

28. Pascault, H.S.; Verdu, J. & Williams, R. J. J. – "Thermosetting Polymers", Marcel Dekker, New York (2002). http://dx.doi.org/10.1201/9780203908402

29. Alves, N. M.; Gómez Ribelles, J. L.; J Gómez Tejedor, A. & Mano, J. F. – Macromolecules, **37**, p.3735 (2004). http://dx.doi.org/10.1021/ma035626z

30. Levchik, S. V. & Weil, E. D. – Polym. Int., **53**, p.1901 (2004). http://dx.doi.org/10.1002/pi.1473

31. Levchik, S. V.; Camino, G.; Luda, M. P. Costa, L.; Costes, B.; Henry, Y.; Morel, E. & Muller, G. – Polym. Adv. Technol., **6**, p.53 (1995). http://dx.doi.org/10.1002/pat.1995.220060201

32. Levchik, S. V.; Camino, G.; Luda, M.P.; Costa, L.; Costes, B.; Henry, Y. & Muller, G. M. E. – Polym. Degrad. Stabil., **48**, p.359 (1995). http://dx.doi.org/10.1016/0141-3910(95)00084-Y

33. Pistor, V.; Soares, B. G. & Mauler, R. S. – Polym. Compos., **33**, p.1438 (2012).

34. Pistor, V.; Barbosa, L. G.; Soares, B. G. & Mauler, R. S. – Polymer, **53**, p.5798 (2012). http://dx.doi.org/10.1016/j.polymer.2012.10.018