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Phenolic matrix nanocomposites based on commercial grade resols: synthesis and characterization

Maurizio Natali, Josè Kenny, Luigi Torre

*University of Perugia, Department of Civil and Environmental Engineering, Loc. Pentima Bassa
21, 05100 Terni - Italy*

Abstract

Polymer layered silicate nanocomposites based on a commercial grade resol were produced using a simple, low labor cost, mechanical approach which allowed to avoid the process of intercalative polymerization of phenol and formaldehyde. Commercial compatibilized montmorillonite was selected as the main nanoreinforcement, while the matrix was a resol diluted in methanol. The aim of this work was to optimize the production technique of the above mentioned nanocomposites. Therefore intercalation of the resin was promoted by high speed mixing, and the processing parameters were varied in order to find the optimum dispersion. The produced nanocomposites were characterized and compared by means of X-ray diffraction, SEM and thermogravimetric analysis. The results of the characterization tests indicated that it was possible to obtain a good degree of dispersion as well as a uniform distribution of the nanoclay platelets. However, TGA measurements showed that the introduction of well dispersed nanoclays did not result in a consistent improvement of thermal stability respect that of the neat resol.

Key words:

1. Introduction

Polymeric ablative composites are key materials in the aerospace sector. Their main function is to protect aerodynamic surfaces and propulsion structures from extreme environments. The walls of a rocket combustion chamber, for example, can experience temperatures as high as 3,000°C and must withstand pressures up to 100 atm. Moreover, ablative materials are also used to protect the space vehicles during the re-entry flight. This protective function is accomplished by a self-

regulating heat and mass transfer process typically known as ablation[1]. Polymeric ablative composites are composed by a continuous phase, the matrix and, a discontinuous phase, which is constituted by the reinforcements and functional fillers, both phases can actively participate to the ablation process. Most polymeric ablators are based on thermosetting resins and, in this group of polymers, phenolic resins are undoubtedly the most employed and important matrices.[2] In fact, beside their exceptional thermal stability, they possess excellent features such as, high dimensional stability and thermal insulation. These properties can be directly related to their high crosslink density and their chemical structure.[3] Furthermore, the high crosslinking density of phenolic matrices improves the mechanical performance of the char, leading a better protection of the inner layers of the ablator.[4]

During last forty years, in order to improve the quality of composites, fillers such as mineral powders or fibers, have been combined to polymers. However, in last twenty years, researchers focused their attention on nanocomposites, i.e. on the use of nanofillers such as nanoclays, nanosilica or, nanofibers. In this class of composites, Polymer Layered Silicate Nanocomposites (PLSN) based on montmorillonite (MMT) have attracted great attention because the introduction of these kind of nanofillers can lead to improved mechanical and barrier properties, [5]-[7] as well as of the thermal features, [8]-[9], without a relevant increase of the specific weight of the neat polymer.

Although phenolic resins are widely used as ablative matrices, few attempts to use these resins as a matrix for layered silicate nanocomposites are present in literature. This fact can be related to difficulty to obtain the exfoliation or even the intercalation of the nanoclay because of the rigid three-dimensional structure of the phenolic resin molecules, particularly, with resols. [10]

To solve this problem, Usuki et al. [11] attempted to synthesize phenolic resin/layered silicate nanocomposites by an intercalative polymerization approach, employing phenol and formaldehyde and a modified montmorillonite. Lee et al., [10] as well as, Choi et al. [12]-[13] synthesized phenolic resin/layered silicate nanocomposites by melt intercalation of a linear novolac. Currently, only fairly limited researches on resol type phenolic resin layered silicate nanocomposites - via in situ polymerization of monomers - have been published. [14]-[16] In fact, it was showed that it is more difficult to obtain exfoliated structures employing resol type phenolic resins than using novolac type phenolic resins. According to literature, this situation can be explained considering that, even before the cure, resols generally possess a more crosslinked structure than novolacs. [17]

However, up now, the mainstream approach to process phenolic resin layered

silicate nanocomposites, is based on the in situ polymerization of monomers i.e., phenol and formaldehyde molecules need to be absorbed into the interlayer spaces of the nanoclay and then, polymerized in situ.[18]-[19] In other words, with this technique - based on a high labor cost chemical approach - it is necessary to employ both phenol and formaldehyde as starting materials.

In this research, PLSN were obtained using a commercial grade resol diluted in methyl alcohol. The employed processing technique was based on a simple mechanical approach (i.e., using a mixing tool) procedure used quite successfully in the preparation of nanocomposites based on other matrices, such as polyester resins. Literature surveys have shown that this is not an usual way to process resol type phenolic matrix nanocomposites. In fact, according to Kaynak and Tasan [20] it seems that up to now, only in their work, the mixing of the clay with the liquid resin was employed as a method to produce PLSN. To our knowledge, no others studies seem to involve the production of resol based nanocomposites. In our research, three processing techniques were evaluated and, in one case, even the effects of an ultrasonic source were considered. The nanocomposites obtained using these three mixing methods were examined by XRD, TGA and SEM analysis.

2. Experimental Section

2.1. Materials

The matrix chosen for the production of nanocomposite specimens was a single stage phenolic resin - a resol - diluted in methyl alcohol (kindly provided by SHA). The nanoclay was Cloisite® 30B, an organic treated MMT with methyl tallow bis-2-hydroxyethyl quaternary ammonium (Southern Clay Products).

2.2. Determination of the curing cycle of the neat resol

Even if phenolic resins are the oldest thermosetting polymers, their processing is rather difficult.[3] In fact, since during the crosslinking process of phenolic matrices the by-product of the polycondensation reaction is mostly water, voids and fractures can be formed during the processing. Moreover, also the solvent in which the resol is diluted may contribute to complicate this problem. Generally, because of their features, resols can be cured both applying a source of heat or also, employing a curing agent. In this work, in order to simplify the production of the nanocomposite samples, phenolic resin was processed by the application of heat. Since during the reaction there is no release of additional gas due to the curing agent, this approach allowed to minimize the creation of voids and

fractures. Another advantage of this curing approach is that, excluding the use of an hardener, very short gel times, which may inhibit the release of gas, are avoided.

The first experimental step of this research was to study the curing cycle of the pristine matrix. Preliminary process parameters were acquired performing a series of Differential Scanning Calorimetry (DSC) analyses on the resol. Measurements were performed on Mettler-Toledo 822e Model. However, in order to minimize the presence of voids and fractures in the cured matrix, the effects of the applied temperature and pressure profiles during the curing cycle, were studied.

First, the resol was polymerized at atmospheric pressure. The following temperature profile was used: 24h @ 60°C and then heating up to 180°C at an heating rate of 10°C/30 min. The obtained specimens are shown Fig.1(a) it is clearly visible that these samples are characterized by the presence of a few macro fractures. In order to obtain a lower degree of voids, it was decided to process the resol under vacuum. The same curing cycle was applied. As a result, the obtained samples were characterized by a great amount of micro bubbles and cracks, which, as is possible to observe in Fig.1(b), were uniformly distributed throughout the bulk of the sample. According to the obtained results, the use of vacuum during the curing cycle, simply introduced another kind of problem. After many different trials, we came to the conclusion that the use of vacuum was not necessary, but conversely, the key approach to obtain a fractures and voids free sample was more related to the temperature profile. Particularly, it was observed that, in order to obtain a good cured material, the most important thing to do was simply to enlarge the first step of the curing cycle - i.e, to delay the gelling of the resin - keeping the resol at a temperature of 60°C for a longer time. In such a way, the production and the trapping of gas was minimized. The main drawback of such curing cycle was that, in order to obtain a sample with no void, very large processing time was necessary. The complete cure of the material required, in fact at least 5 days. Such processing time is not usual for standard series production, but, for the purpose of the study, and in general, for the production of extreme temperature resistant materials, it can be surely considered more than acceptable.

A photograph of a neat resol specimen cured with the optimized cycle, is showed in Fig.2. From this pictures it is possible to observe that the samples produced with the optimized curing cycle were fractures and voids free. In order to better evaluate the effectiveness of such cure cycle, Scanning Electron Microscopy (SEM) was used, a Zeiss Supra 25 SEM was employed, and SEM pictures of a fracture surface of the obtained sample are shown in Fig.3 and Fig.4. It is possible to observe that the SEM analyses on the fracture surface related to the well cured

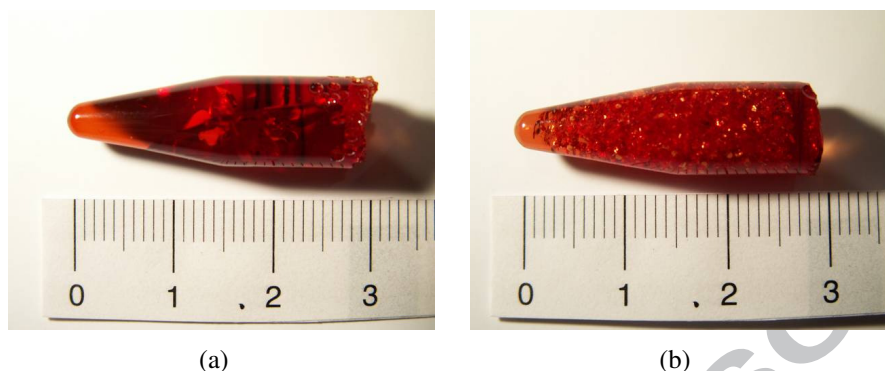


Figure 1: Cured specimens of the neat resol prepared employing a unfavorable processing technique. Fig.1(a) refers to a typical sample obtained with a temperature profile leading to a too short gel time. Fig.1(b) shows a representative neat resol specimen prepared applying both an unfavorable curing cycle and pressure.

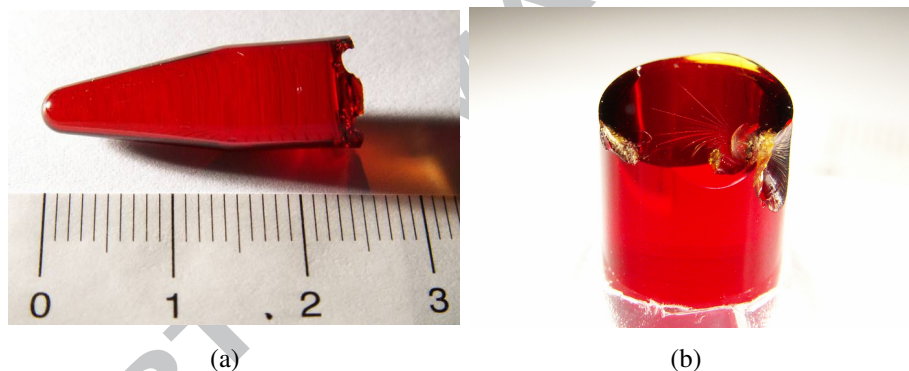


Figure 2: Fig.2(a) typical neat resol specimen prepared employing a favorable curing cycle. No voids or fractures were visible in the samples. Fig.2(b) fracture surface of a well cured pristine resol sample.

neat resol specimen, confirmed that no bubbles or in general defects were generated during the cure. This is a remarkable result especially considering that SEM was not able to detect any voids.

In order to evaluate the degree of cure obtained by the employed curing cycle, DSC tests were performed on the neat resol. In particular, dynamic scans from -30°C up to 350°C at an heating rate of $10^{\circ}\text{C}/\text{min}$. were performed. In order to obtain a readable signal it has been necessary to utilized pressurized pans. Two

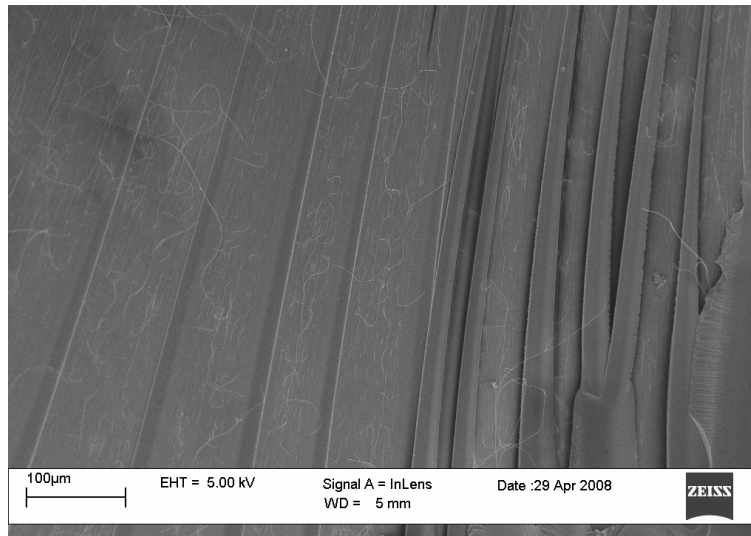


Figure 3: SEM scan of a fracture surface related to a well cured neat resin specimen. No fractures or voids could be detected.

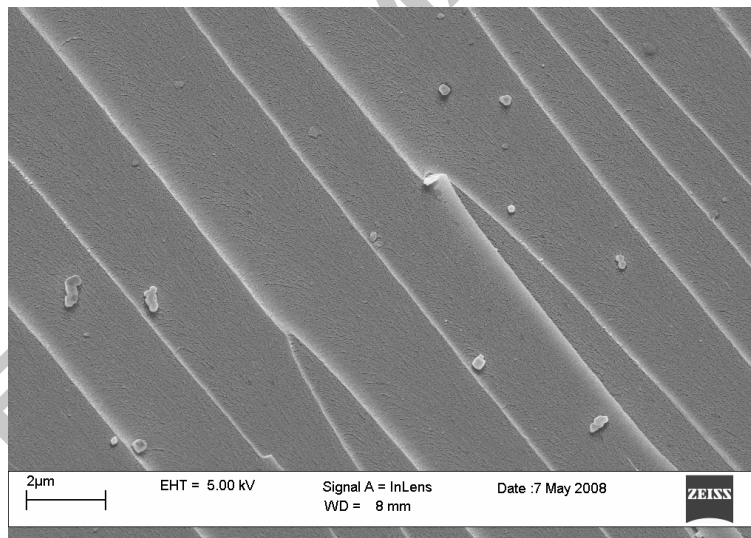


Figure 4: SEM detail of a fracture surface referred to a neat resin sample prepared using a good curing cycle. Even, at higher magnification no defects could be found.

dynamical scan on the liquid and on the cured neat resin, are shown in (Fig.5). From a numerical point of view, the obtained degree of cure related to the specimens treated with the selected temperature profile was 94.3%.

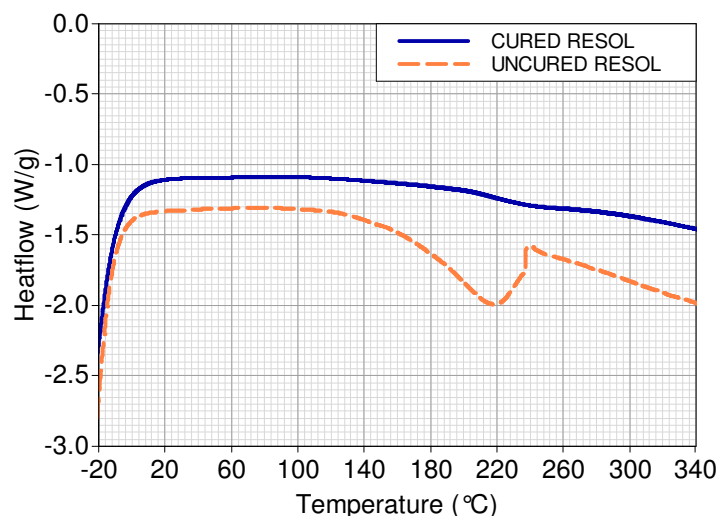


Figure 5: Results of DSC analysis referred to neat resol.

2.3. Preparation of the nanocomposites

In order to produce the nanocomposites, three processing techniques were considered. In the first one a mixture of resol plus the nanoclay was processed using a mechanical mixer set up at a speed of 2,000 rpm. We will refer to this blend as sample 1. In the second process the blend was prepared using the same mixer, at the same speed, but in combination with an ultrasonic source provided by an ultrasonic bath (sample 2). For these two samples, the same mixing impeller (Heidolph RZR 2041) was used. The third blend was processed employing a higher speed mixer i.e., 30,000 rpm (sample 3) which was equipped with a smaller diameter stirring impeller. More in details the ratio between the diameters of the tools used in the first two blends over the one used in the third blend was about 1:3.

In all the cases, the blends were prepared according to the following procedure: first the resol was weighted and then, the selected amount of nanofiller was added. Before its use, the nanoclay was spread on an aluminum plate and then, dried for 48 hours at 60°C. The nanoclay percentage was always 5% in weight (resol:nanofiller, 95:5) and, the mixing time was 3 hours. All stirring operations were performed at room temperature. In order to remove the air introduced in the blends during the mixing process, all mixtures were degassed for 40 min at a pressure of 0.1 atm. Then, the produced blends were polymerized employing the same curing cycle used for the neat resol.

3. Results and discussion

According to the optical analysis, all the produced specimens showed no presence of voids or fractures. Furthermore, no phase separation between the matrix and the nanoclay could be observed. Pictures related to the three produced blends are showed in figure (sample 1, Fig.6(a) and Fig.6(b)), figure (sample2, Fig.7(a) and Fig.7(b)) and figure (sample 3, Fig.8(a) and Fig.8(b)). It should be underlined that, the cure cycle adopted, was characterized by a very long residence time under the gel point, such situation, promoting the phase separation between the nanofiller and the matrix, can seriously compromise the homogeneity of the nanocomposites.[20] Therefore having obtained homogeneous and good quality samples can be considered as a very remarkable result.

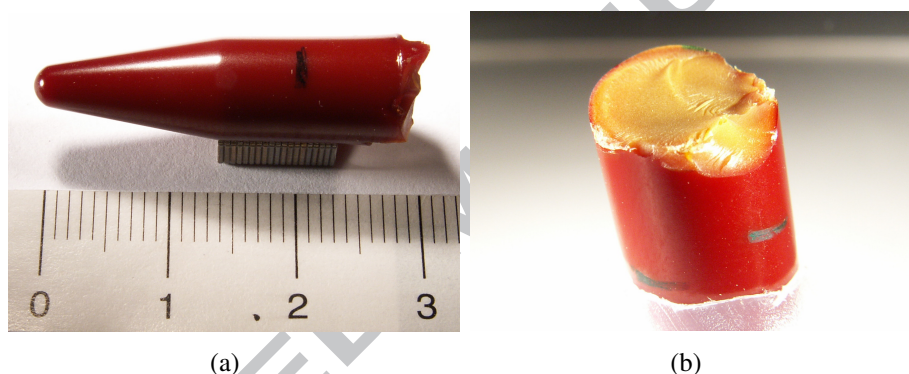


Figure 6: Characteristic appearance of a specimen prepared with the blend produced with first technique which employs a 2,000 rpm mixer. Fig.6(b) fracture surface of the sample. No phase separation between matrix and the filler could be observed.

3.1. SEM characterization

In order to confirm the above statements, the morphology and the dispersion of the clay sheets in the he produced nanocomposites were studied by means of Scanning Electron Microscopy. For each sample studied, two kind of SEM images were produced. The first one, taken at a resolution of $20\mu\text{m}$, was used to observe the overall dispersion of the clay in the matrix. Then, in order to evaluate the degree of disassembly of the stacked layers, other SEM images were acquired at a deepest magnification i.e., $2\mu\text{m}$. The SEM pictures obtained for the nanocomposites produced with the three different techniques, are shown in figures 9 through 14. It is possible to observe from the pictures taken at lower magnification, that

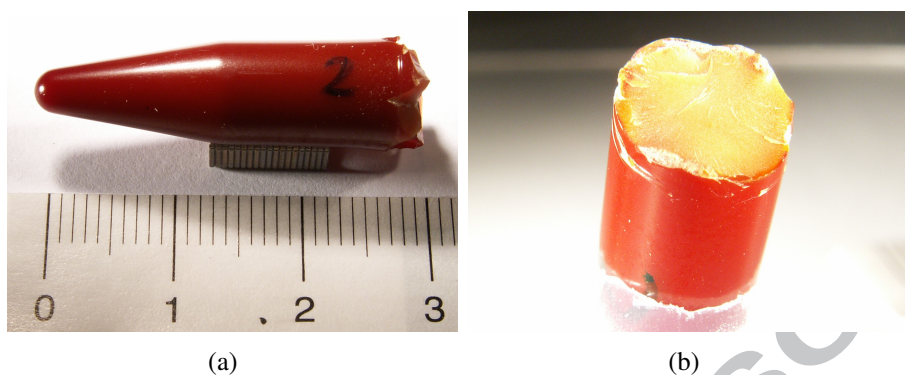


Figure 7: Typical specimen prepared with the blend produced using a 2,000 rpm mixer combined with an ultrasonic source. Fig.7(b) fracture surface of the sample. No phase separation between matrix and the filler could be observed.

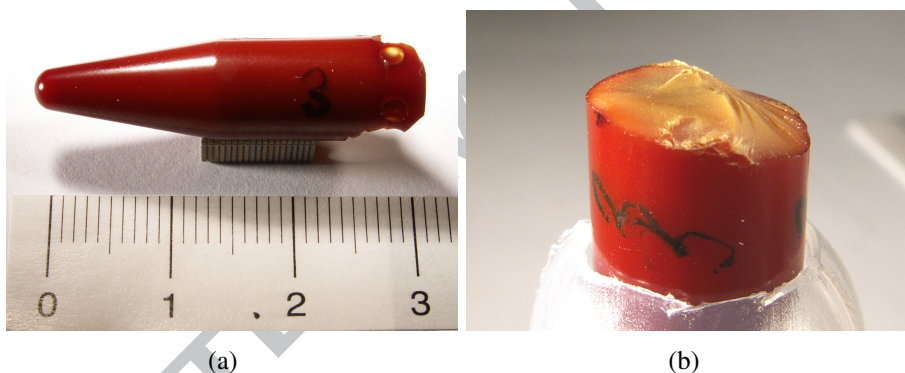


Figure 8: Typical appearance of a nanocomposite specimen produced with the third technique, using a 30,000 rpm mixer. Fig.8(b) fracture surface of the sample. Even in this case, no phase separation between matrix and the nanoclay could be detected.

the homogeneity of the dispersion was of good quality (blend 1, Fig.9, blend 2, Fig.10 and blend 3, Fig.11). Higher resolution pictures (sample 1, Fig.12, sample 2, Fig.13 and sample 3, Fig.14) confirmed that the platelets have lost their original ordered stacked structure to assume a disordered intercalated structure.

All the produced nanocomposites did not show any presence of voids as in the case of the neat resol, confirming that, the curing cycle used to polymerize neat matrix yielded good quality samples also in the case of the nanocomposites.

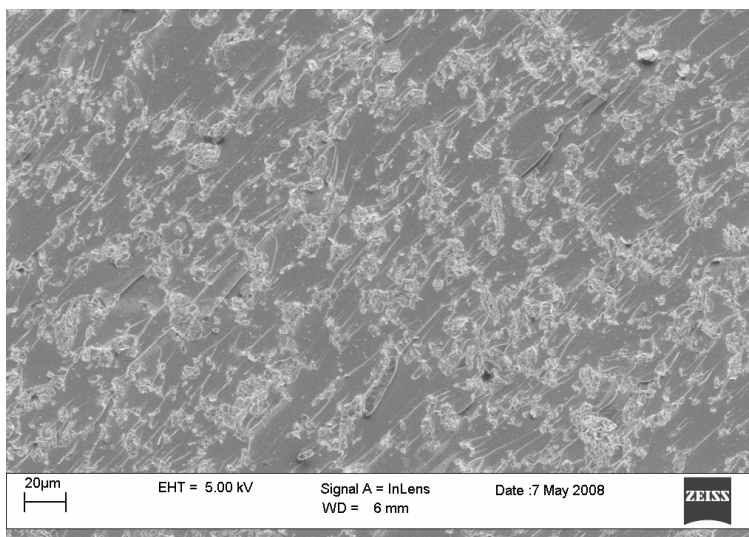


Figure 9: SEM picture of nanocomposite 1. Nanoclay platelets are homogeneously distributed. No clay agglomerations could be detected.

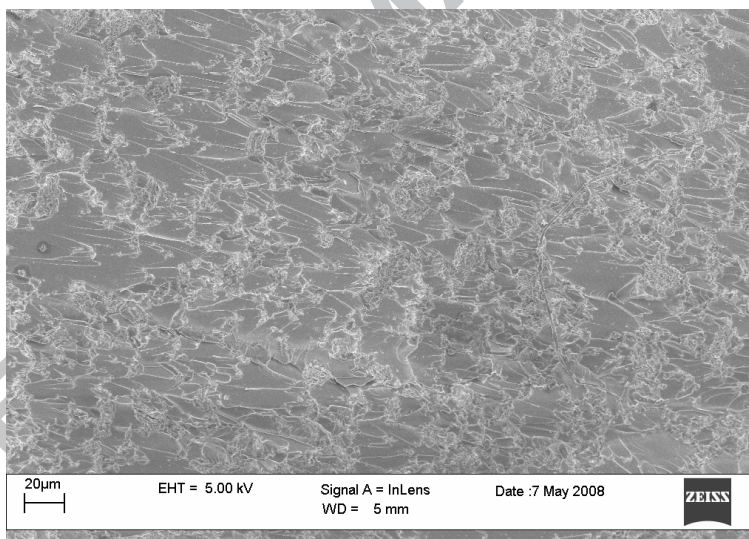


Figure 10: SEM picture of nanocomposite prepared with second technique. Nanoclay sheets are both finely dispersed as well as distributed in the matrix. No clay agglomerations could be detected.

3.2. XRD characterization

Figure 15 shows the X-ray diffraction patterns of the produced blends. In order to evaluate the degree of disaggregation of nanoclay tactoids, the XRD profile

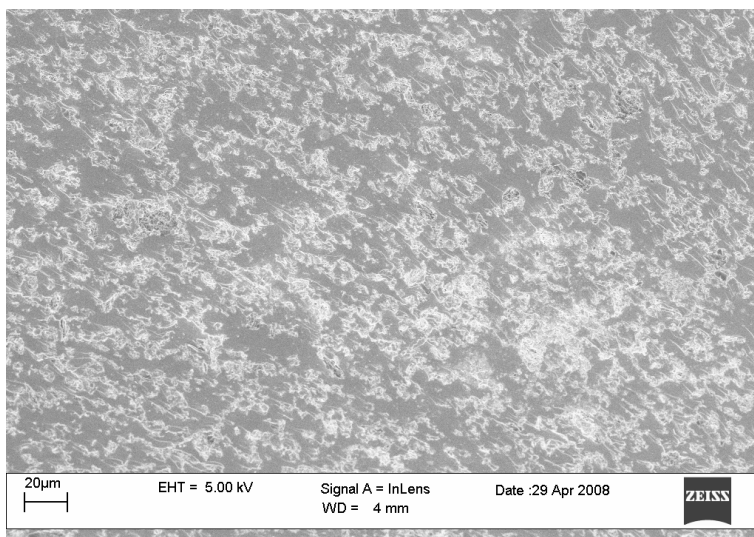


Figure 11: SEM picture of nanocomposite prepared with the higher speed mixer. Even in this situation, nanoclay platelets are uniformly dispersed.

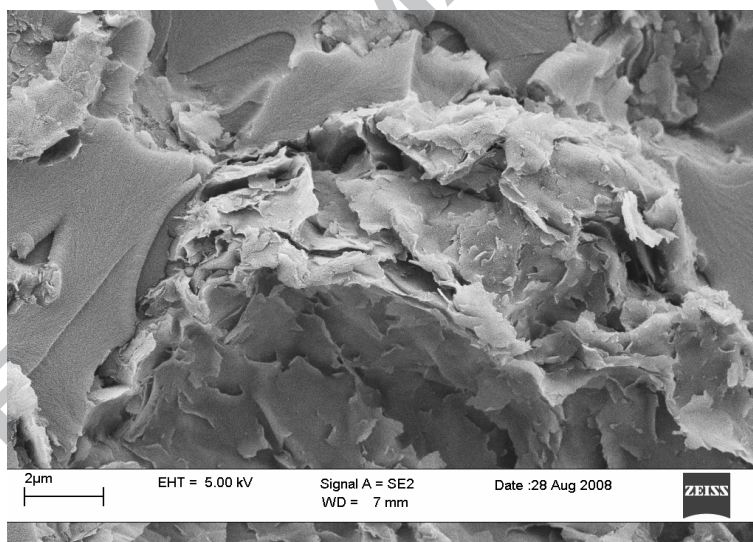


Figure 12: Detail of some nanoclay platelets dispersed in the first blend. The scale is the same of Figure 4.

of neat nanoclay was used as reference. According to experimental results, the basal spacing of the Cloisite® 30B is about 1.79 nm. Concerning the evaluated blends, in all of them, the interlamellar spacing between the nanoclay sheets was

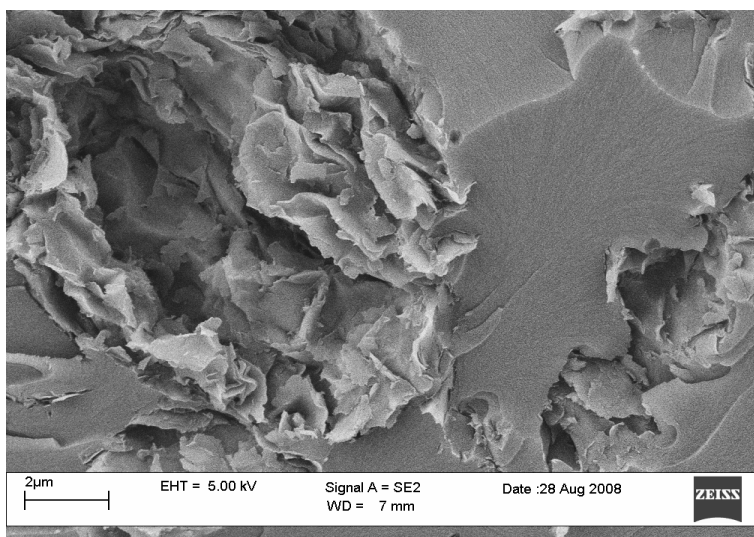


Figure 13: Detail of some nanoclay platelets of the second sample.

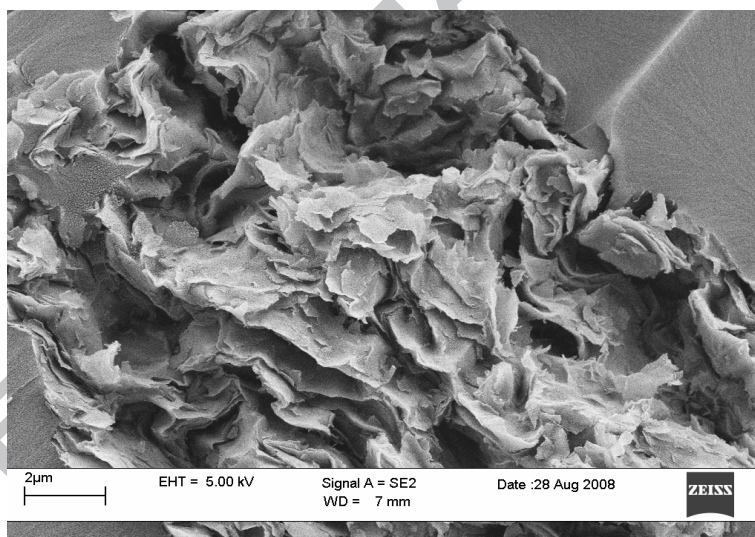


Figure 14: Detail of some nanoclay platelets of the third blend.

increased when the nanofiller was introduced and mixed into the phenolic matrix. Although an increase of the interlayer distance, or the absence of a peak in the X-Ray diffraction pattern, can be considered a necessary, but not sufficient condition for the exfoliation of nanoclay [21], the increase of the d-spacing observed

in the figure coupled with the indication of the SEM give an encouraging insight that the resin molecules have penetrated into the layers of the nanoclay i.e., that a certain degree of intercalation or even exfoliation was obtained. Regarding the employed processing techniques, XRD measurements confirmed the effectiveness of all three mixing methods. The contribution of low power ultrasounds bath (second technique i.e., sample 2) did not result very relevant. Finally, XRD plot related to nanocomposite obtained with the highest speed mixing (sample 3) showed no remarkable differences with the other two. Concluding, according to XRD analysis, it resulted that the simplest technique - using the 2,000 rpm mixer - could be considered the most appropriate. In fact, this approach showed the minimum ratio between complexity of the processing technique and obtained results.

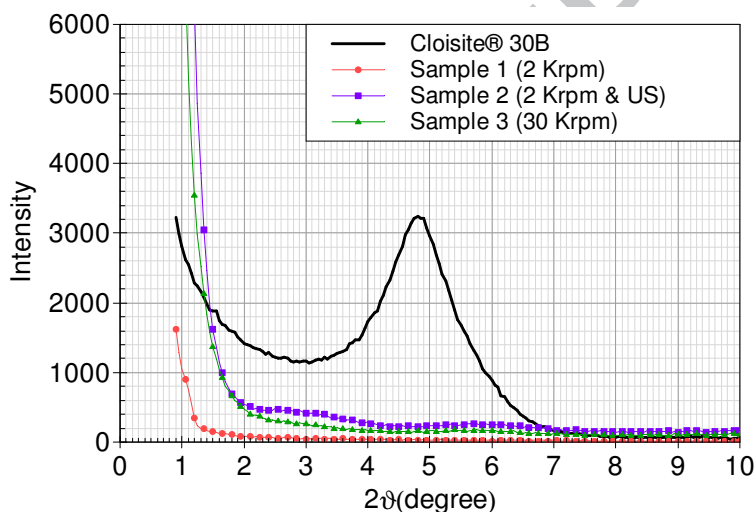


Figure 15: X-Ray patterns of the produced nanocomposites.

3.3. Thermogravimetric analysis

In order to evaluate the thermal behavior of the produced materials as a function of temperature, a series of thermogravimetric analyses was performed. In order to get a good repeatability, nanocomposite specimens were milled up to get a narrow particle diameter distribution of about 200μm. Then, samples of about (10±2)mg were characterized. The measurements were performed in a not oxidative atmosphere (i.e., in nitrogen), applying a linearly growing temperature ramp, at an heating rate of 20°C/min. Measurements were performed on Seiko Exstar

6000 TGA. Fig.16 shows the TGA patterns obtained for the studied materials. Fig.17 shows the corresponding DTA traces.

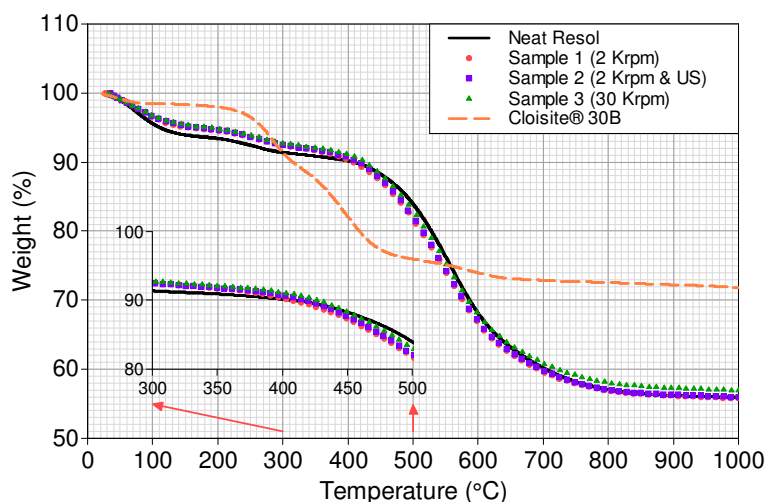


Figure 16: TGA traces of the produced nanocomposites.

According to the obtained results, all produced nanocomposites showed a very similar behavior until about 350°C. In this range of temperatures, the degradation rate of all nanocomposites was generally lower than the neat resol. Over this temperature, sample 1 and sample 2 started to exhibit a worse performance than the neat resol i.e., a greater degradation velocity. Furthermore, after this temperature, sample 3 showed a degradation rate very close to neat resol. However, once a temperature of about 425°C, was reached, the third nanocomposite began to loose its mass at a velocity lower than each other material. At a temperature of about 475°C, even sample 1 and sample 2, began to show a lower degradation rate than the pristine resol. Then, starting from this temperature up to 1,000°C, all nanocomposites always shown a lower degradation velocity than the neat matrix.

A similar degradation behavior, was found by other researchers, such as by Choi et al., [22]. At date, the decrease in thermal stability of neat resol loaded with silicate is not clear.

However, because of its thermal features, sample 3 can be considered the most performing material. In fact, the thermal stability of this nanocomposite was superior than the other studied systems and finally, even its residual mass at 1,000°C was slightly greater than any other material.

If we define the oxidation temperature T_o as the value at which the derivate of the weight W with respect to T is maximum i.e., referring to T_o as the temperature of the maximum rate of oxidation, it is possible to affirm that the effect of the nanoclays on the thermal stability of the system is appreciable only on the degradation rate and not on the temperature T_o .

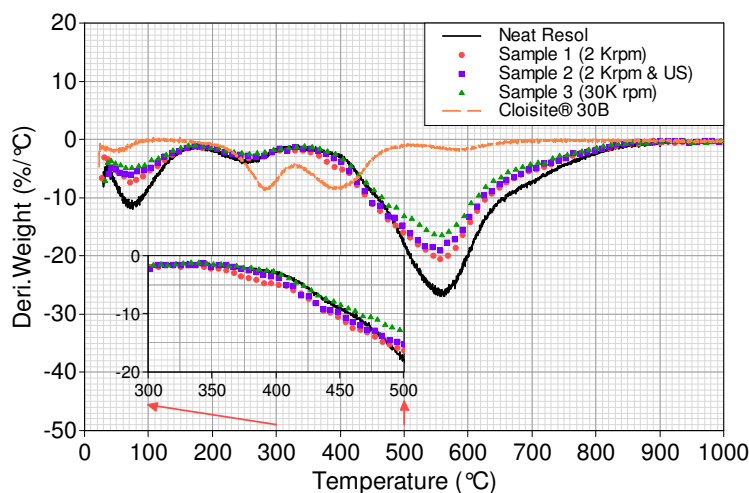


Figure 17: Degradation rate trends of the produced nanocomposites. Sample 3 shown the best resistance to thermal degradation.

4. Conclusions

In this research three different kind of nanocomposites based on a liquid, commercial grade resol were prepared. They were produced using a simple mechanical approach i.e., using a stirring tool. The main advantage of such process lays in the fact that it was not necessary to employ the intercalative polymerization of phenol and formaldehyde. Because of the nature of phenolic resins, the first step of the research was related to the optimization of a suitable curing cycle, which could avoid the production of fractures and voids in the specimens. An effective temperature profile for the cure of the neat matrix was found and, the same method, was successfully employed for the nanocomposites. All the produced neat resols and nanocomposite samples showed no voids, even at a micrometric scale. Furthermore, even if this curing method was based on the extension of the gel time, in no case, this condition led to phase separation between the

nanoclay and matrix. SEM results showed that all three mixing techniques were effective i.e., they were able to promote good dispersion as well as distribution of the clay platelets. The intercalation of the nanoclay sheets was confirmed by X-ray diffraction analyses. In comparison with pristine resol, TGA measurements showed a lower degradation rate of all nanocomposites until about 350°C and over about 475°C. However, only nanocomposite produced with the higher speed mixing showed a residual mass slightly greater than neat resol.

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