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Encapsulation of solvent into halloysite nanotubes to promote self-healing ability in polymers

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Microcracking during service is a critical problem, which can be particularly detrimental to the durability of polymers and polymer composite structures. Materials with self-healing ability are capable to partially or completely repair damages, thus increasing the life of the structural component. One of the self-healing approaches involves the use of solvents as healing agent, which reacts with the polymer healing microcracks. The objective of this research is to investigate a procedure to encapsulate solvents into halloysite nanotubes (HNT) to promote self-healing ability in epoxy. Autonomic healing would be triggered by crack propagation through the embedded nanotubes in the polymer, releasing the liquid solvent into the crack plane. Two solvents were considered in this work: dimethylsulfoxide (DMSO) and nitrobenzene. A procedure was developed to fill HNT with the solvents, which were then coated using the layer-by-layer technique of oppositely charged polyelectrolytes. Solvent encapsulation was verified by X-ray diffraction, Fourier transform infrared analysis, thermogravimetry, specific surface area (BET), and scanning electron microscopy. The results suggest that the procedure was successful to encapsulate DMSO into the nanotubes.

Keywords: self-healing materials; composite materials; nanotubes; halloysite

1. Introduction

Epoxy-based carbon fiber-reinforced composite materials are increasingly being used in aircraft primary and secondary structures. The long-term durability of these materials is greatly influenced by the properties of the polymer matrix and the fiber/matrix interface.[1–5] Matrix microcracking during service is a critical problem, which can be particularly detrimental to the durability, affecting fatigue life and damage tolerance.[6] The microcracks are often located deep within a structural component and therefore are difficult to detect. Yet, they may propagate and eventually lead to mechanical failure.

Materials with self-healing ability are capable of repairing damages, thus increasing the life of the structural component.[7] The self-healing process can be classified according to its nature as autonomic or non-autonomic. While non-autonomic self-healing materials require an external trigger- such as heat- to produce healing, autonomic healing does not require any stimulus in addition to the damage itself. For polymers

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that do not present an intrinsic ability for self-healing, an extrinsic healing process can be achieved with the addition of microcapsules,[8,9] vascular network,[10,11] or nanoreservoirs,[12] embedded on the material to deliver a healing agent. In the case of nanoreservoirs, the idea is to repair nanoscale damage at very early stages. There is also a potential to prevent reduction in mechanical properties normally caused by the microcapsules.

Crack healing in epoxies can be successfully achieved by monomer release after a mechanical damage is inflicted on the material.[13] The monomer polymerizes in the crack plane with the help of a catalyst. Crack healing can also be accomplished through the use of solvents. Solvents such as ethanol and methanol have been used to seal the cracks of thermoplastic polymers.[14] The ability of solvents to repair thermoset polymers (epoxy) has also been investigated.[15] Among the solvents considered to repair epoxy, the best results were obtained with nitrobenzene, N-methylpyrrolidinone, dimethylacetamide, dimethylformamide, and dimethylsulfoxide (DMSO). In this case, the mechanism of healing is still under investigation, but it has been suggested that the solvent may plasticize the epoxy matrix to allow molecular mobility that promotes further curing reactions.

Nanoparticles and nanotubes have been added to polymers for enhancing their physical and mechanical properties. Carbon nanotube networks formed in an epoxy polymer matrix can be utilized as sensors for detecting the onset, nature, and evolution of damage in advanced polymer-based composites.[6] Clays have been the most widely studied materials to be used as nanofillers for polymers [16–18] and montmorillonite (MMT) has been the most commonly used among them.[19,20] MMT has the same layered and crystalline structure as talc and mica but a different layer charge. Its crystal lattice consists of a central octahedral sheet of alumina or magnesium hydroxide between two tetrahedral silica sheets.

Halloysite nanotubes (HNTs) have become the subject of great research interest due to the potential to improve mechanical, thermal, and fire-retardant properties of polymers.[21–28] Halloysite is a naturally occurring two-layered aluminosilicate chemically similar to kaolin. The adjacent alumina and silica layers create a packing disorder, which causes them to curve and form a tubular structure. The size of halloysite tubes vary within 1–15 μm of length and 10–150 nm of inner diameter, depending on the deposit.[29] HNT are capable of entrapping a range of active agents within the inner lumen, as well as within the spaces of the multilayered shell. HNT have been described as promising nanostructures for large-scale production, due to their low cost and easy availability in natural deposits.[30] Therefore, halloysite is a good candidate to encapsulate solvents and promote self-healing ability to polymers.

The objective of this research is to investigate a procedure to encapsulate solvents into HNT to promote self-healing ability in epoxy.

2. Experimental

2.1. Materials

- Halloysite nanotubes (HNT) from Sigma-Aldrich. The material was used as provided by the supplier, with no further treatment.
- Solvents: Dimethylsulfoxide (DMSO) analytical grade and Nitrobenzene analytical grade from Impex.

- Polyelectrolytes: Sodium polyacrylate (type Polysal) from BASF and Cetyltrimethylammonium bromide (CTAB) from Alfa Aesar.
- NaCl from Vetec.

2.2. Procedure

2.2.1. Insertion of solvent into nanotubes

Initially HNT were dispersed in the selected solvent (10 mg/mL) during 40 min using a magnetic stirrer. After homogenization, the mixture was kept under vacuum (40 cmHg) during approximately 1 h to remove air and introduce the solvent into the HNTs. After removal of bubbles, the dispersion was centrifuged to remove excess solvent. The centrifugation process was repeated twice. After each centrifugation, 1% of the initial mass of halloysite was added to the centrifugation precipitate in order to compensate for the residues left in the beaker and centrifuge tubes. After the last centrifugation, the precipitate was taken out of the equipment and submitted to the encapsulation process.

2.2.2. Nanotubes encapsulation

Encapsulation process is performed to block the ends of the HNT in order to trap the solvent inside the structure. In this work, a procedure similar to that described in the literature [31,32] was performed. However, in these previous works, the combination of nanoreservoirs, solvents, and polyelectrolytes proposed in the present study has not been investigated. Figure 1 shows schematically the methodology used in this study.

In order to promote sealing of the nanotube ends, different types of polyelectrolytes with opposite charges were used to enhance interaction between the electrolytes themselves and mainly between the electrolyte layers and the HNT surface. Coating was applied both as a single layer, when only one of the polyelectrolytes was used, and as a double layer, in order to improve sealing of HNT ends.

In order to form the layer surrounding the nanotubes, 1 g of HNTs loaded with the selected solvent was dispersed in 100 mL of aqueous solution of sodium chloride (0.5 M). Then 4 g of the selected polyelectrolyte were added and mixed using a magnetic stirrer for 40 min to adhere on nanoparticles. In order to separate the nanocapsules from the solution, centrifugation was carried out. For bilayered samples, the procedure was repeated by replacing the polyelectrolyte used by the one with opposite charge. Nanotubes precipitated by centrifugation were dried in an oven at a temperature of 80 °C for 2 h in order to be characterized.

Experiments using reference samples of HNT which were not loaded with any solvent were performed so that a comparison of the influence of the solvent on the formation of polyelectrolyte layers could be drawn.

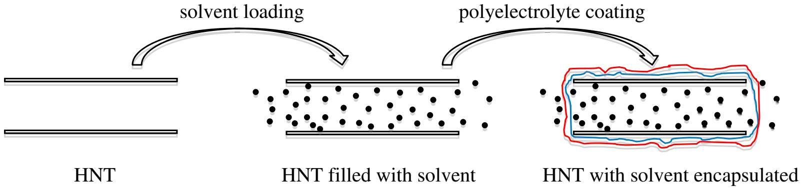

Figure 1. Encapsulation process of solvent into HNTs.

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Table 1 shows designations of samples investigated in this study. The nomenclature followed the processing route employed for each sample.

2.2.3. Characterization

Several experimental techniques were employed to verify the existence of solvent inside the nanotubes. Physical, chemical, and morphological characterization were carried out using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), specific surface area (BET), and scanning electron microscopy (SEM).

2.2.4. X-ray diffraction (XRD)

XRD experiments were carried out using a Shimadzu equipment model XRD-6000. Intensity vs. scattering angle (2θ) were recorded at room temperature in the range 5°–80° (2θ), with scanning rate of 2°/min, temperature approximately 22 °C, Cu (Ka) radiation as X-ray, with wave length of 0,15,418 nm. The technique was used to verify changes in the structure of the HNT.

2.2.5. FTIR spectroscopy

FTIR spectroscopy analysis was performed on a Bomem MB100 equipment with transmittance mode in the range of 400–4000 1/cm in KBr. The proportion used was approximately 10% of sample. The aim of this analysis was to investigate functional groups in halloysite through the identification of the bands obtained. The spectrum of the HNT sample was compared with the spectra of other samples in order to identify bands possibly related to the polyelectrolytes and/or solvents.

2.2.6. Thermogravimetry (TG)

The thermal behavior of the samples was analyzed by TG. Measurements were carried out in a Netzsch equipment model STA 449 F3 using N_2 and a heating up rate of

Table 1. Designation of investigated samples.

		Introduced solvents		Polyelectrolytes for encapsulation	
Sample	Nanotube Halloysite	Nitrobenzene	Dimethylsulfoxide	Sodium polyacrylate	CTAB
HNT	X				
HNT Nitro	X	X			
HNT DMSO	X		X		
HNT Poly	X			X	
Poly N	X	X		X	
Poly D	X		X	X	
HNT CTAB	X				X
CTAB N	X	X			X
CTAB D	X		X		X
HNT PC	X			X	X
PC N	X	X		X	X
PC D	X		X	X	X

2 °C/min, over a temperature range of 25 to 650 °C. Mass variation (%) was calculated from the TG curve, based on the initial mass of the sample. In this way, loss of solvents and polyelectrolytes and changes in the structure of the HNT can be detected.

2.2.7. Specific surface area (BET)

The specific surface area of the samples was quantified by BET technique with nitrogen adsorption/desorption by using a Quantachrome NOVA 2000. Initially, samples were dried in an oven at 80 °C for two hours. After that, samples were placed in the analytical equipment during 12 h, being 6 h with adsorption and 6 h with desorption of nitrogen. The surface area of the samples is expected to decrease when compared to HNT if the nanotube inner cavity is filled with solvent or their ends are blocked by polyelectrolytes.

2.2.8. Scanning electron microscopy (SEM)

SEM samples were analyzed with a Shimadzu equipment model SSX-550 using an accelerating voltage VA between 15 and 20 KV. As samples are non-conductive, gold plating was employed on particles with a Shimadzu equipment IC50 for 5 min with 6 mA current and pressure of 20 Pa. SEM analysis was carried out in order to compare microstructures and evaluate particle agglomeration under the influence of solvents. Changes in shape of the particles, which could characterize the formation of nanocapsules with the possible adhesion of polyelectrolytes around the HNT, were evaluated as well.

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3. Results

3.1. Solvent loading

The samples loaded with the selected solvents were characterized in order to verify if the procedure was successful. The samples compared were named as HNT (without solvent), HNT Nitro (with nitrobenzene), and HNT DMSO (with DMSO). X-ray diffractograms of investigated samples are shown in Figure 2 over the 5–15 range for 2θ, which is the region where peaks related to wall spacing of the nanotubes are found.

According to the diffractograms, the peaks of the samples HNT and HNT Nitro are practically in the same position as 12 (2θ). For the sample HNT DMSO, the behavior is quite different. Halloysite with an XRD peak next to 8–9 (2θ) can be classified as a structure with 1 nm width or hydrated, i.e. the walls inside the nanotubes are separated by a distance of approximately 1 nm.[33] As the starting material is a dehydrated halloysite with approximately 0.7 nm wall spacing, the diffractogram of the HNT DMSO sample indicates there was an increase of the space in between the nanotube walls, which suggests that the solvent DMSO penetrated into the nanotube cavity with the employed procedure. The remaining peak at 12 (2θ) is related to a small amount of nanotubes which were not filled with the solvent.

The same sample HNT DMSO was once more analyzed by XRD after a period of two months, in order to verify if the peak would return to the 12 (2θ) position, which would indicate evaporation of the solvent. The peak remained at 8 (2θ), which suggests the capacity of the HNT to retain the solvent even before encapsulation. There was no difference observed on the entire X-ray pattern (2θ over the range of 5–15 degrees) after the period of two months.

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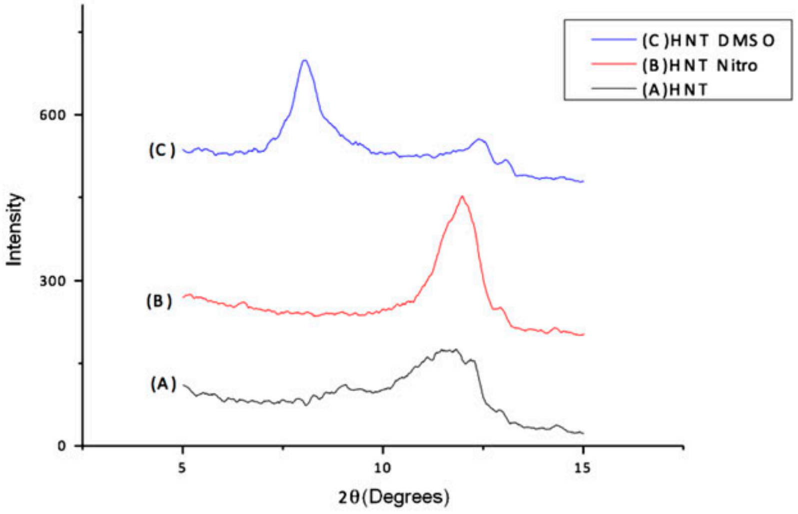

Figure 2. X-ray diffractograms of the samples (A) HNT, (B) HNT Nitro and (C) HNT DMSO.

The peak of the HNT Nitro sample remained in the same position as for the untreated HNT. This suggests that the employed procedure was not successful in filling nitrobenzene into the HNTs. One of the possible reasons for this is that the time period for which the dispersion remained under vacuum was not long enough to fulfill the objective in this case. Another factor that may have added to this is the shape of the nitrobenzene molecule, which may have implied difficulties to the penetration into the nanotube, besides viscosity and chemical affinity. It is known that nitrobenzene has higher density and molar mass than DMSO.

A common effect observed in the diffractograms of both samples treated with solvents was the decrease in peak width and increase in peak length, which indicates a more ordered structure of the material. In the case of nitrobenzene, which possibly did not penetrate into the nanotube, it is possible that the solvent accommodated on the surface of the HNTs, which implies a more pronounced separation between nanotubes and would explain the change in shape of the peaks.

Further results suggest that halloysite was filled with DMSO. Figure 3 shows the mass loss of the investigated samples.

The curves for mass loss show that the samples which were submitted to solvent loading exhibit similar characteristics when compared to the HNT sample. All curves show mass losses at 100, 240, and 470 °C. The slight mass loss around 100 °C is probably due to loss of weakly linked water molecules.[34] The mass loss around 240 °C may be attributed to loss of intercalated water among nanotube walls. In this case, HNT samples still show some moisture present, which is common to most clay minerals, but the material is not hydrated halloysite. The mass loss around 470 °C is probably due to the transformation of halloysite into methahalloysite.[33]

Nevertheless, samples HNT Nitro and HNT DMSO show greater mass loss when compared to HNT sample. Over the temperature range of 150–250 °C, where the boiling point of the solvents is located, there is a difference in the slope of the curves, especially in the HNT DMSO curve. XRD results (Figure 2) suggested that there was an increase in spacing of nanotube walls in this sample. The increased mass loss rate

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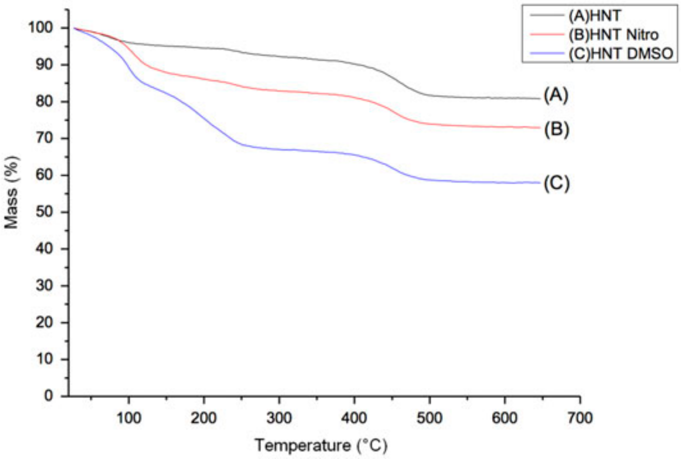

Figure 3. Curves for thermogravimetric analysis of the samples (A) HNT, (B) HNT Nitro, and (C) HNT DMSO.

of HNT DMSO as compared to HNT Nitro suggests that DMSO solvent filled the nanotubes and increased interplanar spacing. Therefore, the solvent was released at higher temperatures, as indicated by the thermal analysis (Figure 3). The sample NHT Nitro showed increased mass loss as compared to the sample HNT. This could be attributed to loss of impregnated solvent among nanotubes.

The surface area of the samples submitted to solvent loading was significantly changed, as seen by adsorption and desorption of nitrogen by BET surface area analysis. Table 2 shows the results obtained for the investigated samples.

The values for surface area of the samples HNT Nitro and HNT DMSO decreased as compared to the surface area of the HNT sample. The lower value found for the HNT DMSO sample is an additional indication that the solvent filled the nanotube, as suggested by XRD (Figure 2) and thermal analysis (Figure 3). The DMSO solvent inside the nanotube possibly made nitrogen adsorption inside HNT difficult. On the other hand, if the nanotube is empty, as it is the case of the HNT sample, the surface area for adsorption is larger, as confirmed by the results obtained for this sample. In case of the HNT Nitro, where XRD (Figure 2) and thermal analysis (Figure 3) indicate that nitrobenzene did not fill in the nanotubes, the lower value found for surface area as compared to the sample HNT suggests that nitrobenzene was impregnated in the clay. In this case, the nanotubes were covered by the nitrobenzene, which made nitrogen adsorption inside HNT difficult. In the case of the nanotubes with DMSO, the reduction in surface area when compared to the HNTs was smaller because the solvent did not cover the nanotubes; instead, the solvent penetrated the inner lumen and produced an increase in interlayer spacing. Agglomeration of the particles of the sample

Table 2. Values for surface area of the investigated samples.

Sample	HNT	HNT Nitro	HNT DMSO
Area (m^2/g)	46,51	16,01	25,42

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was observed with both solvents (nitrobenzene and DMSO). This reduces the area available for nitrogen adsorption.

Sample micrographs confirm that particle agglomeration took place after solvent loading. Figure 4 shows SEM micrographs of the investigated samples. The SEM micrographs suggest that the starting material has an average tube diameter of 100 nm and length of 0.5 μm.

The micrographs obtained (Figure 4) can be related to results for specific surface area (Table 2). The sample HNT shows less agglomerated particles (Figure 4(A)), as compared to HNT Nitro (Figure 4(B)). The sample HNT Nitro is more agglomerated, with various particles aggregates. This is probably the reason for the lower superficial area of the samples HNT Nitro as compared to the value obtained for the sample HNT.

The sample HNT DMSO shows lower superficial area and more agglomerates (Figure 4(C)) as compared to the sample HNT (Figure 4(A)). This lower superficial area may be explained by the agglomerates formed by solvent loading and by penetration of the solvent into the nanotubes, which was also suggested by XRD and thermal analysis.

3.2. Nanotubes encapsulation

The procedure employed for the encapsulation of the nanotubes was evaluated by the characterization of the prepared samples. At first, the procedure using NaCl solution 0.5 M was evaluated. The objective was to form sodium polyacrylate and CTAB layers to encapsulate the nanotubes. Layers of each polyelectrolyte and bilayers of one polyelectrolyte over the other were produced. Figure 5 shows XRD results of the investigated samples. Samples with nitrobenzene are Poly N and CTAB N. The samples with

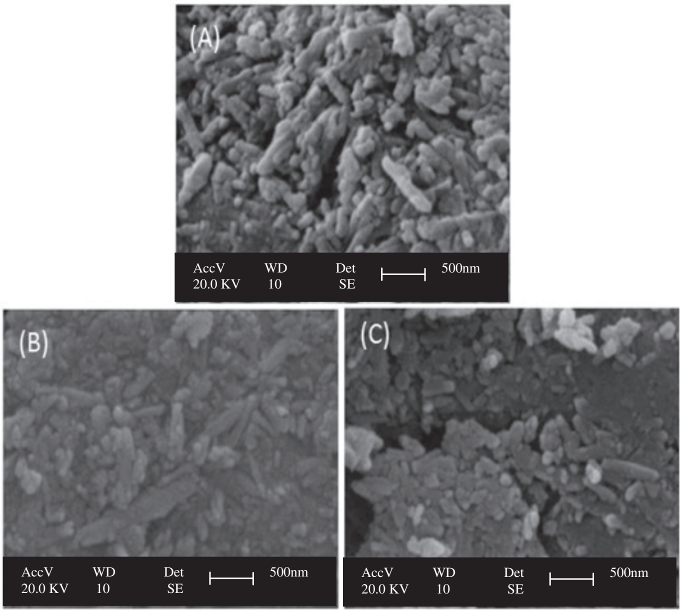

Figure 4. SEM micrographs of samples (A) HNT, (B) HNT Nitro, and (C) HNT DMSO.

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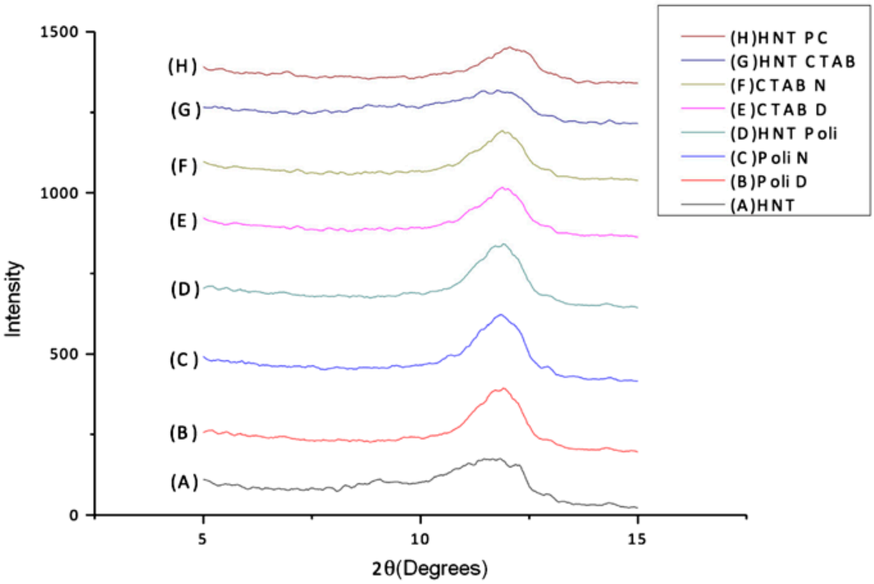

Figure 5. X-ray diffractograms of the samples (A) HNT; (B) Poli D (HNT, DMSO and Polyacrylate); (C) Poly N (HNT, Nitrobenzene and Polyacrylate); (D) HNT Poly (HNT and Polyacrylate); (E) CTAB D (HNT, DMSO and CTAB); (F) CTAB N (HNT, Nitrobenzene and CTAB); (G) HNT CTAB (HNT and CTAB); (H) HNT PC (HNT, Polyacrylate and CTAB).

DMSO are Poly D and CTAB D. Samples which were not submitted to solvent loading were HNT, HNT Poly, HNT CTAB and HNT PC.

Among investigated samples, there was no change of peak position at 12 (2θ), which is related to interplanar distance in between walls inside the halloysite nanotube.[28,29] Even samples filled with DMSO, which showed the peak at 8 (2θ) before encapsulation (Figure 2), showed the peak at 12 (2θ) after encapsulation. This change may be attributed to affinity of the solvent (DMSO) to water. Thus, the solvent may have been removed with the NaCl solution during centrifugation.

As the NaCl solution may have contributed to the removal of the water soluble solvents from the cavity of the nanotube, the encapsulation process via DMSO solvent was employed and its efficiency was compared to the method with the NaCl solution. DMSO was chosen as the dispersion media because results indicated that the cavities of nanotubes subjected to solvent loading with DMSO were filled with that solvent. On the other hand, samples subjected to solvent loading with nitrobenzene seemed to be only aggregated with that solvent. Therefore, further studies involving solvent loading and encapsulation with nitrobenzene were not taken into consideration.

Samples were produced by the same encapsulation method, but this time the process was adapted to DMSO. XRD results of the samples produced are shown Figure 6.

The samples subjected to DMSO loading were HNT D, CTAB D, and PC D. The samples without solvent were HNT and HNT CTAB. The samples encapsulated with CTAB were HNT CTAB and CTAB D. The sample PC D was developed in order to allow encapsulation with a layer of sodium polyacrylate over the CTAB layer. Samples encapsulated only by polyacrylate layers could not be obtained because when the polyelectrolyte was added to the DMSO dispersion, coagulation of the material took place, which hindered it from adhering to the halloysite.

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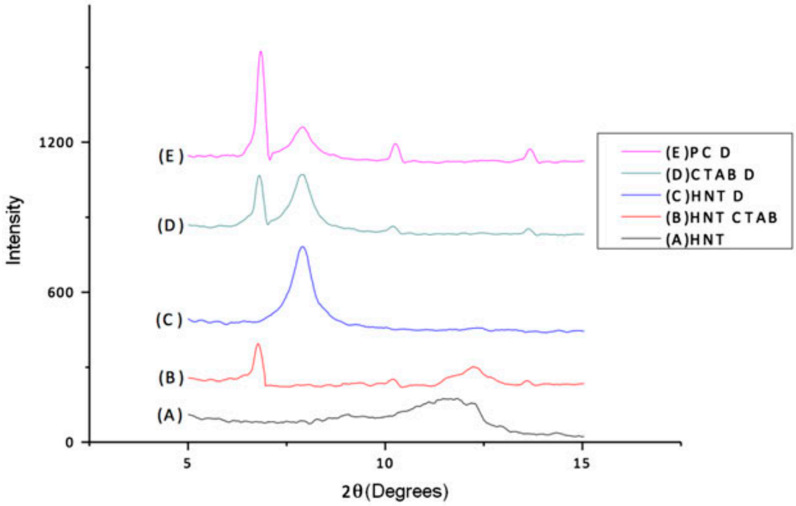

Figure 6. X-ray Diffractograms of samples encapsulated via DMSO solvent. (A) HNT, (B) HNT CTAB (HNT and CTAB), (C) HNT D (HNT and DMSO), (D) CTAB D (HNT, DMSO, and CTAB), (E) PC D (HNT, DMSO, CTAB, and Polyacrylate).

Figure 6 shows that samples not loaded with solvent exhibit a peak at 12 (2*θ*), which is related to the distance in between nanotube walls. The samples loaded with DMSO exhibited peaks shifted to 8 (2*θ*), even after the encapsulation process. Using NaCl solution, the peaks returned to 12 (2*θ*), which may be attributed to the mixing of the solvent with the NaCl solution. The results also suggest that the polyelectrolyte CTAB is present in the encapsulated samples. Peaks at 7, 10, and 14 (2*θ*) were identified as diffractions due to the polyelectrolyte. The presence of the polyelectrolyte is also suggested by the results of thermal analysis in Figure 7.

TGA results (Figure 7) show the expected behavior of halloysite with the transformation into methahalloysite at around 470 °C. This behavior is seen for all investigated samples. The sample HNT CTAB, which was not loaded with DMSO, shows mass loss related to the decomposition of CTAB around 190 °C.[35] CTAB D and PC D samples exhibit the same behavior but, as these samples were loaded with DMSO, they show a mass loss around 150–200 °C related to evaporation of that solvent. This behavior is similar to that seen for the sample HNT D (Figure 7). By analyzing specifically the sample PC D, which is composed by the polyelectrolytes CTAB and sodium polyacrylate, the curve shows mass loss around 100 °C, which is probably related to decomposition of polyacrylate.[36]

Infrared spectroscopy suggests the presence of the layer of polyelectrolyte on HNTs for the processing via DMSO solvent. Figure 8 shows infrared spectra of investigated samples.

It can be observed that samples with polyelectrolytes (PC D and CTAB D) have the same characteristics, as well as non-encapsulated samples (HNT e HNT D), which showed only spectra related to halloysite.[29] It was not possible to identify any peak related to DMSO solvent in HNT D, CTAB D, and PC D samples, however other peaks that are not related to HNT were identified in CTAB D and PC D samples.

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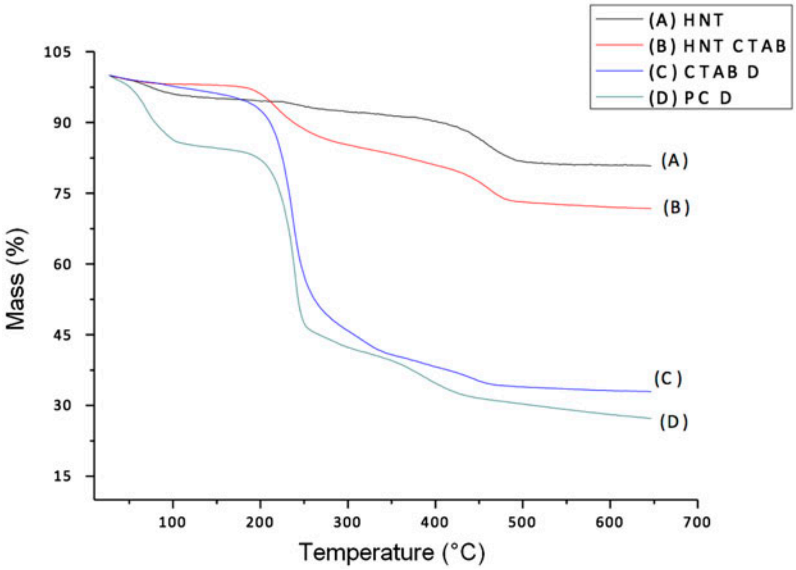

Figure 7. Thermogravimetric analysis of encapsulated samples via DMSO. (A) HNT, (B) HNT CTAB (HNT and CTAB), (C) CTAB D (HNT, DMSO, and CTAB), (D) PC D (HNT, DMSO, CTAB, and polyacrylate).

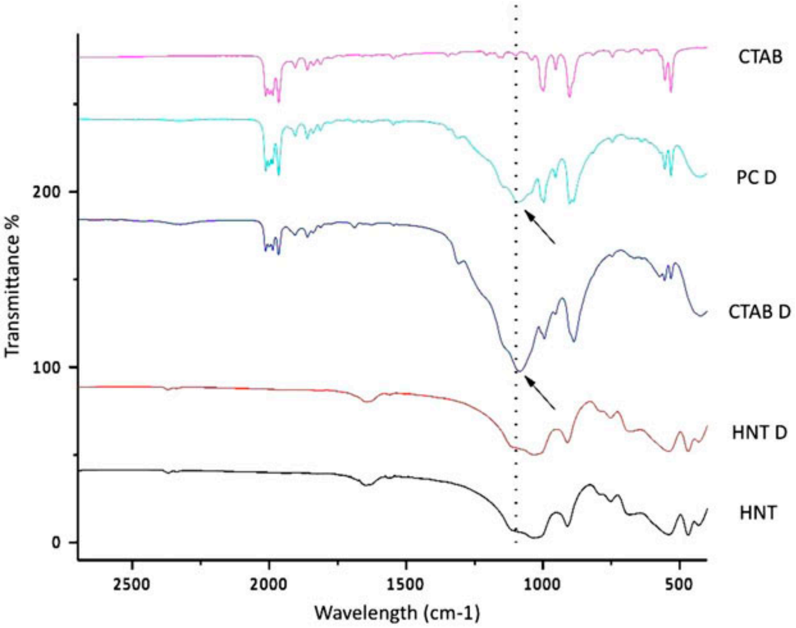

Figure 8. Infrared spectra of encapsulated samples via DMSO. (A) HNT, (B) HNT D (HNT and DMSO), (C) CTAB D (HNT, DMSO, and CTAB), (D) PC D (HNT, DMSO, CTAB, and Polyacrylate), (E) CTAB (Polyelectrolyte CTAB).

In encapsulated samples (CTAB D and PC D), peaks at 2000, 950, and 550 cm^{-1} are related to CTAB. Peaks attributed to sodium polyacrylate have not been identified, suggesting that there was no interference of the polyelectrolyte in the spectra of the samples. However, in both encapsulated samples, it is possible to identify a peak that is not related to the polyelectrolytes or to halloysite. However, a peak at 1090 cm^{-1} suggests bonds between CTAB and halloysite. In this spectrum range it is possible to attribute peaks related to Carbon/Oxygen (CO), Carbon/Nitrogen (CH), or Carbon/Oxygen/Carbon (COC) bonds, which can be formed between CTAB molecules and hydroxyls on the halloysite surface.[37] Thus, FTIR spectra suggests layer of polyelectrolyte for the processing via solvent DMSO.

4. Conclusions

A procedure to encapsulate solvents into HNT was developed, where nitrobenzene and DMSO were evaluated. Results indicate an increase in the spacing between the inner walls of halloysite, which was attributed to infiltration of DMSO. Infiltration of nitrobenezene into the nanotubes was not achieved. The encapsulation process via saline solution did not provide the polyelectrolyte coating of the nanotubes to lock up the introduced solvent. The encapsulation process using DMSO was more efficient as compared to the process employing saline solution. Results suggest that the solvent remained inside the nanotubes after the encapsulation procedure. The presence of a polyelectrolyte CTAB coating on the HNT was indicated by the results obtained, as well as their chemical interaction. Such observations were not seen for sodium polyacrylate.

The efficiency of these nanotubes with encapsulated solvent in repairing microcracks in epoxy still needs to be evaluated. Foreseen applications of the encapsulated nanotubes comprise healing of microcracks at the ply interface of laminates with the possibility of interlaminar reinforcement, as well as healing of surface damage in secondary structural members such as fairings. Ultimately, nanotubes filled with solvents can prove as a feasible approach to heal cracks in thermoset materials in an autonomic fashion, thus increasing durability.

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