

CN102286189A Method for preparing graphene oxide/epoxide resin nano composite material

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Method for preparing graphene oxide / epoxy resin nano composite material

Technical field

The invention belongs to the field of preparation of resin-based nanocomposite materials, and in particular relates to a preparation method of graphene oxide / epoxy resin nanocomposite materials.

technical background

In recent years, due to graphene's excellent thermal conductivity (5000W-1m-1), mechanical properties (destructive strength: 125GPa, Young's modulus: 1000GPa) and high charge mobility (200000cm²g⁻¹), Scientists have paid great attention. At the same time, scientists also added graphene as a functional filler to the polymer resin to improve the thermal, mechanical and electrical properties of the resin matrix. At present, the main preparation methods of graphene are: 1. Mechanical peeling method; 2. Chemical reduction graphene oxide method; 3. Carbon nanotube axial cutting method; 4. Electrochemical reduction method; 5. Chemical vapor deposition method; 6. Microwave method; 7, solvothermal method; 8, arc discharge method; 9, epitaxial growth method; 10, liquid phase peeling graphite method. However, as a resin-based filler, it is necessary to be able to prepare graphene in large quantities. The main method of preparing graphene in large quantities is chemical or thermal reduction of graphite oxide. However, for graphene to exert a good reinforcement effect on the resin matrix, it is required that graphene can be well dispersed into the resin matrix and have a good interface with the resin matrix. However, graphene, like carbon nanotubes, is very easy to agglomerate, and it is difficult to evenly disperse it into the resin matrix. There are many epoxy groups, carboxyl groups and hydroxyl groups on the surface of graphene oxide, so it can not only be polar solvents but also have good affinity with epoxy resins. At present, the reported method of combining graphene oxide and epoxy resin mainly uses acetone or water as a solvent. Acetone is toxic and pollutes the environment. However, water is used as a solvent. Since water and epoxy are not miscible, they can only be made in low content. Composite material of graphene oxide and epoxy resin.

Summary of the invention

The object of the present invention is to provide a method for uniformly dispersing graphene oxide into an epoxy resin matrix to prepare graphene oxide / epoxy resin nanocomposites. This method uses ethanol as a solvent to ultrasonically strip graphite oxide to obtain a homogeneously stable graphene oxide solution, and then dissolves the epoxy resin in the resulting solution. For the mixed solution, ultrasonic treatment is performed, the ethanol is evaporated, and then a curing agent is added, Heating and curing to obtain graphene oxide / epoxy resin nanocomposites.

The technical solution of the present invention is as follows:

The preparation method of the graphene oxide / epoxy resin nanocomposite provided by the present invention has the following steps:

1) Dissolve graphite oxide in ethanol to prepare a graphite oxide ethanol solution with a concentration of 0.01-20g / L. Then, ultrasonically treat the graphite oxide ethanol solution with an ultrasonic device with a power of 300-1000W for 0.5-5 hours to obtain Ethanol solution of graphene oxide; (The scanned photograph of graphene oxide is shown in Figure 1);

2) Add the epoxy resin to the graphene oxide ethanol solution obtained in step 1) to obtain a mixed liquid, and stir the mixed liquid for 5-30 minutes with a magnetic stirrer, and then perform the mixed liquid with an ultrasonic equipment with a power of 300-1000W Ultrasonic treatment for 0.5-5 hours;

3) Step 2) Put the ultrasonically-treated mixture in an oven with a temperature of 50-80 degrees Celsius, bake for 10-48 hours, and then use a vacuum pump to extract the ethanol solvent in the mixture until the mixture is free of bubbles;

4) Add a chemical equivalent of curing agent to the mixed solution in step 3), magnetically stir at room temperature for 10-20 minutes to obtain a mixture, and then use a vacuum pump to draw bubbles in the mixture while magnetically stirring, until there are no bubbles in the mixture;

5) The mixture obtained in step 4) is cast into a mold with a preheating temperature of 50-80 degrees Celsius, and then placed in an oven for curing. The curing conditions are: 50-80 ° C for 3-12 hours, and then heated to 130-150 ° C. After curing for 2-20 hours, the graphene oxide / epoxy resin nanocomposite is obtained; the cross-sectional scanning photo of the obtained nanocomposite is shown in Figure 2, and it can be seen that the graphene oxide and epoxy resin have a good interface combination;

The weight ratio of the epoxy resin, curing agent and graphite oxide is 100: 23.6-60: 0.001-2.

The epoxy resin is a bisphenol F type epoxy resin or a bisphenol A type epoxy resin.

The curing agent is an amine curing agent or an acid anhydride curing agent. The amine curing agent is DETDA or GY-051.

The acid anhydride curing agent is methyltetrahydrophthalic anhydride or methylhexahydrophthalic anhydride.

Compared with the prior art, the advantages of the method for preparing graphene oxide / epoxy resin nanocomposite provided by the present invention are as follows:

1、 In the process of preparing graphene oxide / epoxy resin nanocomposites, no toxic solvents such as acetone, DMF, or tetrahydrofuran are used, and ethanol is used, which avoids physical harm to the operator and the environment. create pollution.

2、 Because there are many carboxyl and hydroxyl groups on the surface of graphene oxide, ethanol can not only infiltrate graphene oxide very well, but also ethanol is a polar organic solvent and can dissolve epoxy resin very well. Therefore, compared with water as a solvent, it can better disperse graphene oxide into the epoxy resin matrix, and can make more graphene oxide added to the system.

BRIEF DESCRIPTION

Figure 1 is a scanned photo of graphene oxide;

FIG. 2 is a cross-sectional scanning photograph of graphene oxide / epoxy resin nanocomposite material of the present invention. It can be seen that graphene oxide and epoxy resin have a good interface combination.

detailed description

Example 1

Weighing: graphite oxide 0.001g;

100g of bisphenol A epoxy resin;

Methylhexahydrophthalic anhydride 50g

Tetrabutylammonium bromide 1g;

1、 Dissolve the weighed 0.001g graphite oxide in ethanol, configure a concentration of 0.01g / L graphite oxide ethanol solution 100ml, and then sonicate the graphite oxide ethanol solution with an ultrasonic device with a power of 300W for 0.5 hours to obtain graphite oxide Enol solution;

- 2、 Add 100g of bisphenol A epoxy resin to the graphene oxide ethanol solution obtained in step 1 to obtain a mixed solution, and stir for 5 minutes with a magnetic stirrer, and then sonicate the mixed solution with an ultrasonic device with a power of 300W for 0.5 hours;
- 3、 Put the mixed solution obtained in step 2 in an oven with an oven temperature of 50 degrees Celsius and bake for 48 hours, and then use a vacuum pump to extract the remaining solvent of the mixed solution until the system is free of bubbles;
- 4、 To the mixed solution of step 3), 50 g of methylhexahydrophthalic anhydride (curing agent) and 1 g of tetrabutylammonium bromide are added, and the mixture is magnetically stirred for 10 minutes at room temperature to obtain a mixture, and then the mixture is extracted with a vacuum pump while magnetically stirring Bubbles until there are no bubbles in the mixture.
- 5、 The mixture obtained in step 4 is cast into a mold with a preheating temperature of 50 degrees Celsius, and then placed in an oven for curing. The curing condition is 50 ° C for 3 hours, and then the temperature is raised to 150 ° C for 3 hours to obtain the oxidation of this embodiment Graphene / epoxy nanocomposites. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 50: 0.001.

Example 2

Weighing: 0.01g graphite oxide; 100g bisphenol A epoxy resin; 60g methyltetrahydrophthalic anhydride and 1g tetrabutylammonium bromide;

- 1、 Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.1 g / L of 100 ml, and then it was sonicated for 0.5 hours with an ultrasonic device with a power of 1000 W.
- 2、 100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 10 minutes, and then it was sonicated for 0.5 hours with an ultrasonic device with a power of 1000 W.
- 3、 Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.
- 4、 Add 50g of curing agent methyltetrahydrophthalic anhydride and 1g of tetrabutylammonium bromide to the mixture obtained in step 3, magnetically stir at room temperature for 10 minutes to obtain a mixture, and then use a vacuum pump to extract bubbles in the mixture while magnetically stirring, to There are no bubbles in the mixture.
- 5、 The mixture obtained in step 4 is cast into a mold with a preheating temperature of 50 degrees Celsius, and then placed in an oven for curing. The curing condition is curing at 50 ° C for 3 hours, and then heating to 150 ° C for 3 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 60: 0.01.

Example 3

Weighing: 0.02g graphite oxide; 100g bisphenol A epoxy resin; 50g methylhexahydrophthalic anhydride and 1g tetrabutylammonium bromide;

- 1、 Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.2g / L of 100ml, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.
- 2、 100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.
- 3、 Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.
- 4、 Add 50g of epoxy resin curing agent methylhexahydrophthalic anhydride and 1g of tetrabutylammonium bromide to the mixture obtained in step 3, magnetically stir at room temperature for 20 minutes to obtain a

177 mixture, and then extract the mixture with a vacuum pump while magnetically stirring Bubbles until there are no
178 bubbles in the mixture.

179
180 5、The mixture obtained in step 4 is cast into a mold with a preheating temperature of 50 degrees Celsius, and
181 then placed in an oven for curing. The curing condition is curing at 50 ° C for 3 hours, and then heating to 150 °
182 C for 3 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 50:
183 0.02.

184 185 Example 4

186
187 Weighing: graphite oxide 0.03g; bisphenol F epoxy resin 100g; methylhexahydrophthalic anhydride 50g and
188 tetrabutylammonium bromide 1g;

189
190 1、Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.3g / L of 100ml, and
191 then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.

192
193 2、100 g of bisphenol F epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic
194 stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.

195
196 3、Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48
197 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.

198
199 4、To the mixture obtained in step 3, 60 g of epoxy resin curing agent methylhexahydrophthalic anhydride and
200 1 g of tetrabutylammonium bromide were added, and the mixture was magnetically stirred for 30 minutes at
201 room temperature to obtain a mixture, and then the mixture was extracted with a vacuum pump while
202 magnetically stirring Bubbles until there are no bubbles in the mixture.

203
204 5、The mixture obtained in step 4 is cast into a mold with a preheating temperature of 50 degrees Celsius, and
205 then placed in an oven for curing. The curing condition is curing at 50 ° C for 3 hours, and then heating to 150 °
206 C for 3 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 50:
207 0.03.

208 209 Example 5

210
211 Weighing: graphite oxide 0.02g; bisphenol A epoxy resin 100g; epoxy resin curing agent DETDA 23.6g;

212
213 1、Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.2g / L of 100ml, and
214 then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.

215
216 2、100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic
217 stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.

218
219 3、Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48
220 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.

221
222 4、23.6g of epoxy resin curing agent DETDA was added to the mixture obtained in step 3, and the mixture was
223 magnetically stirred at room temperature for 20 minutes to obtain a mixture, and then the bubbles in the mixture
224 were extracted with a vacuum pump while the magnetic stirring was completed, until there were no bubbles in
225 the mixture.

226
227 5、The mixture obtained in step 4 is cast into a mold with a preheating temperature of 50 degrees Celsius, and
228 then placed in an oven for curing at a curing condition of 80 ° C for 8 hours, and then heated to 130 ° C for 12
229 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 23.6: 0.02.

230 231 Example 6

232
233 Weighing: graphite oxide 0.05g; bisphenol F epoxy resin 100g; epoxy resin curing agent DETDA 23.6g;

1、Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.5g / L of 100ml, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.

2、100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.

3、Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.

4、Add 23.6g of epoxy resin curing agent DETDA to the mixture obtained in step 3, and stir magnetically at room temperature for 30 minutes to obtain a mixture. Then, while stirring magnetically, extract the bubbles in the mixture with a vacuum pump until there are no bubbles in the mixture.

5、The mixture obtained in step 4 is cast into a mold with a preheating temperature of 80 degrees Celsius, and then placed in an oven for curing. The curing condition is 80 degrees Celsius for 8 hours, and then the temperature is raised to 130 degrees Celsius for 12 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 23.6: 0.05.

Example 7

Weighing: graphite oxide 0.05g; bisphenol F epoxy resin 100g; epoxy resin curing agent DETDA 23.6g;

1、Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 0.5g / L of 100ml, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.

2、100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.

3、Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.

4、Add 23.6g of epoxy resin curing agent DETDA to the mixture obtained in step 3, and stir magnetically at room temperature for 30 minutes to obtain a mixture. Then, while stirring magnetically, extract the bubbles in the mixture with a vacuum pump until there are no bubbles in the mixture.

5、The mixture obtained in step 4 is cast into a mold with a preheating temperature of 80 degrees Celsius, and then placed in an oven for curing. The curing condition is 80 degrees Celsius for 8 hours, and then the temperature is raised to 130 degrees Celsius for 12 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 23.6: 0.05.

Example 8

Weighing: graphite oxide 2g; bisphenol F epoxy resin 100g; epoxy resin curing agent DETDA 23.6g;

1、Graphite oxide was dissolved in ethanol to prepare a solution with a concentration of 20g / L of 100ml, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000W.

2、100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 30 minutes, and then it was sonicated for 5 hours with an ultrasonic device with a power of 1000 W.

3、Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles.

4、Add 23.6g of epoxy resin curing agent DETDA to the mixture obtained in step 3, and stir magnetically at room temperature for 30 minutes to obtain a mixture. Then, while stirring magnetically, extract the bubbles in the mixture with a vacuum pump until there are no bubbles in the mixture.

5、 The mixture obtained in step 4 is cast into a mold with a preheating temperature of 80 degrees Celsius, and then placed in an oven for curing. The curing condition is 80 degrees Celsius for 8 hours, and then the temperature is raised to 130 degrees Celsius for 12 hours. The weight ratio of epoxy resin, curing agent and graphite oxide in this embodiment is 100: 23.6: 2.

Comparative Example 1

Dissolve 0.05g of graphite oxide in acetone and prepare a solution with a concentration of 0.5g / L of 100ml. Then, sonicate it with an ultrasonic device with a power of 1000W for 1 hour. However, compared with Example 7, the formed graphene oxide solution was not stable enough, and after standing for 6 hours, it was found that there was a precipitate at the bottom, but Example 7 did not produce a precipitate, indicating that ethanol has a better wetting of graphene oxide than acetone. Sex.

Comparative Example 2

1、 Dissolve 0.05g of graphite oxide in water and prepare a solution with a concentration of 0.5g / L of 100ml. Then, sonicate it with an ultrasonic device with a power of 1000W for 1 hour.

2、 100 g of bisphenol A epoxy resin was added to the solution obtained in step 1, and stirred with a magnetic stirrer for 10 minutes, and then it was sonicated for 1 hour with an ultrasonic device with a power of 1000 W.

3、 Put the mixed solution obtained in step 2 in an oven at an oven temperature of 60 degrees Celsius for 48 hours, and then use a vacuum pump to extract the remaining solvent until the system is free of bubbles. In the mixture formed at this time, there were many agglomerated graphene oxides in large flakes, but no precipitation occurred in Example 7 to form a homogeneous mixture.

CN103627139A Preparation method of functionalized graphene oxide/epoxy resin nanocomposite

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Method for preparing functionalized graphene oxide/epoxy resin nano composite material

Technical field

The invention relates to the technical field of polymer-based nano composite materials, and more particularly to a surface chemical modification of graphene oxide and a preparation method of graphene/polymer nano composite material.

Background technique

Graphene is a carbonaceous material in which carbon atoms are closely packed into a single-layer two-dimensional honeycomb lattice structure. It is a crystal with only one atom thick. Since the first discovery of graphene by Geim in 2004, graphene has become The focus in the nanomaterials community. It can be rolled into zero-dimensional fullerenes, one-dimensional carbon nanotubes, or stacked into three-dimensional graphite. Therefore, graphene is the basic unit constituting other carbon allotropes. Due to the special structure and excellent properties of graphene, such as high Young's modulus and breaking strength (up to 1100GPa and 125GPa, respectively), excellent thermal conductivity (5300 W m^{-1}) and specific surface area ($2600 \text{ m}^2 \text{ g}^{-1}$), unique electrical properties (electron mobility is $200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

A method for preparing graphene has been reported as a tape stripping method [Novoselov KS, Geim AK. et al. Science. 2004; 306 (5696): 666-669], chemical vapor deposition [Li, X. S.; Cai, W W. et al. Science 2009; 324, 1312-1314], epitaxial growth method [Berger C, Song Z. et al. The Journal of Physical Chemistry B. 2004; 108(52): 19912-19916] and others Some improved preparation methods [US2012/0228556] and the like. However, the industrial preparation of graphene by the existing method still has great difficulty. The preparation of graphene using graphene oxide as a precursor is now a more common method because graphene oxide is not only easy to prepare, but also has excellent properties by surface chemical modification using surface oxidation groups. Therefore, graphene oxide may enter real applications earlier than graphene [Cai DY and Song M. J. Mater. Chem. 2010, 20, 7906-7915].

At present, graphene oxide, especially modified graphene oxide, is widely used in the preparation of high performance polymer nanocomposites. For example, after the modification of graphene oxide with p-phenylenediamine by Ma et al., the conductivity of the polymer is significantly improved [Ma HL, Zhang HB. et al. ACS Applied Materials & Interfaces. 2012; 4(4): 1948-1953] Zhang et al. synthesized graphene oxide containing isocyanate functional groups and used them to modify polyimide. The results showed that the addition of 0.75 wt% modified graphene oxide increased the tensile strength of polyimide by about 60%. [Zhang LB, Wang JQ. et al. Composites Part A: Applied Science and Manufacturing. 2012; 43(9): 1537-1545].

Chinese patent CN 102153877 A discloses a graphene composite material and a preparation method thereof, the invention uses an organosilane modified graphene, and a graphene polymer nanocomposite is prepared, although the dispersibility of the modified graphene is improved. However, since the surface hydroxyl group content of the graphene itself is small, the number of organosilane molecules grafted on the surface of the graphene is relatively small, and the interface between the graphene sheet and the polymer matrix cannot be well improved.

Chinese Patent Publication No. 201310138360 discloses a graphene oxide microsphere epoxy resin composite material and a preparation method thereof, but the filler involved in the method is graphene microspheres, and the graphene microspheres are completely different from graphene oxide. The form, structure and nature are two different substances.

Bortz et al. directly added graphene oxide to epoxy resin to prepare composite materials. The results showed that the mechanical properties of the resin matrix were significantly improved; however, the surface treatment of graphene oxide was not mentioned [Macromolecules 2012;45(1):238 -245].

Wang Zhou et al. modified exemplified graphene oxide with silane coupling agent KH560 and sodium dodecyl sulfate SDS, and prepared SDS functionalized graphene oxide/epoxy composite, but modified oxide graphene for KH560 to prepare epoxy. Resin composites and their effects on the mechanical properties of composites are not mentioned [preparation and characterization of epoxy resin/graphene oxide nanocomposites, Master Thesis, Beijing University of Chemical Technology, 2010].

In summary, in order to exert the excellent mechanical properties of graphene oxide, improve the dispersibility of graphene oxide in the polymer and the interface quality with the matrix, the preparation of a functionalized graphene oxide/epoxy nanocomposite was developed. The method is very necessary.

Summary of the invention

In order to effectively solve the dispersion and interface problem of graphene in epoxy resin, the invention provides a preparation method of functionalized graphene oxide/epoxy resin nano composite material, and the graphene/epoxy resin nano composite prepared by the invention Materials can effectively improve the mechanical and thermal properties of epoxy resins, including strength, stiffness, toughness and thermal stability.

The present invention is achieved by the following technical solutions: a method for preparing a functionalized graphene oxide/epoxy nanocomposite, the preparation method is the following steps: a silane coupling agent modified graphene oxide (f-GO) first ultrasonic treatment for 20 to 40 minutes dispersed in an organic solvent, and then added epoxy resin, after mixing to obtain a masterbatch, under vacuum conditions (0.1MPa-0.5MPa), remove the organic solvent, and then add a curing agent to mix, High temperature curing gives a functionalized graphene oxide/epoxy nanocomposite, as shown in Figure 9.

Preferably, the sonication time is 30 minutes, the high temperature curing temperature is 90 to 180 ° C, and the time is 1 to 6 hours.

Preferably, after adding the epoxy resin, it is uniformly mixed by mechanical mixing method to obtain a masterbatch having a high graphene content and uniform dispersion; the mechanical mixing method is high-speed stirring, twin rolls, planetary ball milling method, and the best mechanical mixing method. For the ball milling method.

The dispersion method combined with the solvent method and the planetary ball milling method enables the present invention to easily and efficiently disperse and exfoliate agglomerates of graphene.

Preferably, after adding the curing agent, the mixture is uniformly mixed by high-speed stirring, and then the uniformly mixed masterbatch, epoxy resin and curing agent are poured into the preheated mold, and solidified in a temperature-programmed oven to obtain graphite. Arene/epoxy nanocomposites.

The epoxy resin is selected from the group consisting of bisphenol A epoxy resin, phenolic epoxy resin, bisphenol F epoxy resin, polyphenol type glycidyl ether epoxy resin, aliphatic glycidyl ether epoxy resin and silicone modification One or several of the epoxy resins.

The curing agent is selected from one or more of an acid anhydride, an alicyclic amine or an aliphatic amine. Preferably, the acid anhydride of the curing agent is selected from the group consisting of trimellitic anhydride and methyltetrahydrophthalic anhydride, and the alicyclic amine or aliphatic amine of the curing agent is selected from the group consisting of diethylenetriamine, tetraethylenepentamine, methylhexa One of hydrogen phthalic anhydride.

The amount of graphene oxide modified by the silane coupling agent is 0.01 to 2.0% of the mass of the composite material, and the mass of the composite material and the sum of the quality of the graphene oxide, the epoxy resin and the curing agent modified by the silane coupling agent. The amount of curing agent is determined by the epoxy value of the epoxy resin and the type of curing agent and its reactive groups, and should ensure that the epoxy resin is sufficiently crosslinked. The theoretical addition amount of the curing agent is calculated according to the stoichiometric ratio of the epoxy group to the curing agent functional group; for the acid anhydride curing agent such as methyl hexahydrophthalic anhydride and the tertiary amine (wherein the mass ratio of methyl hexahydrophthalic anhydride to tertiary amine) 100:1), the preferred mass ratio of epoxy resin to curing agent is 185:170; for amine curing agent such as diaminodiphenyl sulfone, the preferred mass ratio of epoxy resin to curing agent is 100:33; The preferred mass ratio of the imidazole curing agent such as 2-ethyl-4-methylimidazole to epoxy resin to curing agent is 100:3.

The invention utilizes the modified graphene oxide of the silicone to improve the mechanical properties (including tensile strength, bending strength, fracture toughness and storage modulus) and thermal properties of the polymer matrix. In particular, a class of silane coupling agent-modified graphene oxide having an epoxy group at one end thereof improves the fracture toughness, modulus and thermal properties of the polymer matrix.

The method for preparing the silane coupling agent-modified graphene oxide of the present invention is the following step: first, the graphene oxide (GO) is ultrasonically treated for 30 to 70 minutes and dispersed in an organic solvent to obtain a graphene oxide suspension, while stirring. The silane coupling agent is added dropwise to the suspension, and after heating under the protection of an inert gas, the obtained product is washed, filtered, and the unreacted silane coupling agent is removed, and dried to obtain a silane coupling of a black solid powder. Linkage modified graphene oxide (f-GO).

Preferably, the graphene oxide (GO) is made of graphite, and the GO atom-containing sp² hybridized carbon atom fraction prepared by the Hummer method has a carbon atom fraction of 10% to 50%, and the rest is sp³ hybridized carbon atoms. The GO surface contains a large amount of oxidizing groups such as a hydroxyl group, a carboxyl group, and an epoxy group.

In order to obtain good dispersion of graphene oxide in an organic solvent without damaging its structure and size, it is preferred that the sonication time is 40 to 60 minutes, and the optimum ultrasonic time is 45 minutes.

The heating reaction temperature is 50 to 90 ° C, and the reaction time is 3 to 7 hours. Preferably, the reaction temperature is 60 to 80 ° C, the optimum reaction temperature is 70 ° C, the reaction time is 4 to 6 hours, and the optimum reaction time is 5 hours.

Preferably, the silane coupling agent is added dropwise to the solution under the action of mechanical agitation.

The inert gas is preferably nitrogen or argon.

Preferably, the drying is carried out in a vacuum drying oven.

The silane coupling agent has an epoxy group at one end and a bisalkoxy or trialkoxysilane coupling agent at the other end, and the mass ratio of the silane coupling agent to the graphene oxide is 4 to 15:1. Preferably, the silane coupling agent is selected from the group consisting of γ -glycidyloxypropyltrimethoxysilane (KH560), γ -glycidyloxypropyltriethoxysilane, and β -(3,4-epoxycyclohexyl) One or more of ethyltrimethoxysilane and methyl (γ -glycidyloxy)diethoxysilane.

The above organic solvent is selected from the group consisting of acetone, toluene, tetrahydrofuran, pyridine, dimethyl sulfoxide, N-methylpyrrolidone, N,N-dimethylformamide, methyl ethyl ketone, ethanol, dichloromethane, diethyl ether and chloroform. Or several.

The invention not only includes a class of silane coupling agent modified graphene oxide having an epoxy group at one end thereof, but also a modified graphene oxide to improve the thermal, tensile and bending properties and fracture of the epoxy resin composite material. Resilience, etc.; the two are interrelated. We can modify the surface of the graphene oxide to give a lot of epoxy groups on the surface, which will greatly improve the compatibility of graphene oxide with epoxy resin matrix. (Dispersion peeling and interface quality), thereby being able to improve various properties of the resin matrix. The observed graphene oxide was uniformly dispersed in the epoxy resin by optical microscopy, and no significant agglomerates were present. The mechanical and thermal properties of the prepared graphene/epoxy nanocomposites were tested. The results show that the graphene oxide modified by silane coupling agent can be significantly improved at very low content (0.1 wt%). The mechanical properties of epoxy resin, including strength, stiffness and toughness; the thermal decomposition temperature of epoxy resin by graphene oxide modified by silane coupling agent is obviously improved, and the thermal stability of the composite is improved.

Compared with the prior art, the invention has the beneficial effects that the graphene nano composite material prepared by the invention can effectively improve the mechanical and thermal properties of the epoxy resin, including strength, stiffness, toughness and thermal stability.

DRAWINGS

Figure 1 is a Raman spectrum of graphite, GO and f-GO;

Figure 2 is a photoelectron spectrum of graphite, GO and f-GO;

Figure 3 (a) is a transmission electron microscope image GO, (b) is a transmission electron microscope image of f-GO, (c) is an optical microscope image of a composite material having a GO content of 0.1 wt%, and (d) is f-GO. An optical microscope image of a composite material having a content of 0.1 wt%;

4 is a tensile diagram of a material, wherein (a) is an epoxy resin, (b) is a composite material having a GO content of 0.1% by weight, and (c) is a composite material having an f-GO content of 0.1% by weight;

Figure 5 is a comparison of tensile strength of different contents of GO and f-GO;

Figure 6 is a comparison of bending strength of different contents of GO and f-GO;

Figure 7 is the critical stress intensity factor of different filler composites and the storage modulus at 25 ° C;

Figure 8 is the thermal stability of different content of f-GO composite;

Figure 9 is a schematic illustration of the preparation process of the present invention.

Detailed ways

The invention will now be further described in detail by way of specific examples. The materials used in the examples were commercially available.

Example 1

(1) The obtained GO was prepared by the Hummer method using graphite as a raw material, and then 500 mg of GO was first dispersed in toluene and ultrasonicated for 1 hour to obtain a graphene oxide suspension, which was under the protection of nitrogen at a temperature of 70 ° C under mechanical stirring. 2.4 g of the silane coupling agent KH560 was added dropwise to the suspension for 5 hours. After the reaction was completed, it was filtered, washed, and dried in a vacuum oven to obtain a black solid powder f-GO.

(2) The silane coupling agent modified graphene oxide (f-GO) in step (1) was sonicated for 30 min, and then dispersed in acetone, then 93.7 g of bisphenol A epoxy resin was added, and the planetary ball mill (250 rpm) was 6 h. After the masterbatch was obtained, the organic solvent was removed under vacuum (0.1 MPa), and 86.1 g of a curing agent (a mixture of methyl hexahydrophthalic anhydride and N,N-dimethylbenzylamine in a mass ratio of 100:1) was added. The high temperature (120 ° C 1 h, 160 ° C 2 h) curing gave a functionalized graphene oxide / epoxy resin nanocomposite with a filler content of 0.10 wt%.

Comparative example 1

0.18 g of graphene oxide (GO) was sonicated for 30 min, then dispersed in acetone, then 93.7 g of bisphenol A epoxy resin was added, and a masterbatch was obtained after 6 h of planetary ball milling (250 rpm) under vacuum (0.1 MPa). The organic solvent was removed, and 86.1 g of a curing agent (a mixture of methyl hexahydrophthalic anhydride and N,N-dimethylbenzylamine in a mass ratio of 100:1) was added, and the mixture was cured at a high temperature (120 ° C for 1 h, 160 ° C for 2 h). An epoxy nanocomposite having a filler content of 0.10% by weight.

Test example 1

The Raman spectrum of the graphene oxide (GO) prepared in Example 1 and the graphene oxide (f-GO) modified by the silane coupling agent prepared in Example 1 is shown in Fig. 1, and the photoelectron spectrum is as shown in Fig. 2. It can be found from the photoelectron spectroscopy that, as shown in Fig. 2, two new peaks appear in the graphene oxide modified by the silane coupling agent, namely Si 2p and Si 2s, respectively, indicating that the silane coupling agent has been successfully obtained. Grafted onto the surface of the graphene oxide. As shown in Fig. 1, the intensity of D peak is obviously enhanced after the oxidized graphite, but the ratio of D peak to G does not change greatly after modification with silane coupling agent,

indicating that the introduction of silane coupling agent is not significantly destroys the structure of the graphene oxide itself.

As can be seen from Fig. 3(a)(b), the surface structure of the graphene oxide is flat, and many wrinkles appear on the surface of the modified graphene oxide. After mechanical ball milling, as shown in Fig. 3 (c) (d), the size of the agglomerates of the modified GO in the epoxy resin was remarkably reduced and the dispersion was better than that of the unmodified GO.

This embodiment specifically illustrates the mechanical properties of the functionalized graphene oxide/epoxy nanocomposite in the present invention with a filler content of 0.10 wt%. Tensile performance test according to ASTM-D638 standard, the instrument uses universal stretching machine (Ametek Ls100plus), at room temperature, the tensile rate is 1.0 mm / min, from the tensile stress-strain curve of Figure 4 can be seen: The materials are all brittle fracture modes, but compared with the composite materials with GO as filler and pure epoxy resin, the functionalized graphene oxide/epoxy nanocomposites with f-GO as filler are broken. The extension load is higher. It can be further seen from the tensile strength of the material of Fig. 5 that the graphene oxide modified by the silane coupling agent can significantly improve the tensile strength of the epoxy resin. If the content of 0.10 wt% of f-GO is added, the tensile strength of the epoxy resin is increased by 40%.

Bending performance test according to ASTM-D790 standard, the instrument uses a universal stretcher (Ametek Ls100plus), at room temperature, the rate is 2.0 mm / min. Figure 6 shows the flexural strength of the material. It can be seen that at ultra-low content (0.10 wt%), f-GO can significantly improve the flexural strength of epoxy resin, while the unmodified GO is not obvious, high content. There is even a certain decline.

The storage modulus was obtained by a dynamic mechanical thermal analyzer (NETZSCH, DMA 242), and the fracture toughness test was obtained by a compact tensile test according to the ASTM-D5045 standard. The thermal stability of the material was measured by a thermogravimetric analyzer (TA Q500) at a heating rate of 20 ° C/min in a nitrogen atmosphere. As shown in Fig. 7, both GO and f-GO can improve the fracture toughness of epoxy resin; in comparison, f-GO toughening effect is more obvious. Similarly, the storage modulus of the f-GO modified epoxy resin has also been greatly improved. For example, when 0.10 wt% of f-GO is added, the storage modulus of the epoxy resin is increased by 15%. The thermogravimetric curve of the functionalized graphene oxide/epoxy nanocomposite is shown in Figure 8. The thermal decomposition temperature (5wt%) of the functionalized graphene oxide/epoxy nanocomposite is added by adding 0.10 wt% of f-GO. The temperature corresponding to the weight loss is significantly improved, indicating that the addition of f-GO improves the thermal stability of the epoxy resin.

Example 2

(1) Using graphite as raw material, the prepared GO was prepared by the Hummer method, and then 500 mg of GO was first dispersed in toluene and ultrasonicated for 1 h to obtain a graphene oxide suspension, which was under the protection of nitrogen at a temperature of 70 ° C under mechanical stirring. 2.4 g of the silane coupling agent KH560 was added dropwise to the suspension for 5 hours. After the reaction was completed, the mixture was filtered, washed, and dried in a vacuum oven to obtain a black solid powder f-GO.

(2) The silane coupling agent-modified graphene oxide (f-GO) prepared in the step (1) was ultrasonicated for 30 min., and then dispersed in acetone, and then bisphenol A epoxy resin 33.79 g, planetary ball mill (250) was added. After 6h, the masterbatch was obtained. Under vacuum conditions (0.5MPa), the organic solvent was removed, and 31.05g of curing agent was added separately. The high temperature (120°C 1h, 160°C2h) solidified to obtain the filler content of 0.25wt%. Graphene oxide modified epoxy resin based nanocomposites.

Comparative example 2

0.16.3 g of graphene oxide (GO) was sonicated for 30 min, then dispersed in acetone, then 33.79 g of bisphenol A epoxy resin was added, and a masterbatch was obtained after 6 h of planetary ball milling (250 rpm) under vacuum (0.5 MPa). The organic solvent was removed, and 31.05 g of the curing agent was separately added and solidified at a high temperature (120 ° C for 1 h, 160 ° C for 2 h) to obtain an epoxy-based nanocomposite having a filler content of 0.25 wt%.

Test example 2

This embodiment specifically illustrates the mechanical properties and thermal stability of the functionalized graphene oxide/epoxy nanocomposite having a filler content of 0.25 wt% in the present invention. Tensile properties of functionalized graphene oxide/epoxy nanocomposites According to ASTM-D638, the instrument uses a universal stretching machine (Ametek Ls100plus) at a tensile rate of 1.0 mm/min at room temperature. 5 It can be seen that under the same content (0.25wt%), the increase of tensile strength of epoxy resin by f-GO is more obvious than that of GO. However, the relative increase is relatively low relative to the low content (0.10 wt%). Bending performance test of functionalized graphene oxide/epoxy nanocomposites According to ASTM-D790 standard, the instrument adopts universal stretching machine (Ametek Ls100plus), and the temperature is 2.0 mm/min at room temperature, as can be seen from Fig. 6. Out, at the same content (0.25wt%), f-GO improves the flexural strength of epoxy resin much higher than GO. The thermal stability of the functionalized graphene oxide/epoxy nanocomposite with a filler content of 0.25 wt% was measured by a thermogravimetric analyzer (TA Q500) at a heating rate of 20 ° C/min in a nitrogen atmosphere. It can be seen from Fig. 8 that the thermal decomposition temperature of the 0.25 wt% f-GO modified resin composite is higher than that of the pure epoxy resin and 0.10 wt% f-GO modified epoxy composite, indicating that f- GO can more effectively improve the thermal stability of composite materials.

Example 3

(1) The obtained GO was prepared by the Hummer method using graphite as a raw material, and then 500 mg of GO was first dispersed in toluene and ultrasonicated for 1 hour to obtain a graphene oxide suspension, which was under the protection of nitrogen at a temperature of 70 ° C under mechanical stirring. 7.5 g of methyl (γ-glycidoxo) diethoxysilane was added dropwise to the suspension for 5 h. After the reaction was completed, it was filtered, washed, and dried in a vacuum oven to obtain a black solid powder. f-GO.

(2) The silane coupling agent-modified graphene oxide (f-GO) prepared in the step (1) was sonicated for 30 min., and then dispersed in acetone, and then bisphenol A epoxy resin 33.70 g was added, and the planetary ball mill (250) After 6 hours, the masterbatch was obtained. Under vacuum conditions (0.3 MPa), the organic solvent was removed, and then 30.97 g of curing agent was added and mixed at high temperature (120 ° C for 1 h, 160 ° C for 2 h) to obtain a filler content of 0.50 wt%. Graphene oxide/epoxy resin nanocomposites.

Comparative example 3

The graphene oxide (GO) 0.325 g was sonicated for 30 min., then dispersed in acetone, then 33.70 g of bisphenol A epoxy resin was added, and the masterbatch was obtained after 6 h of planetary ball milling (250 rpm) under vacuum conditions (0.3 MPa). The organic solvent was removed, and then added with 30.97 curing agent, and solidified at a high temperature (120 ° C for 1 h, 160 ° C for 2 h) to obtain an epoxy-based nanocomposite having a filler content of 0.50 wt%.

Test Example 3

This embodiment specifically illustrates the mechanical properties and thermal stability of the functionalized graphene oxide/epoxy nanocomposite having a filler content of 0.50 wt% in the present invention. Tensile properties of functionalized graphene oxide/epoxy nanocomposites According to ASTM-D638, the instrument uses a universal stretching machine (Ametek Ls100plus) at a tensile rate of 1.0 mm/min at room temperature. 5 It can be seen that under the same content (0.50wt%), the increase of tensile strength of epoxy resin by f-GO is more obvious than that of GO. However, the strength of the modified composite is somewhat reduced relative to the low content (0.10 wt% and 0.25 wt%), which should be due to the secondary agglomeration of graphene at high levels. The flexural properties of the composites were tested according to ASTM-D790, using a universal stretcher (Ametek Ls100plus) at a rate of 2.0 mm/min at room temperature, as can be seen from Figure 6, although filled with 0.50 wt% GO and f -GO has reduced the bending strength of epoxy resin to a certain extent, but the strength of f-GO/epoxy composite is still higher than that of GO/epoxy composite. The thermal stability of the functionalized graphene oxide/epoxy nanocomposite with a filler content of 0.50 wt% was measured by a thermogravimetric analyzer (TA Q500) at a heating rate of 20 ° C/min in a nitrogen atmosphere. It can be seen from Fig. 8 that the decomposition temperature of the composite with a filler content of 0.50 wt% is higher than that of the pure epoxy resin and the low-content (0.10 and 0.25 wt%) f-GO modified composites, indicating a higher At the time of content (0.50 wt%), f-GO can still improve the thermal stability of the composite to a large extent.

Example 4

(1) The prepared GO was prepared by the Hummer method using graphite as a raw material, and then 500 mg of GO was first dispersed in N-methylpyrrolidone and ultrasonicated for 70 min to obtain a graphene oxide suspension under the protection of argon at a temperature of 90 °C. 2 g γ -glycidoxypolytriethoxysilane was added dropwise to the suspension under mechanical stirring at a reaction time of 7 hours. After the reaction was completed, it was filtered, washed, dried in a vacuum drying oven to obtain a black solid. Powder f-GO.

(2) The silane coupling agent-modified graphene oxide (f-GO) prepared in the step (1) was sonicated for 0.1 min for 40 min., and then dispersed in ethanol, and then 33.79 g of a phenolic epoxy resin was added, and a planetary ball mill (250 rpm) for 6 h was added. After the masterbatch is obtained, under vacuum conditions (0.5 MPa), the organic solvent is removed, and 11.15 g of curing agent (diaminodiphenyl sulfone) is separately added and mixed at a high temperature (160 °C for 0.5 h, 180 °C for 2 h, 200 °C for 2 h). A functionalized graphene oxide/epoxy nanocomposite having a filler content of 0.25 wt% was obtained.

Comparative example 4

The graphene oxide (GO) 0.1125g was sonicated for 40min, then dispersed in ethanol, then 33.79g of phenolic epoxy resin was added, and the ballast was obtained by planetary ball milling (250 rpm) for 6h. Under vacuum condition (0.5MPa), organic was removed. The solvent was further mixed with 11.15 g of a curing agent (diaminodiphenyl sulfone), and cured at a high temperature (160 °C for 0.5 h, 180 °C for 2 h, 200 °C for 2 h) to obtain an epoxy-based nanocomposite having a filler content of 0.25 wt%.

Test Example 4

This embodiment specifically illustrates the mechanical properties and thermal stability of the functionalized graphene oxide/epoxy nanocomposite having a filler content of 0.25 wt% in the present invention. Tensile performance test according to ASTM D638 standard, the instrument uses universal stretching machine (Ametek Ls100plus), at room temperature, the tensile rate is 1.0 mm / min, the same content (0.25 wt%), f-GO to epoxy resin The increase in tensile strength is more pronounced than in GO. The bending performance test is based on the ASTM D790 standard. The instrument uses a universal stretching machine (Ametek Ls100plus). At room temperature, the rate is 2.0 mm/min. The bending strength of the epoxy resin is also much higher than that of GO. The thermal stability of the functionalized graphene oxide/epoxy nanocomposite with a filler content of 0.25 wt% was measured by a thermogravimetric analyzer (TA, Q500) at a heating rate of 20 °C/min in a nitrogen atmosphere. The thermal decomposition temperature of the 0.25 wt% f-GO/epoxy composite is higher than that of the pure epoxy and 0.25 wt% GO/epoxy composite, indicating that the surface functionalization of GO further improves the thermal stability of the composite.

Example 5

(1) The obtained GO was prepared by the Hummer method using graphite as a raw material, and then 500 mg of GO was first dispersed in toluene and ultrasonicated for 30 min to obtain a graphene oxide suspension, which was under the protection of nitrogen at a temperature of 70 °C under mechanical stirring. 7.5 g of methyl (γ -glycidoxy) diethoxysilane was added dropwise to the suspension for 5 h. After the reaction was completed, it was filtered, washed, and dried in a vacuum oven to obtain a black solid powder. f-GO.

(2) The silane coupling agent-modified graphene oxide (f-GO) prepared in the step (1) was subjected to sonication for 50 min., and then dispersed in N,N-dimethylformamide, followed by the addition of bisphenol F epoxy resin. 33.70g, after ball milling (250 rpm) for 6h, the masterbatch was obtained. Under vacuum conditions (0.3MPa), the organic solvent was removed, and then 1.011g of curing agent (2-ethyl-4-methylimidazole) was added and mixed. (90 °C 0.5 h, 120 °C 1.5 h, 140 °C 1.5 h) curing to obtain a filler content of 0.25 wt% of functionalized graphene oxide / epoxy resin nanocomposites.

Comparative example 5

The graphene oxide (GO) 0.175 g g was sonicated for 50 min., and then dispersed in N,N-dimethylformamide, then 33.70 g of bisphenol F epoxy resin was added, and a planetary ball mill (250 rpm) for 6 h to obtain a master batch. Under vacuum conditions (0.3 MPa), remove the organic solvent, and then add 1.011g of curing agent (2-ethyl-4-methylimidazole), respectively, high temperature (90 °C 0.5h, 120 °C 1.5h, 140 °C 1.5 h) Curing to obtain an epoxy-based nanocomposite having a filler content of 0.25 wt%.

Test Example 5

This embodiment specifically illustrates the mechanical properties and thermal stability of the functionalized graphene oxide/epoxy nanocomposite having a filler content of 0.25 wt% in the present invention. Tensile performance test according to ASTM-D638 standard, the instrument adopts universal stretching machine (Ametek Ls100plus), the tensile rate is 1.0 mm/min at room temperature, and the tensile strength of epoxy resin is improved by f-GO at the same content. The amplitude is more obvious than GO. Bending performance test according to ASTM-D790 standard, the instrument uses universal stretching machine (Ametek Ls100plus), at room temperature, the rate is 2.0 mm / min, GO and f-GO have little effect on the bending strength of epoxy resin. The thermal stability of the functionalized graphene oxide/epoxy nanocomposite with a filler content of 0.25 wt% was measured by a thermogravimetric analyzer (TA, Q500) at a heating rate of 20 ° C/min in a nitrogen atmosphere. The thermal decomposition temperature of the composite with f-GO content of 0.25wt% is much higher than that of the corresponding content of GO, indicating that the surface treatment of GO can greatly improve the thermal stability of the composite.

Otimização do processo de dispersão de nanotubos de carbono em poliuretano termorrígido

Optimization of carbon nanotubes dispersion process in thermoset polyurethane

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Resumo

Neste trabalho foi desenvolvido um processo empregando misturador de alto cisalhamento e moinho de rolos para dispersar MWCNTs (multiwalled carbon nanotubes) puros e modificados em poliálcool visando a preparação de concentrados de 3% em massa. Condições otimizadas no trabalho permitiram a obtenção de suspensões com menor número e tamanho de agregados de MWCNTs. Compósitos contendo 0,5% em massa de MWCNTs foram preparados por diluição dos concentrados em poliálcool usando mistura mecânica seguida de cura. Resultados de microscopia indicaram que as melhores dispersões foram obtidas com os MWCNTs modificados, os quais permitiram um aumento na tensão na ruptura, no alongamento e uma melhor preservação da estabilidade térmica. Além disso, valores de condutividade elétrica sugerem que o compósito possa ser empregado para dissipação eletrostática. Dessa forma, os resultados obtidos demonstram que a modificação covalente da superfície dos MWCNTs e a utilização de estratégias eficientes de dispersão são essenciais para melhorar as propriedades finais dos nanocompósitos.

Palavras-chave: *dispersão de nanotubos de carbono, nanotubos de carbono modificados, propriedades mecânicas, poliuretano termorrígido elastomérico.*

Abstract

A process employing high shear mixer and roll mill to disperse pristine and modified MWCNTs (multiwalled carbon nanotubes) in polyol was developed in order to prepare 3 wt% masterbatches. The optimum process conditions resulted in suspensions with smaller number and size of nanotube aggregates. Composites containing 0.5 wt% of MWCNTs were prepared by dilution of polyol masterbatches by simple mechanical mixing followed by cure. Microscopy data revealed better dispersion of modified carbon nanotubes in the polymer matrix, which promoted an increase in the tensile strength, elongation and a better preservation of thermal stability. Furthermore, electric conductivity values indicated that the composites can be used for electrostatic dissipation. These results demonstrate that the covalent modification of MWCNTs surface and the use of efficient dispersion strategies are essential to improve nanocomposites' final properties.

Keywords: *carbon nanotubes dispersion, modified carbon nanotubes, thermoset polyurethane elastomer, mechanical properties.*

1. Introdução

A primeira descrição relacionada ao processo de produção de poliuretanos (PUs) baseado na reação de um diisocianato com um diol foi a patente alemã depositada pela I.G. Farben (subdivisão da Bayer) em 1937, tendo Otto Bayer como um dos inventores.^[1]

As propriedades dos PUs e portanto sua aplicação final, dependem do isocianato e diol empregados (e da proporção entre eles), além de outros reagentes como extensores de cadeia, agentes de cura, aditivos, entre outros, bem como do processo envolvido na sua síntese. Esse processo pode acontecer em uma etapa (*one shot*), no qual todos os

reagentes são adicionados no início da reação ou em duas etapas, via produção de um pré-polímero (reação entre o isocianato e poliálcool) que é posteriormente reagido com o extensor de cadeia ou agente de cura (sistemas com um ou dois componentes)^[1,2]. Podem ser produzidos poliuretanos termoplásticos ou termorrígidos, preparando-se desde espumas rígidas ou flexíveis, passando por revestimentos resistentes a produtos químicos, adesivos especiais, selantes, pequenos componentes de máquinas como engrenagens, rodízios e roldanas, até grandes peças industriais de alto desempenho mecânico^[1,2,3].

A presença de ligações covalentes entre as cadeias (ligações cruzadas) fornecem aos PUs termorrígidos propriedades superiores às verificadas para os PUs termoplásticos como resistências à tração, compressão, impacto, abrasão e à degradação causada por ácidos, bases e solventes orgânicos, mantendo as características elastoméricas^[4]. Esses polímeros são geralmente preparados via processamento de pré-polímero, uma vez que possibilita um melhor controle da reação química antes da etapa de reticulação, empregando-se proporções molares da ordem de 1,00 mol de diol para 1,60-2,25 mols de isocianato^[2,3]. Os poliuretanos termorrígidos elastoméricos com excelentes propriedades de resistência ao desgaste são utilizados nas indústrias de mineração, óleo e gás, apresentando grandes vantagens financeiras, sendo utilizados na fabricação de peças estruturais de alto desempenho tais como esteiras de mineração, laminados de interior de aviões ou peças de recepção de grandes tubulações em alto mar (enrijecedores de curvatura)^[5,6].

Os nanotubos de carbono (CNTs) são considerados como um dos materiais mais resistentes já sintetizados pelo homem. Apresentam propriedades elétricas e térmicas extraordinárias somadas a uma boa estabilidade química, o que vem despertando grande interesse na sua utilização em diversas aplicações, principalmente no preparo de compósitos poliméricos com elevada resistência mecânica, por exemplo à tração e flexão, assim como grande estabilidade térmica^[7,8]. Os nanotubos de carbono de paredes múltiplas (MWCNTs) possuem características elétricas entre metal e semicondutor, apresentam módulo de elasticidade de 0,27-0,95 TPa, resistência à tração de 11-63 GPa e condutividade entre 200-3000 W/mK (MWCNTs isolados)^[9-11]. A adição de CNTs em matrizes poliméricas permite melhorias nas suas propriedades mecânicas, térmicas, elétricas, entre outras^[10-12]. A redução no preço dos nanotubos de carbono, especialmente para os MWCNTs, tem contribuído para sua utilização em maiores escalas^[13].

Como o processamento dos poliuretanos termorrígidos é completamente distinto, a dispersão de CNTs nessa matriz para o preparo de compósitos exige técnicas de misturas específicas e seu estudo ainda encontra-se em fase incipiente quando comparado às pesquisas com PUs termoplásticos.

Além das características relacionadas ao nanotubo e ao poliuretano discutidas anteriormente, o processo empregado na dispersão dos CNTs é determinante para as propriedades finais do compósito obtido. Os poucos trabalhos voltados para o preparo de nanocompósitos CNTs/PUs termorrígidos encontrados na literatura são baseados na síntese do polímero em duas etapas (via pré-polímero) com a dispersão dos nanotubos no isocianato ou no polioli com o auxílio de dispersores de alto cisalhamento ou ultrassom^[14-17]. Foram utilizados nanotubos do tipo SWCNTs (nanotubos de carbono de parede simples) e MWCNTs, purificados, modificados e não modificados quimicamente^[15-18]. Nesses trabalhos, os compósitos foram preparados diretamente na concentração de interesse.

No intuito de contribuir para o tema e acrescentar novos dados ao universo de compósitos com poliuretanos termorrígidos, nosso grupo propôs uma metodologia de preparação de compósito PU termorrígido elastomérico/MWCNT por meio

da dispersão dos MWCNTs em pré-polímero empregando dispersor de alto cisalhamento e moinho de rolos a partir de concentrados (*masterbatches*) que posteriormente foram diluídos para a concentração desejada^[19,20]. Como continuação desse estudo, o presente trabalho tem como objetivo avaliar um procedimento de dispersão de CNTs por meio da avaliação da morfologia, propriedades térmicas, elétricas e mecânicas dos nanocompósitos obtidos. Foram utilizados MWCNTs não modificados e modificados (com grupos carboxílicos) em polioli por meio de preparação de concentrados (3,0% em massa de MWCNTs). Esse trabalho visa contribuir para a introdução de nanotubos de carbono no setor produtivo de poliuretanos termorrígidos buscando diminuir o impacto negativo (financeiro e de saúde, meio ambiente e segurança - SMS) na cadeia de valores do produto final.

2. Materiais e Métodos

2.1 Materiais

Foram utilizados MWCNTs adquiridos da empresa Timesnano (China) com pureza >95%, diâmetro externo e comprimento de 2-8 nm e 1-30 µm, respectivamente. Dois tipos de nanotubos foram utilizados: não modificado e modificado com grupos carboxilados (4% de acordo com o fornecedor). Para a síntese do PUE (poliuretano termorrígido elastomérico), foram empregados poli(tetrametileno éter glicol) (PTMG-1000) proveniente da SAFE Chemicals LLC, 2,4-diisocianato de tolueno (TDI) (nome IUPAC 2,4-diisocianato-1-metil benzeno) fornecido pela Bayer S.A., 1,4-butano diol como extensor de cadeia (nome IUPAC butano-1,4-diol) proveniente da M.Cassab Comercio e Indústria LTDA e 4,4-metileno-bis-orto-cloroanilina (MOCA) como agente de cura (nome IUPAC [(4-amino-3-clorofenil) metil]-2-cloroanilina) adquirido da M.Cassab Comercio e Indústria LTDA. Todos os reagentes foram utilizados como recebidos.

2.2 Métodos

2.2.1 Dispersão de MWCNTs em polioli

Inicialmente os MWCNTs modificados e não modificados foram secos em estufa a vácuo por um período de 10 horas a temperatura de 110 °C de forma a garantir a ausência de umidade. Posteriormente, a massa desejada de nanotubos (modificados e não modificados) foi dispersa em PTMG-1000 previamente aquecido a 60 °C. Esta mistura originou um concentrado (*masterbatch*) com teor de 3% em massa de MWCNTs em Polioli. A dispersão foi realizada através de um misturador de alto cisalhamento (Turrax®) a uma velocidade de 20000 rpm por 10 min. Após esta etapa a mistura foi processada em moinho de rolos com separação entre os rolos de 10 e 5 µm e velocidade de 100 rpm a 60 °C. A Figura 1 mostra as etapas usadas na dispersão.

2.2.2 Síntese dos nanocompósitos

Os nanocompósitos foram produzidos em um processo que envolve a síntese de um pré-polímero e sua posterior cura (Figura 1b). A reação para obtenção do pré-polímero foi realizada em um reator de aço inox equipado com agitador mecânico sob vácuo após diluição do concentrado (pela adição de PTMG) para 0,5% em massa de MWCNTs. Foram adicionadas

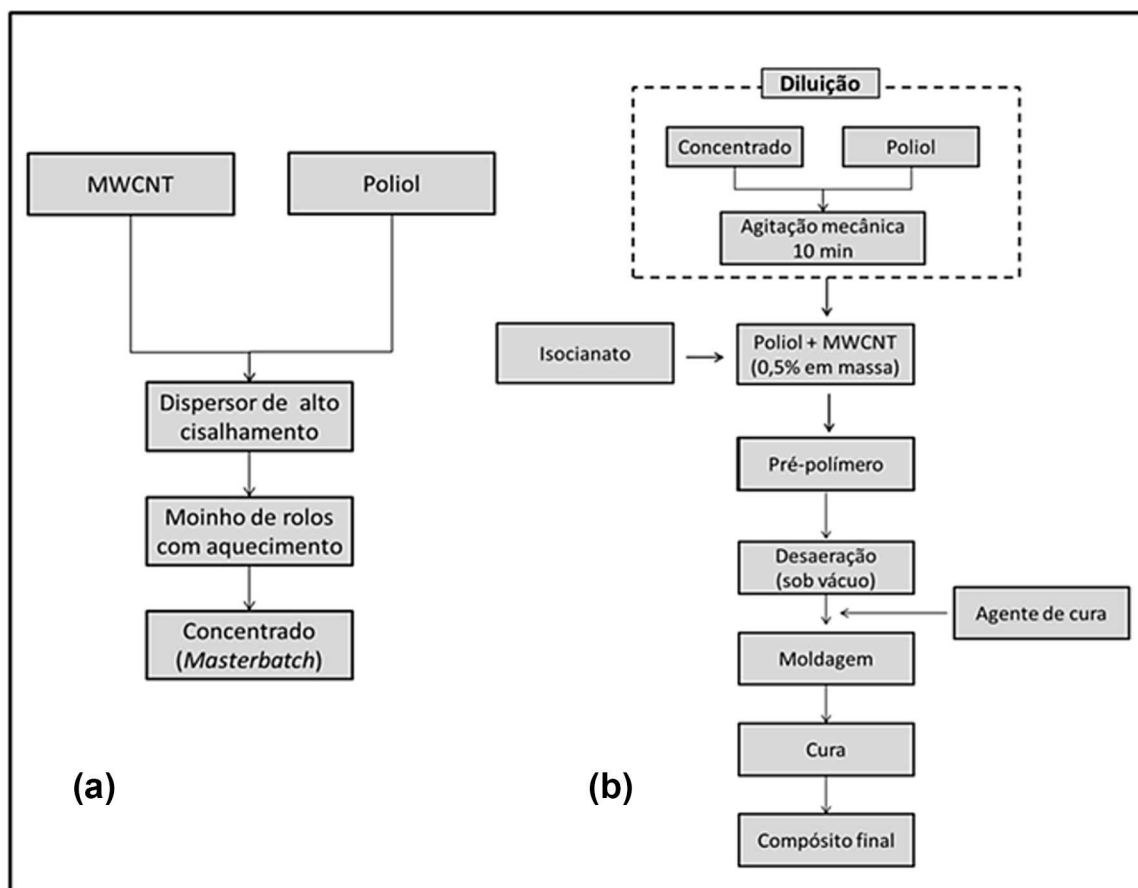


Figura 1. (a) Processo de dispersão dos nanotubos de carbono em poliuretano em duas etapas, primeiro com o agitador mecânico e posteriormente com o moinho de rolos e (b) produção dos compósitos^[21].

quantidades estequiométricas de PTMG 1000/MWCNTs/TDI e o sistema foi mantido a 70 °C por 2 horas com posterior adição de 1,4-butanodiol com a finalidade de aumentar a massa molar do pré-polímero^[22]. Após 2 horas de reação, obteve-se o pré-polímero com teor de NCO livre em torno de 7,4% determinado por titulação com N-dibutilamina^[23]. A segunda etapa do processo de síntese dos nanocompósitos inicia-se com a desaeração do pré-polímero em câmara de vácuo por 90 min. Antes de adicionar o agente de cura (MOCA) o pré-polímero foi reaquecido a 80 °C. A massa de MOCA utilizada foi proporcional à quantidade de NCO livre presente no pré-polímero. Após a adição do MOCA, a mistura foi homogeneizada através de uma agitação suave por aproximadamente 1 min tomando-se o devido cuidado de não inserir bolhas no sistema. Em seguida a mistura foi vertida em moldes que, posteriormente, passaram pelo processo de cura a 100 °C por 10 h. Posteriormente o processo de pós-cura final foi conduzido mantendo as amostras por 15 dias a temperatura ambiente^[20].

2.2.3 Caracterização

A caracterização detalhada das amostras de nanotubos modificados e não modificados foi descrita em um trabalho prévio do nosso grupo^[20].

Os nanocompósitos foram caracterizados por microscopia óptica (MO) utilizando um microscópio Olympus, modelo BX50F-e. Sua morfologia foi examinada por microscopia eletrônica de varredura (MEV) utilizando microscópio com canhão de emissão por efeito de campo (Quanta 200 - FEG/FEI). Para esta análise as amostras foram fraturadas em nitrogênio líquido e suas superfícies de fratura foram recobertas por uma fina camada de ouro. Com o propósito de avaliar a dispersão micrométrica e nanométrica dos MWCNTs na matriz de PUE foi utilizada microscopia eletrônica de transmissão (MET) em microscópio Tecnai – G2-20/FEI. Para esta análise, as amostras foram preparadas com o auxílio da técnica de criomicrotomia.

Espectros de absorção no infravermelho do PUE e dos nanocompósitos foram obtidos utilizando espectrômetro FTIR (dispositivo de ATR, modelo 380 Nicolet Thermo Scientific) com uma faixa espectral de 4000-680 cm⁻¹. Foram realizadas 32 varreduras com resolução de 4 cm⁻¹. Medidas elétricas nestas mesmas amostras foram feitas a 25 °C utilizando um potenciostato Autolab PGSTAT30 Ecochemie. Foi utilizada uma célula experimental de impedancimetria modelo AN8080 da marca Analógica possuindo dois eletrodos bloqueantes de aço inox de área 0,27 cm². A faixa de frequência usada foi entre 1 MHz e 0,5 Hz, sob 0 V e amplitude de perturbação

de 10 mV. As amostras foram medidas na forma de filmes com espessura de 0,3 mm.

O PUE e os nanocompósitos foram submetidos a ensaios de tração e medição da dureza (Shore D). Os ensaios de tração foram realizados em máquina de ensaio Kratos modelo TRCv59D-USB com célula de carga de 100 Kgf, velocidade de deslocamento de 500 mm/min a temperatura de 22,0 °C e umidade relativa de 44,0% empregando-se um número mínimo de 03 ensaios para cada amostra. Análises termogravimétricas (TGA) destas amostras foram realizadas em atmosfera de nitrogênio com razão de aquecimento de 10 °C/min utilizando o equipamento TGA Q5000 dentro de um intervalo de temperatura de 20 a 800 °C.

3. Resultados e Discussões

3.1 Dispersão dos MWCNTs em polioli

Na síntese de poliuretanos empregando-se reação em duas etapas, uma primeira avaliação da dispersão dos nanotubos de carbono pode ser realizada através de imagens

obtidas por microscopia ótica. Essa técnica é muito útil para verificar se há presença de agregados de CNTs, inferir sobre o número e tamanho dos mesmos e assim julgar a eficiência do processo de dispersão utilizado^[24,25].

A Figura 2 mostra as etapas do processo de dispersão dos nanotubos de carbono obtidas no presente trabalho e as imagens de microscopia ótica do sistema em cada etapa.

Como descrito na literatura, o grande desafio no preparo de nanocompósito poliméricos é a dispersão eficiente dos nanotubos de carbono na matriz, tanto em suspensão quanto no estado sólido^[26]. A imagem de MO (Figura 2b) mostra a sedimentação dos nanotubos de carbono (MWCNT modificado) após sua adição ao polioli e agitação simples. Para diminuir a viscosidade do meio e melhorar a processabilidade, o sistema foi aquecido a 60 °C. Na primeira etapa, a suspensão foi submetida a um dispersor de alto cisalhamento (Turrax®) e a melhor dispersão foi obtida após 10 min na velocidade de 20000 rpm. No entanto, constata-se que existem vários agregados de diferentes tamanhos (na faixa de 3 µm até 67 µm) de nanotubos de carbono não dispersos, o que indica

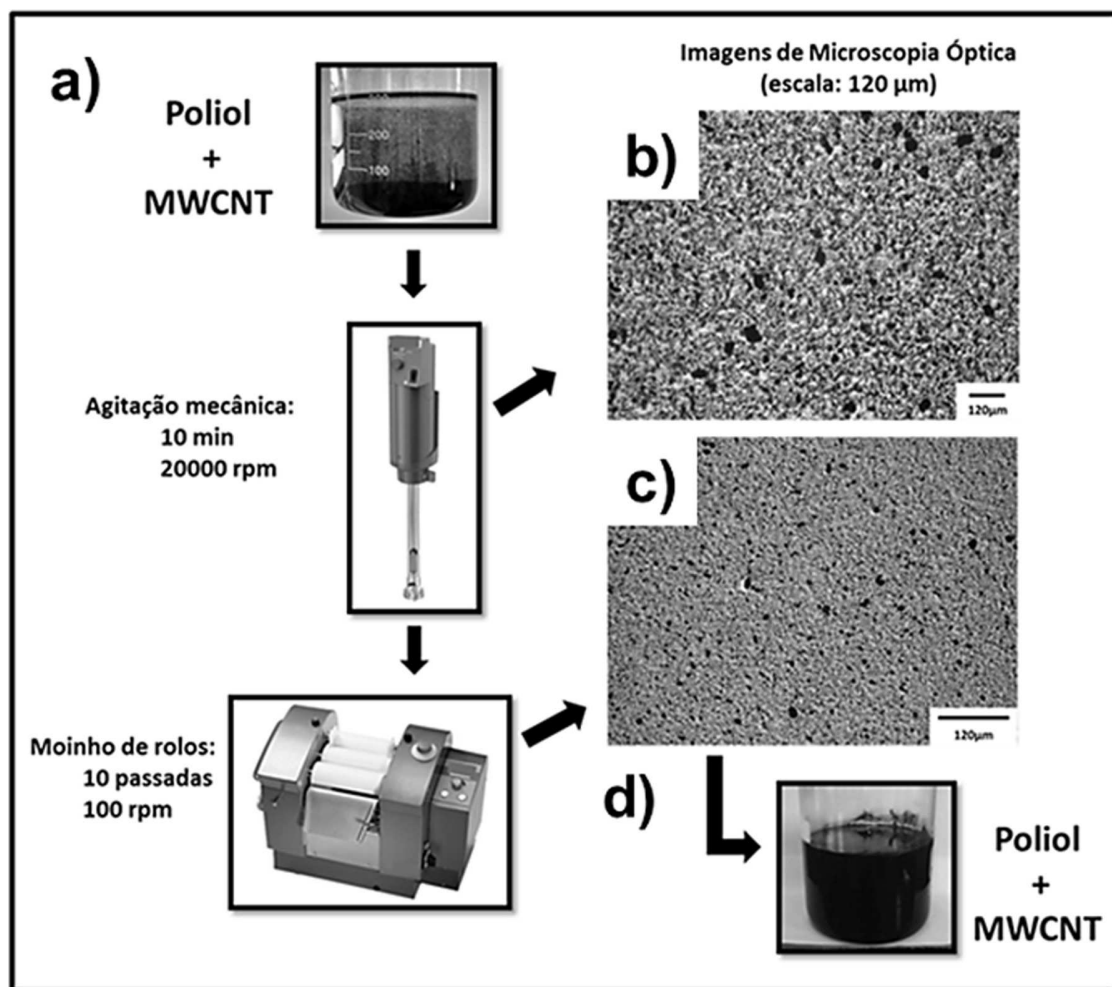


Figura 2. Processo de dispersão dos nanotubos de carbono em polioli em duas etapas: primeiro com o agitador mecânico e posteriormente com o moinho de rolos. (a) Polioli e nanotubo formando duas fases, (b) imagem de MO da dispersão dos CNTs em polioli utilizando apenas agitador mecânico, (c) imagem de MO da dispersão dos CNTs em polioli após as duas etapas de uso do agitador mecânico e do moinho de rolos, (d) CNTs dispersos em polioli formando uma única fase.

que apenas a utilização do dispersor não é suficiente para atingir o efeito desejado. Na sequência, o sistema foi levado a um moinho de rolos e submetido a diferentes condições de processamento, variando-se a separação entre os rolos, a velocidade de rotação do moinho e o número de vezes pelo qual determinada quantidade de material era submetida aos três rolos (“ciclos”). A imagem de MO (Figura 2c) mostra a dispersão obtida (MWCNT modificado) com separação entre os rolos de 10 e 5 μm , velocidade de rotação de 100 rpm após 10 ciclos. Embora ainda existam pequenos agregados (entre 0,7 e 21 μm), verifica-se que a quantidade de material disperso aumentou com a introdução da etapa de moagem. O aspecto da dispersão final é mostrado na Figura 2d. Para o MWCNT não modificado, esta também é a melhor condição de dispersão, embora tenham sido observados agregados maiores e em maior número que para o MWCNT modificado. A melhor dispersão dos MWCNTs modificados está relacionada à sua melhor interação com o PTMG, o que previne a reagregação.

A vantagem do processo de dispersão do nanotubo em polioli em relação ao realizado em pré-polímero é que o controle da umidade não precisa ser rigoroso, o que facilita o transporte e armazenamento do produto. Como já mencionado, a proporção isocianato/polioli é crucial para a obtenção de PUE com propriedades desejadas. Após a reação de formação do pré-polímero, a manutenção da quantidade de isocianato livre calculada para permitir a reação com o agente de cura é importante. A presença de vapor de água altera consideravelmente o teor de NCO livre, e, portanto, exerce grande influência nas características do compósito final.

As imagens de MO mostradas na Figura 2 são relativas ao concentrado (*masterbatch*) contendo 3% em massa de CNT funcionalizado. Esse concentrado pode ser armazenado por vários dias sem que nenhuma sedimentação ocorra.

Para preparo dos compósitos, o *masterbatch* pode ser diluído para a concentração desejada pelo emprego de agitação mecânica simples. Isso facilita a introdução dos CNTs na cadeia produtiva de produtos/peças de poliuretanos termorrígidos, uma vez que não há necessidade de utilização de equipamentos específicos, pois os CNTs já estarão devidamente dispersos no concentrado, nem problemas relacionados à SMS, porque não haverá risco de presença de material particulado sólido suspenso no ar no ambiente de produção.

3.2 Caracterização dos nanocompósitos

Para o preparo dos nanocompósitos, os concentrados contendo ambos os MWCNTs (modificados e não modificados) foram diluídos em polioli para concentração de 0,5% em massa e curados. Os materiais foram caracterizados após 15 dias de pós-cura (temperatura ambiente).

A dispersão dos MWCNTs na matriz e a morfologia dos nanocompósitos foram avaliadas por MO, MEV e MET.

Na Figura 3a, b são apresentadas as imagens de MO para os compósitos preparados com MWCNTs modificados e não modificados. Pode-se constatar que não houve mudança substancial na dispersão/distribuição dos nanotubos no estado sólido em relação aquela verificada para as suspensões em PTMG, ou seja, com as etapas de reação para a síntese de

pré-polímero e cura não houve reagregação dos nanotubos de carbono. Tal fato é resultante da eficiência do processo empregado na dispersão para ambos os nanotubos. Como nas suspensões, pode-se observar a presença de aglomerados menores de MWCNTs modificados (entre 0,6 e 12 μm) em relação aos MWCNTs não modificados (faixa de 0,8 μm até 27,0 μm), provavelmente devido a sua melhor interação com a matriz de PUE.

As imagens de MEV (Figura 3c, d) corroboram o que foi pressuposto a partir das imagens de MO. Percebe-se que os MWCNTs modificados apresentaram uma melhor adesão à matriz polimérica como resultado da interação MWCNT-COOH:PUE.

Além disso, como destacado por McClory e colaboradores^[15], outro indício dessa interação é que as imagens foram obtidas na superfície de fratura e não foram observadas regiões que indicassem que o MWCNT foi puxado para fora da matriz no momento da fratura. De fato, essa interface MWCNT:matriz é essencial para o reforço mecânico no sistema. As imagens das Figura 3c, d exibem MWCNTs curvados e entrelaçados na matriz polimérica, ligando “pontos” da superfície fraturada. Essa morfologia, verificada em outros compósitos nanotubo:PUs (termorrígido ou termoplástico), é essencial para a transferência de tensão entre os CNTs e a matriz quando o material é sujeito a uma sollicitação mecânica^[15,27]. Como evidência do recobrimento pelo polímero, o diâmetro dos nanotubos de carbono visíveis nas imagens é da ordem de 23 nm a 34,0 nm nos compósitos com MWCNTs não modificados e de 12,0 nm a 36,0 nm nos compósitos com MWCNTs modificados. Valores bem menores foram observados para esses nanotubos isolados (diâmetro na faixa de 5,0 nm a 15,0 nm). Além disso, como os MWCNTs possuem apenas 4% de funcionalização, não deve haver prejuízo considerável às suas propriedades elétricas, e a morfologia verificada também é propícia à obtenção de boas propriedades elétricas para os compósitos.

A melhor dispersão dos MWCNTs modificados também foi evidenciada nas imagens de MET (Figura 3e, f). Para o nanocompósito preparado com MWCNTs não modificados (Figura 3e), observou-se uma baixa distribuição nanométrica destas cargas com presença significativa de agregados. No caso de utilização de MWCNTs modificados (Figura 3f), pode ser verificada uma melhor distribuição dos MWCNTs por toda a região do nanocompósito, uma vez que, além de agregados nanométricos, há a presença de nanotubos individuais dispersos ao longo da matriz^[16].

Assim, constata-se que o método de preparo dos nanocompósitos a partir de *masterbatch* propicia uma boa dispersão dos nanotubos de carbono na matriz de PUE e que os MWCNTs modificados apresentam-se como materiais mais indicados para preparação de compósitos com propriedades melhoradas.

Segundo a literatura^[18], com o tratamento ácido são gerados grupos oxigenados quimisorvidos à superfície dos nanotubos de carbono, como os anidridos de ácido, carbonilas, hidroxilas, grupos carboxílicos, fenólicos e lactônicos, sendo esses três últimos os principais. Os grupos fenólicos, carboxílicos e álcoois são de particular interesse uma vez que podem participar da reação de polimerização com o isocianato originando grupos amida e uretano que

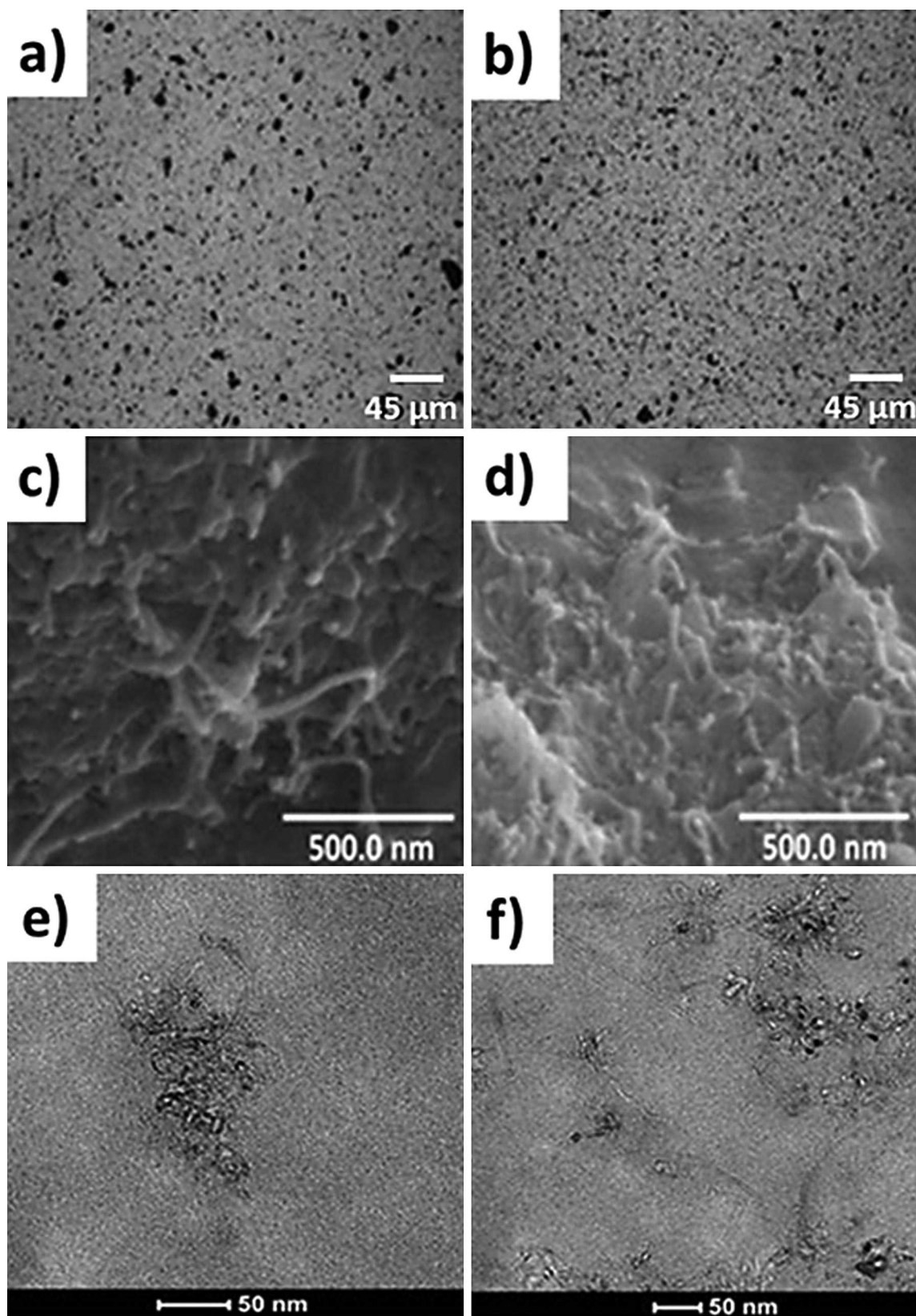


Figura 3. Imagens de MO da superfície dos compósitos contendo 0,5% em massa de: (a) MWCNTs não modificados e (b) MWCNTs modificados. Imagens de MEV da superfície da fratura dos nanocompósitos contendo 0,5% em massa de: (c) MWCNT não modificados e (d) MWCNTs modificados e imagens de MET de cortes de criomicrotomia dos nanocompósitos contendo 0,5% em massa de: (e) MWCNTs não modificados e (f) MWCNTs modificados.

contribuem para a formação de ligações cruzadas no material final^[18]. Diante disso, a espectroscopia vibracional na região do infravermelho foi utilizada para estudar os diferentes materiais.

A Figura 4 apresenta o espectro de FTIR do PUE e dos nanocompósitos contendo nanotubos de carbono modificados e não modificados.

Através da análise da Figura 4 pode-se observar uma banda larga de baixa intensidade em 3277 cm^{-1} característica da própria deformação axial da ligação de hidrogênio do grupo N-H com o oxigênio derivado o grupo éter do segmento flexível^[16,28,29]. Uma banda na região de 2937 cm^{-1} corresponde à deformação axial assimétrica de C-H dos grupos CH_2 ^[30]. Em 2854 cm^{-1} foi observada banda de baixa intensidade correspondente à deformação axial de CH_2 alifático^[30]. Em 1695 cm^{-1} observa-se banda característica de baixa intensidade correspondente à deformação axial C=O interagindo com ligação de hidrogênio. As bandas agudas que aparecem em 1525 e 1220 cm^{-1} podem ser atribuídas às ligações C-N de grupos uretanos^[30]. A banda em 1101 cm^{-1} corresponde à deformação axial assimétrica e simétrica da ligação C-O-C^[30,31]. Para os nanocompósitos, não foram observadas bandas adicionais ou deslocamentos consideráveis em relação à PUE, nem diferenças devido à funcionalização dos nanotubos. Possivelmente isso está relacionado à baixa concentração de nanotubos utilizada, bem como à presença de apenas 4% de grupos carboxílicos no MWCNT modificado. Dessa forma não foi possível avaliar a diferença entre os MWCNTs, nem se há interação preferencial com os domínios rígidos ou flexíveis do poliuretano termorrígido.

A degradação térmica de poliuretanos é um processo complexo e pode ocorrer em pelo menos duas etapas conforme relatado na literatura^[32]. A primeira etapa está relacionada à decomposição térmica dos segmentos rígidos e a segunda à degradação dos segmentos flexíveis^[32-34]. As curvas TG e DTG para o PUE e os nanocompósitos são apresentadas na Figura 5. Por meio da curva DTG, pode-se observar que a degradação térmica do PUE acontece em pelo menos três estágios, com máximos em 287 , 340 , 405 °C .

A decomposição térmica dos nanocompósitos também ocorre em três estágios, apresentando pequenas variações de temperatura quando comparados ao PUE. Os resultados mostraram que a estabilidade térmica dos nanocompósitos diminuiu em ~ 12 e 9 °C para os nanocompósitos contendo MWCNTs não modificados e modificados, respectivamente. O decréscimo na temperatura de degradação para as amostras de MWCNTs não modificados possivelmente ocorreu devido à dispersão dos mesmos na matriz com presença de maiores agregados, observada pelas imagens de microscopias, e à presença de impurezas adsorvidas nas paredes externas dos tubos que contribuíram para um aumento na velocidade de degradação dos segmentos rígidos deste nanocompósito^[29,35]. Já para os nanocompósitos contendo MWCNTs modificados, a menor variação provavelmente é devido à melhor dispersão e remoção de impurezas adsorvidas nas superfícies dos tubos como consequência do processo de modificação química.

A fim de avaliar a influência dos MWCNTs nas propriedades mecânicas da matriz de PUE, ensaios de tração e dureza foram realizados. Os resultados obtidos para o PUE

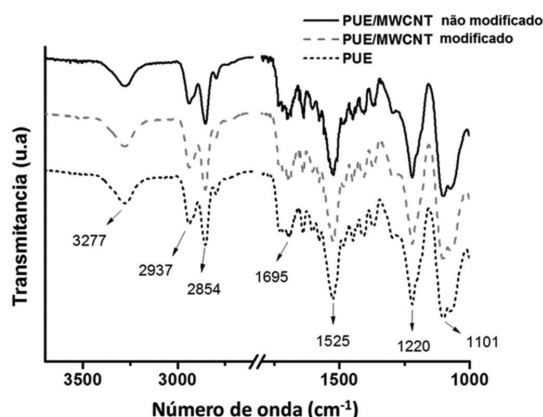


Figura 4. Espectros de FTIR do PUE e dos nanocompósitos contendo 0,5% em massa de MWCNTs modificados e não modificados.

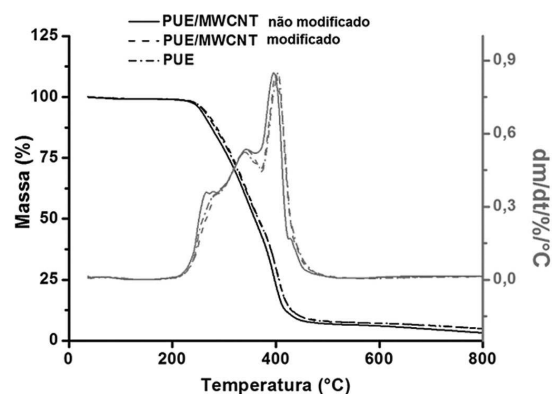


Figura 5. Curva TG e DTG para a PUE e nanocompósitos em atmosfera de N_2 .

e nanocompósitos produzidos com MWCNTs modificados e não modificados são apresentados na Figura 6.

Como já discutido, além das características dos nanotubos de carbono e do procedimento utilizado na dispersão dos mesmos, a natureza da matriz polimérica tem grande influência nas propriedades dos nanocompósitos poliméricos. Portanto, utilizou-se como estratégia para dispersão dos MWCNTs e aumento nas propriedades mecânicas, avaliar a influência do processo pela comparação entre as propriedades dos compósitos preparados com a mesma matriz e nanotubos modificados e não modificados.

A tensão na ruptura reduziu cerca de 7% com a introdução de MWCNTs não modificados. Já no nanocompósito produzido a partir de MWCNTs modificados verificou-se um aumento em torno de 10% em relação à matriz de PUE (Figura 6a). O alongamento na ruptura apresentou um comportamento semelhante, com uma redução de cerca de 3% para o nanocompósito produzido a partir de MWCNTs não modificados e um aumento em torno de 10% para o nanocompósito com MWCNTs modificados, comparando-se aos valores da PUE (Figura 6b). Para o módulo de elasticidade há uma diminuição de cerca de 17%

no nanocompósito preparado com MWCNT não modificado e de aproximadamente 8% para o nanocompósito com MWCNT modificado (Figura 6c). Através da Figura 6d, pode-se verificar que os nanotubos de carbono exercem pouca influência na dureza (Shore D) da matriz.

Esses resultados corroboram com o que foi observado nos estudos de microscopia, uma vez que mostram que os MWCNTs modificados por tratamento ácido são mais indicados como carga de reforço devido a melhor interação com a matriz e formação de uma interface propícia para a transferência de tensão entre o nanotubo de carbono e o polímero quando o compósito é submetido à tensão mecânica. Esse comportamento foi mostrado na literatura para compósitos preparados com matrizes termorrígidas distintas da utilizada no presente trabalho^[18,36].

Para compósitos poliméricos em geral, termoplásticos ou termorrígidos, com MWCNTs, a tendência mais frequente é o aumento no módulo de elasticidade e a diminuição no alongamento de ruptura devido à inserção de uma carga rígida. No entanto, as potenciais influências dos MWCNTs são amplas e também é possível um aumento no alongamento concomitante ao módulo de elasticidade, como já foi relatado para sistemas de PUE/MWCNTs^[14], bem como o aumento no alongamento com redução no módulo^[37,38]. O efeito nas propriedades é específico para cada sistema,

considerando tipo de nanotubo e tipo de matriz polimérica. Guo e colaboradores relataram uma diminuição do módulo e um aumento do alongamento para compósitos de epóxi (termorrígido de alto módulo) de forma proporcional à concentração utilizada de MWCNTs funcionalizados^[38]. Eles discutiram que o aumento na deformação pode ser resultante do deslizamento de camadas internas dos MWCNTs. Portanto, neste caso os nanotubos de carbono atuaram como aditivo para melhorar a ductilidade e não a rigidez do sistema epóxi. Através da funcionalização, esse deslizamento pode ser favorecido devido à camada externa de MWCNTs ser mais defeituosa, a qual interage de forma mais fraca com as camadas internas.

Outro fator importante para as propriedades observadas é que a formulação de PUE estudada apresenta um módulo muito elevado, de 290 MPa (valor obtido pela extrapolação da secante a 2% de deformação), enquanto os demais trabalhos na literatura sobre PUE/MWCNTs reportam PUE com módulos abaixo de 10 MPa^[14,16,17]. Assim, apesar dos MWCNTs resultarem em redução no módulo, seu valor ainda é mantido em um patamar elevado com a introdução de MWCNTs funcionalizados.

A introdução de MWCNTs funcionalizados propiciou um aumento da ductilidade do material e o aumento na tensão na ruptura em 10%, o que é o resultado de ganho

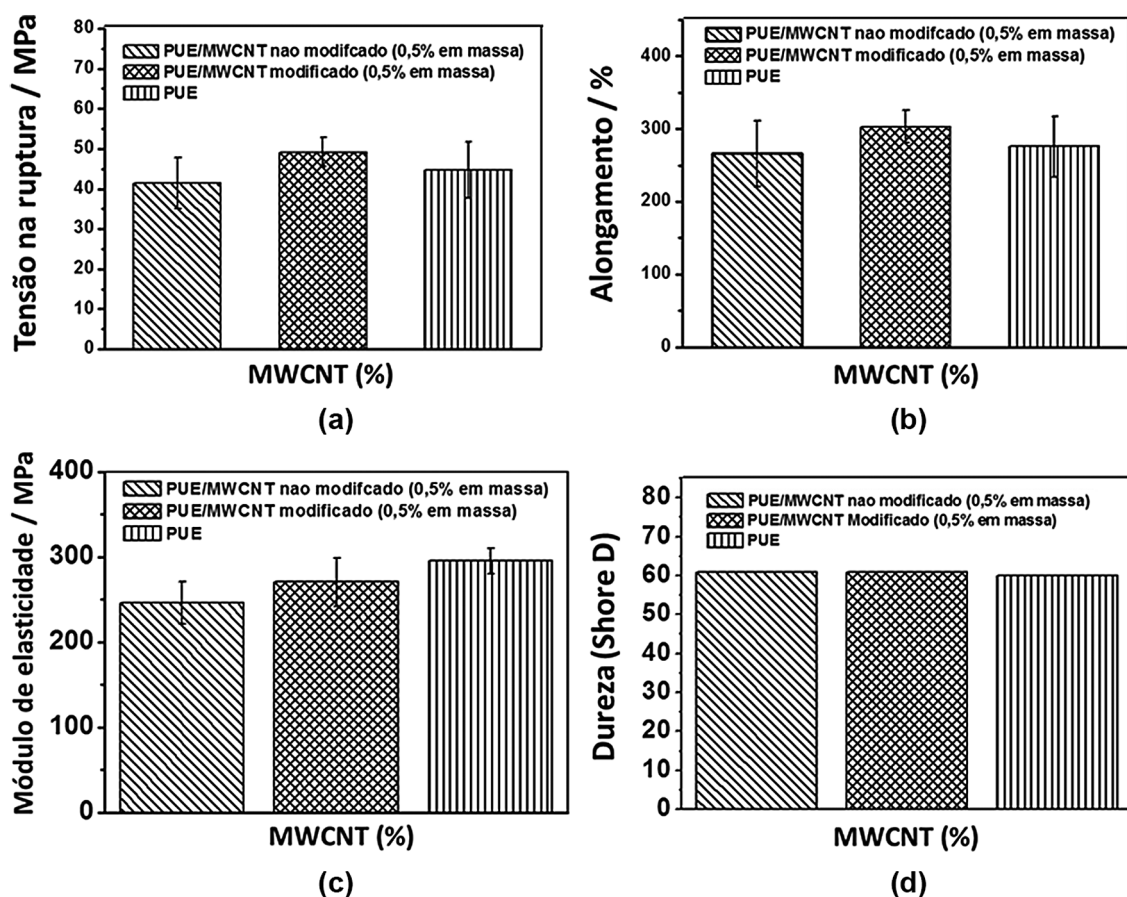


Figura 6. Propriedades mecânicas das amostras estudadas. (a) Tensão na ruptura, (b) alongamento percentual na ruptura, (c) módulo de elasticidade (secante a 2%) e (d) dureza (Shore D).

mais significativo. No caso deste tipo de termorrígido um ganho nesta faixa já é de relevância para considerar-se a aplicação do compósito em projetos de engenharia exigentes. Quando a dispersão de MWCNTs é ineficaz e o compósito é formado por aglomerados grandes, estes atuam como concentradores de tensão, que facilitam a propagação de trincas e reduzem a tensão na ruptura do material^[17]. Portanto, somente uma nanocarga especial pode promover algum ganho em propriedades mecânicas para polímeros desta classe.

Embora aumentos modestos tenham sido verificados em relação a alguns desses trabalhos, o procedimento descrito permite a preparação de quantidades escaláveis de concentrado. Um diferencial importante para essa rota de processo, que constitui uma maior viabilidade para introdução na indústria, é a utilização de moinho de rolos como equipamento principal de processamento. As referências de PUE/MWCNTs relatam a incorporação da nanocarga por ultrassom ou dispersores de alto cisalhamento^[14-16]. No entanto, essas técnicas são baseadas em fontes de dispersão localizadas (nos transdutores ultrassônicos ou nas pontas dos dispersores de alto cisalhamento) e, portanto, apresentam dificuldades no aumento de escala sem resultar em heterogeneidades no processamento. O moinho de rolos garante um processamento homogêneo, onde todo o material é submetido a uma mesma tensão de cisalhamento, sendo uma técnica de alto interesse tecnológico para o aumento de escala. Além disso, os nanotubos de carbono utilizados foram modificados com apenas 4% de grupos carboxílicos (segundo dados do fornecedor e confirmados por TGA). Nosso grupo desenvolveu uma metodologia de funcionalização por tratamento ácido em escala que possibilita a obtenção de nanotubos de carbono com maiores graus de funcionalização sem variação drástica na sua razão de aspecto e com a utilização de quantidades muito pequenas de ácido^[21]. Esse procedimento de modificação de superfície dos nanotubos de carbono é muito mais simples dos que as utilizadas nos trabalhos citados anteriormente^[37,38]. Assim, acredita-se que a utilização de nanotubos com maior grau de funcionalização aliado ao processo de dispersão otimizado no presente trabalho, trarão efeitos mais significativos nas propriedades mecânicas.

A dispersão de nanocargas em polímeros isolantes produz um aumento significativo na condutividade elétrica do material quando a concentração dos nanotubos de carbono atinge o limiar de percolação (aumento de várias ordens de grandeza na condutividade do material em relação à matriz polimérica). Os nanocompósitos obtidos neste trabalho foram estudados por espectroscopia de impedância eletroquímica e a condutividade elétrica foi obtida com o emprego da Equação 1^[27,39].

$$C = \frac{l}{A \times R} \quad (1)$$

sendo l a espessura, A a área e R a resistência dos filmes.

A Tabela 1 mostra os resultados de condutividade para todas as amostras investigadas.

Os nanocompósitos com MWCNTs modificados e não modificados apresentaram valores de condutividades superiores em aproximadamente duas ordens de grandeza em relação ao valor obtido para a matriz polimérica pura. No entanto, esses valores ainda são menores que

Tabela 1. Resultados de condutividade para PUE e para os diferentes nanocompósitos preparados.

Amostras	Condutividade (S/cm)
PUE	$3,4 \times 10^{-6}$
PUE/MWCNT não modificado 0,5% em massa	$9,8 \times 10^{-5}$
PU/MWCNT modificado 0,5% em massa	$8,7 \times 10^{-5}$

usualmente obtidos considerando-se a alta condutividade dos nanotubos de carbono isolados^[40,41]. Segundo Lavall e colaboradores, dependendo da adesão do polímero aos CNTs, há formação de uma camada isolante em torno destas partículas condutoras, diminuindo o contato entre os tubos e, em consequência, as propriedades de condução elétrica^[27]. A condutividade de nanocompósitos do tipo polímero/CNTs depende intrinsecamente dessa relação polímero/nanotubo e é sempre menor do que a condutividade obtida pelo contato direto entre os tubos^[42]. No presente trabalho, além desse efeito, acredita-se que a concentração utilizada (0,5% de MWCNTs) esteja abaixo do limiar de percolação para esse tipo de sistema. Condutividades entre 10^{-7} e 10^{-1} S/cm já foram descritos na literatura para sistemas semelhantes, embora a maioria dos valores estejam na ordem de 10^{-4} S/cm^[42]. Em um trabalho anterior do grupo foram obtidos valores próximos a 10^{-5} S/cm para a condutividade de um sistema baseado em poliuretano termoplástico (TPU) com 1% em massa de nanotubos modificados^[39], mas neste caso o TPU de partida era altamente isolante, apresentando condutividade de 10^{-12} S/cm. Valores de condutividade da ordem obtida no presente trabalho permitem que o compósito possa ser empregado em aplicações nas quais a dissipação eletrostática seja um requisito^[43]. Para atingir condutividades que permitam uso em blindagem eletromagnética deve-se adicionar maior quantidade de nanotubos de carbono, mas será necessário também modificação de estratégia de processamento para produzir dispersões adequadas à percolação elétrica^[39,43].

4. Conclusão

A produção de *masterbatches* de MWCNTs em polioli através de uma combinação de misturador de alto cisalhamento e moinho de rolos, possibilitou a fabricação de nanocompósitos com 0,5% em massa de MWCNTs em PUE após diluição, utilizando somente agitação mecânica, sem prejuízo da dispersão dos nanotubos de carbono. Os MWCNTs modificados com grupos oxigenados resultaram em uma melhor dispersão e adesão dos CNTs à matriz polimérica, que refletiram em melhores resultados mecânicos, como tensão na ruptura e alongamento, além de uma melhor preservação da estabilidade térmica. A condutividade dos nanocompósitos foi aumentada em aproximadamente duas ordens de grandeza, o que possibilita o uso do material em aplicações que demandam dissipação eletrostática. A metodologia utilizada garante um processamento homogêneo, com possibilidade de aumento de escala e alta atratividade tecnológica para inserção na indústria. A avaliação do grau de dispersão dos MWCNTs em PUE pelo método desenvolvido neste trabalho e das propriedades obtidas consequentemente, permitem projetar a fabricação de nanocompósitos com diferentes conjuntos de propriedades através do controle do teor de grupos oxigenados nos MWCNTs, da concentração utilizada de nanocarga e das etapas de processo.

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