Novel Approach for Obtaining Nanocomposites with a High Percentage of Mwcnts Reinforcement and Elastomeric Materials PU/MWCNT

Khaled Chawraba1,2, Abdallah Nassereddine3, Hareth Sleiman1, Joumana Toufaily1, Jacques Lallevée4, and Tayssir Hamieh1∗

1Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA) and LEADDER Laboratory, Faculty of Sciences and EDST, Lebanese University, Hariri Campus, Hadath, Beirut, Lebanon
2CNRS, IS2M UMR 7361, Université de Haute-Alsace, F-68100 Mulhouse, France
3Department of sciences, Paris-Diderot University, Paris, France
4Université de Strasbourg, 67081 Strasbourg, France

Abstract

Novel nanocomposites based on polyurethane/carbon nanotube and incorporation of functional groups (hydroquinone and citric acid) were prepared by “solution casting method”. In this work, a high percentage of carbon-nanotubes (CNTs) was introduced successfully into the polyurethane. The samples were characterized by scanning electron microscopy (SEM); the results obtained showed a high dispersion of CNTs on polymer. Then, the thermal stability of the nanocomposites was evaluated by thermal gravimetric analysis (TGA), and the mechanical properties were evaluated by tensile test. Compared to pure polyurethane, the nanocomposites, with high loading of CNTs, displayed better thermal stability and mechanical properties (high elongation at break-1000%).

Keywords: Dispersion • Elastomers • Mechanical properties • Nanocomposites • Polyurethanes

Introduction

Polyurethane (PU) is one of the most interesting synthetic elastomers [1]. Due to its unique properties, the linear structure of segmented PU appears in the form of (AB)n. The flexible segment B is normally formed of a polyester or a polyether macromolecular molecular weight between 1000 and 3000, and the hard segment A consists of a disocyanate. Because of the difference in chemical structure, micro-Areas forming between the soft segments and the hard segments and joined by a resulting mutual attraction of intermolecular hydrogen bonds. The incorporation of nanoparticles can considerably improve the properties of the polymer nanocomposite [2-4]. Carbon nanotubes (CNT) as an interesting additive due to their superior properties such as electrical, thermal, and mechanical and high length/diameter ratio, low density, and strength make them favorable additives for reinforcement. To fabricate CNT nanocomposites with effective reinforcement a good dispersion is needed, and formation of a strong covalent and noncovalent interaction with the matrix [2,5-7]. the choice of polyurethanes (PU) to preparation of nanocomposites with carbon nanotubes (CNTs), because is having special properties such as high resistance to abrasion, hardness, elastic modulus, tensile strength, and elongation at break, among others [8,9]. These properties promote the choice of this composites to be used in a large variety of fields such as aerospace, automotive, electronics, medical, oil and gas, mining and construction [10,11].

Since their discovery in 1991 by Iijima [12], unique and novel properties of carbon nanotubes (CNTs) and technological possibilities, offering the polymer-CNT composites, such as improved mechanical, electrical and thermal properties, continue to draw the attention of global research. To date, literature studies have been converged on the methods of distribution and dispersion of carbon nanotubes in the polymer matrix and, on the interaction aspects of the polymer chains and carbon nanotubes can be promoted.

Many researchers have studied different PU types reinforced multiwalled carbon nanotubes (MWCNTs) [13,14]. CNTs are most widely used in composites, not only for improving mechanical properties, but also for enhancing electrical, [15] thermal, and electromagnetic interference shielding properties [13].

Nanocomposites of nanotube-polymer composites open opportunities for new multi-functional materials with broad commercial and defense applications. The big challenges encountered in making such a composite are the uniform dispersion of carbon nanotubes in a polymer matrix without agglomerates and entanglements, and the improved nanotubes-resin interface adhesion.

The dispersion of the nanotubes in the PU matrix was always a key issue. The functionalization of the nanotubes leads to a better dispersion of high carbon contents. Bufa and Resasco [16] used the functionalized nanotubes which contain hydroxyl groups to improve the interaction with the urethane groups via hydrogen bonding. The study of composite structure shows that carbon nanotubes can be dispersed in the matrix of polyurethane. Another group of researchers [17] managed to fix on the nanotube carboxylic group COOH by oxidation reaction, thus, chemical bonding of carbon nanotubes in the matrix of the polyurethane was confirmed by infrared spectra Fourier transform (FTIR).

*Address for Correspondence: Tayssir Hamieh, Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA) and LEADDER Laboratory, Faculty of Sciences and EDST, Lebanese University, Hariri Campus, Hadath, Beirut, Lebanon, Email: tayssir.hamieh@ul.edu.lb

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The agglomeration and nonhomogeneous dispersion of the CNTs and poor interaction between the CNTs and polymer matrix are two major problems that occur during the preparation of CNT reinforced composites [18-20]. However, due to low dispersibility of the CNTs in polymeric matrix, the nanotubes aggregate with a polymer in simple mixing process due to van der Waals attraction forces between the carbon nanotubes and the polymer matrix [21-23].

This paper is dedicated to the preparation and characterization of polyurethane-carbon nanotube composite elastomer. Carbon nanotubes were dispersed into polyol by mechanochemical methods. And polyurethane-carbon nanotube nanocomposite was prepared by further in situ polymerization. This study will endeavor to solve the dispersion problem of carbon nanotubes and study the relationship between the structure and properties of PU-CNT composites. The interaction between polyurethane and carbon nanotubes, thermal stability and mechanical properties were also examined.

Materials and Sample Preparation

Polyether Polyol (Mw=1200 and 1750 g/mol with functionality=3) (commercial), polymeric MDI (f=1.43, commercial), dibutyl tin laurate (DBTL) (sigma Aldrich), hydroquinone (sigma Aldrich), citric acid (sigma Aldrich) and sulfuric acid (98%) (Sigma Aldrich). The Carbon nanotube is treated by a mixture of nitric and sulfuric acid (1:1). A mother solution of the high concentration carbon nanotube 24% of the weight polyol was prepared over 40 minutes of agitation. Other polyols, which are loaded carbon nanotubes with smaller percentages, will be synthesized from this mother solution of polyol, samples of different volumes, added to the calculated quantities of pure polyol.

Citric acid or hydroquinone is added to the polyol and are mechanical mixed (500 rotation/minutes) at 120°C for 4 h in an oil bath and homogenized for 24 h, after that the polymeric MDI and dibutyl tin laurate and water were added to the mixture and mixing for 10 min for homogenization, finally cast the solution in the mold and dry for 2 days. Samples contains polyol (MW=1200, 1750 g/mol) and citric acid are designated with a prefix (CAPU-1200-NCO-%CNT) and (CA-PU-1750-%CNT). Samples contain polyol (MW=1200, 1750 g/mol) and hydroquinone are designated with a prefix (HQ-PU-1200-NCO-%CNT) and (HQ-PU-1200-NCO-%CNT).

Chemical reactions

a) Treatment of Carbon Nanotubes by mixing sulfur-nitrile

\[ \text{Carbon Nanotubes} + \text{H}_2\text{SO}_4/\text{HNO}_3 \rightarrow \text{Particles} \]

b) Esterification with the hydroxyl of citric acid and hydroquinone

\[ \text{HO-} + \text{CO}_2 + \text{H}_2\text{O} \]

Experimental characterization: Homogeneities, thermal stability, and elongation

Study of homogeneity by scanning electron microscopy: The homogeneous dispersion of CNTs in the PU matrix is required especially for multilevel; thermal stability, the tendency toward crystallization, glass transition temperature, a good reinforcement for the strength of the material especially tensile strength, and elongation at break, the inhomogeneity can lead to structural flaws in the composite material. Figures 1-6 show photographs taken by microscopy MBE electronic scanning of the crosscuts fracture surfaces of composite materials prepared PU-CNTs. The points and the bright lines are the ends of CNTs broken or aggregated.

Figure 1. Linkage between polyurethanes and carbon nanotube [24].

Figure 2. SEM for nanocomposites a) HQ-PU1200-6%, b) HQ-PU1200-12%, c) HQ-PU1200-18%, d) HQ-PU1200-24%.

Figure 3. SEM for nanocomposites a) CA-PU1200-6%, b) CA-PU1200-12%, c) CA-PU1200-18%, d) CA-PU1200-24%.

Figure 4. SEM for nanocomposites a) HQ-PU1750-6%, b) HQ-PU1750-12%,
c) HQ-PU1750-18%, d) HQ-PU1750-24%

![Figure 5](image.png)

**Figure 5.** SEM for nanocomposites a) CA-PU1750-6%, b) CA-PU1750-12%, c) CA-PU1750-18%, d) CA-PU1750-24%.

![Figure 6](image.png)

**Figure 6.** Dimensions of simples. L=115mm; C=25±1mm; G=25±1mm; R=14±1mm; A=33±mm; D=6mm.

Against the composite by two CA-PU1200-24% (Figure 3) and CA-PU1750-24% (Figure 5), present homogeneous textures and particles aggregated are few. Figure 5 show a very satisfactory dispersion in the morphology of the two foams CA-PU1750-6% and CA-PU1750-12%, less satisfactory dispersion for the composite CA-PU1750-18%. Aggregations are noticed in the micrographs of CA-PU1200-18% and texture relatively well dispersed in the sample matrix CAPU1200-12% (Figure 3). It seems that the interactions established in the mother solution (polyl-24% CNT-Citric Acid) are strong, and the dispersion by the simple addition of pure polyl, is not obvious. The micrographs of all other composites HQ-PU1200-ICNT and HQ-PU1750-ICNT (Figures 2 and 4) show very well dispersed and homogenous phases.

**Thermal stability by thermogravimetric analysis:** The stability of various polymers has been studied by thermogravimetric analysis was carried out on an apparatus (Automatic Multiple Sample Analyzer TGA thermogravimetric-1000-Navas instruments). The tests were performed with a constant flow of nitrogen and at a temperature elevation rate of 10°C/min. We have defined start temperature degradation as the temperature at which the sample lost 10% of its original mass.

**TGA profiles:** Four major variables must be taken into consideration:

- The temperature of the start of degradation and the half-degradation
- The temperature of the half-degradation
- Charcoal remaining percentage at 600°C.
- The temperature of degradation

Samples would lose 10% of their mass and begin to degrade in a temperature range between 314°C and 336°C. The characteristics of the various samples are presented on Tables 1-4.

**Table 1. Sample preparation.**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>T start</th>
<th>T half degradation</th>
<th>T at Maximum speed degradation</th>
<th>Tfinal</th>
<th>DBTL drops</th>
<th>observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-CNT (+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU-1750-0%</td>
<td>325</td>
<td>377</td>
<td>392</td>
<td>602</td>
<td>3</td>
<td>flexible</td>
</tr>
<tr>
<td>PU-1750-3%</td>
<td>333</td>
<td></td>
<td>406</td>
<td>594</td>
<td>3</td>
<td>flexible</td>
</tr>
<tr>
<td>PU-1750-12%</td>
<td>314</td>
<td></td>
<td>408</td>
<td>598</td>
<td>6</td>
<td>flexible</td>
</tr>
<tr>
<td>PU-1750-16%</td>
<td>331</td>
<td></td>
<td>410</td>
<td>591</td>
<td>12.0224</td>
<td>flexible</td>
</tr>
<tr>
<td>PU-1750-24%</td>
<td>336</td>
<td></td>
<td>403</td>
<td>598</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>PU-CNT-Citric acid (+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA-PU1750-6%</td>
<td>316</td>
<td>385</td>
<td>396</td>
<td>593</td>
<td>9.12</td>
<td></td>
</tr>
<tr>
<td>CA-PU1750-12%</td>
<td>298</td>
<td>376</td>
<td>360-414</td>
<td>602</td>
<td>14.35</td>
<td></td>
</tr>
<tr>
<td>CA-PU1750-18%</td>
<td>291</td>
<td>382</td>
<td>407</td>
<td>583</td>
<td>18.27</td>
<td></td>
</tr>
</tbody>
</table>
CA-PU1750-24% & 277 & 371 & 363-405 & 602 & 21.88 \\
PU-CNT-hydroquinone (+) & & & & & \\
HQ-PU1750-6% & 308 & 386 & 406 & 593 & 10.01 \\
HQ-PU1750-12% & 297 & 384 & 405 & 592 & 14.42 \\
HQ-PU1750-18% & 287 & 377 & 403 & 591 & 18.82 \\
HQ-PU1750-24% & 275 & 376 & 403 & 590 & 21.18 \\
(+ ) Functionalized CNTs & & & & & \\

Table 2. TGA Data for PU-1750-ICNT

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>T start</th>
<th>T half degradation</th>
<th>T at Maximum speed degradation</th>
<th>Tfinal</th>
<th>% Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-CNT-Citric acid (+)</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td></td>
</tr>
<tr>
<td>CA-PU-1200-6%</td>
<td>322</td>
<td>387</td>
<td>360-428</td>
<td>602</td>
<td>5.87</td>
</tr>
<tr>
<td>CA-PU1200-12%</td>
<td>312</td>
<td>385</td>
<td>360-412</td>
<td>600</td>
<td>7.68</td>
</tr>
<tr>
<td>CA-PU1200-18%</td>
<td>299</td>
<td>379</td>
<td>360-410</td>
<td>599</td>
<td>10.26</td>
</tr>
<tr>
<td>CA-PU1200-24%</td>
<td>293</td>
<td>378</td>
<td>360-408</td>
<td>597</td>
<td>13.7</td>
</tr>
<tr>
<td>PU-CNT-hydroquinone (+)</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td></td>
</tr>
<tr>
<td>HQ-PU1200-6%</td>
<td>322</td>
<td>380</td>
<td>405</td>
<td>588</td>
<td>7.05</td>
</tr>
<tr>
<td>HQ-PU1200-12%</td>
<td>302</td>
<td>373</td>
<td>401</td>
<td>586</td>
<td>8.38</td>
</tr>
<tr>
<td>HQ-PU1200-18%</td>
<td>286</td>
<td>368</td>
<td>399</td>
<td>601</td>
<td>13.0</td>
</tr>
<tr>
<td>HQ-PU1200-24%</td>
<td>280</td>
<td>366</td>
<td>396</td>
<td>601</td>
<td>12.79</td>
</tr>
<tr>
<td>(+) Functionalized CNTs</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td>&amp;</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. TGA Data of PU-1200-ICNT.

<table>
<thead>
<tr>
<th>HS-PU-1750-0%</th>
<th>AN-PU-1750-18 NCO (F) -6%</th>
<th>KC-PU-1750-16-NCO (+) -6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>377</td>
<td>385</td>
<td>386</td>
</tr>
</tbody>
</table>

Table 4. Comparison between half degradation temperatures.

The temperature of the half-degradation

The temperature of the half degradation determined from the given analysis TGA is the loss of half of their mass. The values of this parameter for the composite PU-CNT show the same trend already seen in the case of deterioration early, increasing the CNT incorporation rate induces a decrease in temperature values of half degradation, and carbon nanotubes facilitate the thermal degradation of materials examined. This indicates that the incorporation of carbon nanotubes to such a relatively low concentration induced a remarkable thermal stabilization of the matrix.

This can be achieved in our work if it meets only compare three samples:

The percentage of coal at 600°C

However, the mass of residual coal at the end of the degradation of all samples of all families increased with the increasing content of carbon nanotubes. This observation reveals the idea that carbon nanotubes can act as a flame retardant. The two Tables 1-4 show the final temperatures of degradation and the remaining mass of coal.

Mechanical properties: The nanotubes MWNT and SWNT have walls consisting of poly-aromatic structures with conjugated π-bonds, which can be held in place by existing electrophilic sites, optionally in the polymer matrix. The introduction of -COOH on the wall surface of MWNT facilitates hydrogen bonding with the functional groups (urethane, ester groups and carboxylic Additional COOH can also contribute to the good interaction between the CNTs and the PU. The considerable improvement of the mechanical properties of materials composite is not related to a simple quantification of molecular interactions, but other more important parameters, such that a homogeneous dispersion of CNTs through the polymer matrix and strong interfacial adhesion between the oxidized nanotubes or esterified and the matrix. The tensile strength, elongation at break, are in good relationship with the interactions between the functionalized nanotubes and the macromolecular chains in the flexible phase of the composite, in other words, the elongation corresponds to average elongations expanding channels between two nodes, which may be formed from more than one source, such as a bypass by a covalent bond, the entanglement of the chains; a localized crystallization induced by the formation of aggregates of nanotubes, which can promote nucleation, and which act as physical crosslinking points, which limit movement of polymer chains.

Tensile tests were performed using two machines; the first is used for cuts of the specimens to be examined, according to well-defined dimensions (AC QUATI-G-VIA-VISMARA-30-ARESE (M) ITALY), the other to perform the tensile tests, a specialized machine called (ACQUATI GIUSEPPE ARESE (MI) A/10 IES). Traction is made at room temperature with an elongation rate of 25 mm/minute. From each sample, two test pieces were cut and examined, and means from two values will be reported.

The results are given in Figures 7 and 8 and show values for each sample elongation, and Stress at the rupture.
The first sample contains the two families (CA-PU1750-%fCNT) and (CA-PU1200-%fCNT) and are a kind of polyurethane that contains nanotubes with COOH functions, ester linkages, the phases are connected by hydrogen bonds and urethane bonds and probably by bridges of hydrogen bonds between ester groups or functions -COOH oxidized carbon nanotubes on the one hand and the -OH functional groups of the flexible segments of the other polyol.

The elongation of the composite loaded with 24% of CNTs, relative to the polyol compound is of the order of 773%, a behavior close to the behavior of pure polyol is not obvious. micrographs of all other composites with COOH/Citric Acid) elongation (%elongation=1000%), and resistance to breakage. The last family made with a molar mass polyol (M=1750) can establish a linear relationship, both between the elongation and the percent elongation at the break on the one hand and the load percentage NTC functionalized other.

The Obtained Results are Satisfactory

The hardness of a PU-CNT composite is a linear function of the proportion of carbon nanotubes inserted into the matrix, the hardness increases with an increasing percentage of carbon, so the presence of derivatives of Si decreases the toughness and makes the material easier to puncture.

The interactions established in the master batch (polyol-24% CNT-COOH/Citric Acid) are strong, and the dispersion by the simple addition of pure polyol is not obvious. micrographs of all other composites with hydroquinone, show very well dispersed phases, the composites made with the molecular weight of polyol (M=1200 gr) have more homogeneous and continuous texture than those made with the molecular weight of polyol (M=1750 gr). For PU that are made with non-functionalized nanotubes, it seems that neither inserting derivatives if neither the percentage of carbon nanotubes present in the matrix of PU has no appreciable effect on the temperature of early degradation.

Samples of four families show a relationship between the temperature of onset of degradation, on one hand, and the rate of incorporation of the nanotubes in the matrix, on the other hand; a high nanotube incorporation rate (24%) promotes the onset of degradation at a low temperature of about 275°C, the temperature increases in a continuous manner, with the decrease in the rate of incorporation CNT, reaching a value of T=308 (or 316) when the percentage by NTC is of the order of 6%.

The temperature of onset of degradation does not characterize the thermal stability of PU, increased stability may be expressed either by a maximum speed of decreasing degradation either by the maximum deflection point of the peak of degradation to slightly greater temperatures. In general, it can be concluded that the introduction of carbon nanotubes leads to an increase of the thermal stability of the material; In the profiles of the samples of PU degradation speed, the maximum speed gradually decreases with increasing percentages of carbon nanotubes, as the temperatures that correspond to the maximums of the peaks increase with the increasing rate of the nanotubes; and the PU degradation speeds containing Si are significantly larger than other polyurethanes and inserting if decreases their stability.

For composites that exhibit strong interfacial interactions, each degradation rate profile has a belly that corresponds to a temperature range of (T=360°C to T=395°C) and wherein the degradation rate is average, it is followed by a maximum speed peak at a higher temperature. It is estimated
that the belly is a phase delay degradation that’s extended is related to the number of interactions between channels, such interaction in our case is proportional to the number of NTC-COOH functions. This estimate will be more credible when you notice a total or partial lack of respect that belly in PU-NTC-composite none functionalized or treated with hydroquinone.

The mass of the residual coal at the end of degradation of all samples of all families increased with increasing content of carbon nanotubes. This observation reveals the idea that carbon nanotubes can act as a flame retardant.

The Mechanical Performance, We Resumed the Following Results

(a) For composites made with the polyol (M=1200 gr) elongation and elongation at rupture are both, the functions of the CNT content in composites, the elongation of the composite loaded with 24% of CNTs, by relative to the polyol compound (10% relative to the weight of PU) is of the order of 773%, a behavior close to the behavior of an elastomer, i.e., 3.75 times the composite elongation charged with 6% by NTC.

(b) The tensile strength expressed as the force applied to the breaking point is inversely proportional to the percentage by CNTs, the least loaded composite nanotube atoms show resistance to the greatest rupture. A material after it has undergone a largely worn elongation shows a resistance lowers breaking another slightly elongate.

(c) The elongation values are slightly greater for the composite treated with hydroquinone, especially the sample containing 24% of CNTs which show the elongation of an elastomer (% elongation>1000%), and the values resistance to breakage.

(d) The last family made with a molar mass polyol (M=1750) can establish a linear relationship, both between the elongation and the percent elongation at the break on the one hand and the load percentage CNT functionalized second.

(e) The large values of the tensile strength of all composites, correspond to low filler contents of CNTs, and at the same time to low values of elongation at break, and the converse is true, a comparison of the resistance at the break of all samples made in the Figure 8 shows that the type of treatment of the nanotubes does not affect the tensile strength of the composite, but this quantity is dependent on the size polyol.

Conclusion

We studied the synthesis and characterization of nanocomposites manufactured from polyurethane loaded carbon nanotubes. A literature review was prepared by highlighting the knowledge developed during the last decade on the topics of composites, especially the manufacture of electrically conductive foam or fibreinreinforced with CNTs, including electroactive polymers with shape memory that may have innovative applications in several areas. We also explained the mechanical and thermal properties of developing materials, trying when possible, to describe the relationship structure-properties of polymers in question, especially the influence of the incorporation of carbon nanotubes in the matrix polymers. Various composite foams were prepared and grouped into six families differently formed; the first two families are obtained with unfunctionalized nanotubes, one of which contains a small amount of a derivative of silicon. Other families with four, are responsible for two types of oxidized nanotubes, the first type is processed, after the oxidation of citric acid, another type will be treated with hydroquinone, the two types of nanotubes functionalized differently are used with two polyols of different molecular weights (M=1200, f=3 and M=1750, f=3) for the four families. Four samples of each family are obtained and contain different amounts of mass nanotubes. The samples were subjected to a hardness test, their homogeneity was examined by scanning electron microscopy (SEM), their stabilities were evaluated by thermogravimetric analysis TGA, and their mechanical performance was measured by tensile tests.

References


