Effect of Amount of Carbon Nanotubes in Polyurethane Dispersions

E. Orgilés-Calpena, F. Arán-Aís, A. M. Torró-Palau, C. Orgilés-Barceló*

Summary: The possibility of incorporating nanotubes to adhesives opens a new range of innovative solutions, due to their unique structure and properties. In this sense, the objective of this work is the addition of carbon nanotubes (CNTs) to waterborne polyurethane adhesives (WBPU) to improve their rheological, viscoelastic, thermal and mechanical properties and even impart some electrical conductive character to adhesives. Specifically, the stability of the dispersion and the influence of the amount of nanotubes on the properties of the adhesive have been studied.

Keywords: adhesives; electrical conductivity; nanocomposites; polyurethanes

Introduction

Carbon nanotubes are an allotrope form of carbon, like diamond, graphite or fullerenes. Its structure can be considered from a graphene sheet rolled upon itself. Depending on the degree of rolling and the conformation of the original sheet, nanotubes are obtained with different diameters and internal geometry.[1,2] Carbon nanotubes are capable of generating a multitude of changes in polymers properties just being added in very small quantities. The use of nanotechnology enables the production of polymeric materials with improved performance and new features, contributing to the development of new applications in traditional and emerging sectors. The incorporation of nanofillers to polymers contributes to a new generation of nanostructured materials. In this sense, carbon nanotubes have become a very attractive material for use as reinforcement at the nanoscale.[3,4] The possibility of incorporating nanotubes to adhesives opens a new range of innovative solutions, due to their unique structure and properties: high aspect ratio, high Young's modulus, excellent mechanical strength and good thermal and electrical conductivity.

The objective of this work is the addition of carbon nanotubes (CNTs) to waterborne polyurethane adhesives (WBPU) to improve their rheological, viscoelastic, thermal and mechanical properties and even impart some electrical conductive character to adhesives.

Experimental Part

Materials and Preparation of WBPU/CNT Adhesives

A dispersion of carbon nanotubes was used, avoiding direct manipulation of nanoparticles in solid state and minimizing the risk associated with handling nanofillers. Multiwalled carbon nanotubes (Figure 1) in aqueous dispersion (Aquacyl®0101) were provided by Nanocyl S.A. (Sambreville, Belgium) whose most important properties are shown in Table 1.

Carbon nanotubes were added to a commercial anionic polyurethane dispersion (Dispercoll® U54) provided by INSOCO S.L. (Alicante, Spain) whose most important properties are shown in Table 2. Several polyurethane adhesives with a different amount of carbon nanotubes (0.1–1 wt%) were prepared by mechanical dispersion (800 rpm, 30 minutes).

INESCOP. Footwear Research Institute. Industrial Zone Campo Alto. 03600 Elda, Alicante, Spain
E-mail: eorgiles@inescop.es

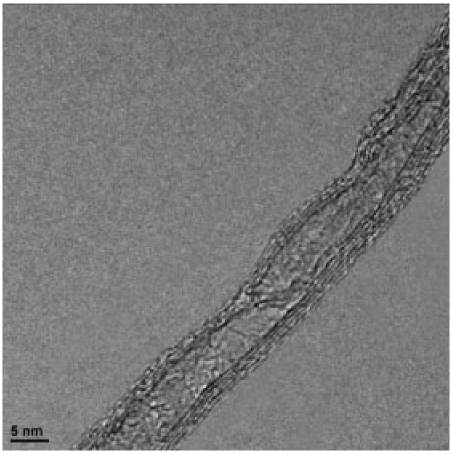

Figure 1.
TEM image of a CNT before incorporating to polyurethane adhesive.

Table 1.
CNTs properties (data supplied by the manufacturer).

Property	Value
Nanotube diameter (TEM)	9.5 nm
Nanotube length (TEM)	1.5 μm
Surface area (BET)	250–300 m^2/g
Carbon purity (TGA)	90%

Table 2.
WBPU properties.

Property	Value
Brookfield Viscosity	337 mPa · s
Solids content	52%
pH	7.0
Mean particle size	166 nm

Characterization Methods

The rheological properties of the polyurethane films were determined in a shear stress-controlled Bohlin CS50 rheometer, using a plate-plate geometry. The thermal properties were analyzed in a differential scanning calorimeter Mettler Toledo DSC 30. Transmission electron microscopy (TEM, JEOL model JEM-2010) was employed to observe the distribution of the carbon nanotubes into the polyurethane matrix. The adhesion properties were studied by T-peel strength tests of leather/polyurethane adhesive/SBR rubber joints according to the standard EN 1392:2007. Electrical conductivity measurements were carried out using a Keithley 2000 picoamperimeter.

Results and Discussion

The DSC thermograms corresponding to the second heating run (Figure 2) showed the T_g of the WBPU/CNT films located at low temperature, followed by the crystallization process (exothermal peak). Finally,

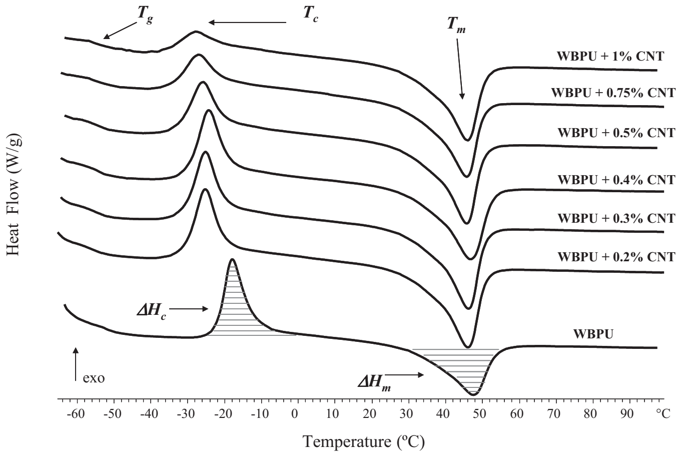

Figure 2.
DSC curves (second heating run) of the polyurethanes with different content of carbon nanotubes.

Table 3.
Some values obtained from DSC thermograms (second heating run) of the polyurethanes with different content of carbon nanotubes.

Adhesive	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
WBPU	−53.4	−18.0	27.4	46.3	31.2
WBPU + 0,2%CNT	−56.5	−24.9	26.5	45.2	44.7
WBPU + 0,3%CNT	−55.4	−24.,9	30.1	45.5	41.5
WBPU + 0,4%CNT	−54.3	−24.0	27.9	46.1	43.3
WBPU + 0,5%CNT	−55.7	−25.5	24.4	44.9	43.0
WBPU + 0,75%CNT	−56.1	−26.9	22.5	45.2	39.7
WBPU + 1%CNT	−55.8	−27.7	14.5	45.4	42.4

an endothermic peak corresponding to melting process is appeared. All the polyurethanes showed a similar value of melting temperature (T_m) of soft segments (Table 3). However, the melting enthalpy values (ΔH_m) increased and the glass transition temperature (T_g) of soft segments, the crystallization temperature (T_c) and enthalpy (ΔH_c) decreased with the incorporation of carbon nanotubes. From these results, it can be concluded that the ability of polyurethane to crystallize is reduced and more energy is required to be melted after the addition of carbon nanotubes due to the steric hindrance they produce.[5–7]

The incorporation of CNTs influenced the rheological properties of WBPU, producing an increase in elastic (G′) modulus, more markedly by increasing the nanotube content and especially from a certain value (Figure 3). This remarkable change in the structure of the polyurethane occurs at a certain level of concentration of nanotubes, which is related to rheological percolation.[5,8–10] This indicated the existence of a more reinforced structure and a reduction of polymer chains movement due to the mobility restrictions imposed by the presence of nanotubes.[5,8]

On the other hand, the CNTs did not significantly influence the adhesive properties; only a slight decrease in T-peel strength is produced[11] as it is shown in Figure 4; however the obtained results satisfactorily meet the quality requirements according to the standard UNE-EN 15307:2007.[12]

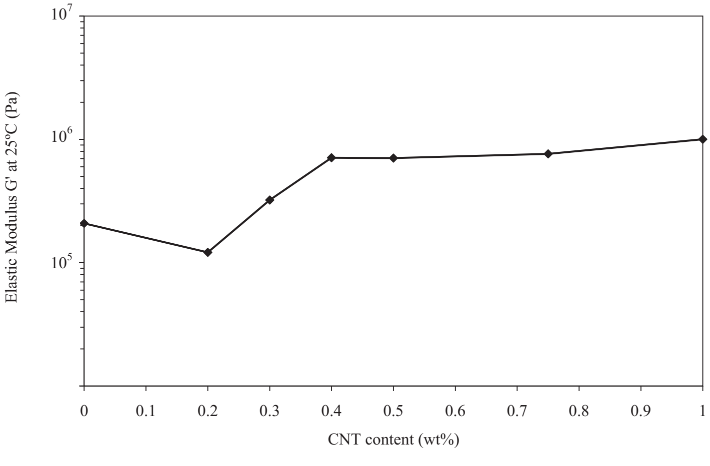

Figure 3.
Evolution of elastic modulus (G’) at 25°C of the polyurethanes as a function of carbon nanotubes content.

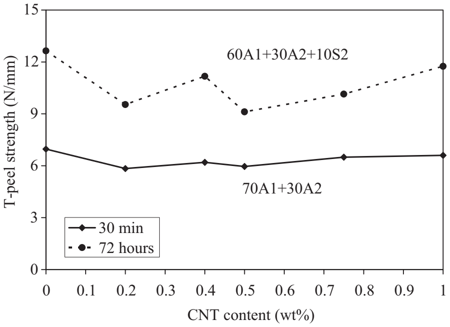

Figure 4.
T-peel strength values of roughened leather/polyurethane adhesive/roughened and halogenated SBR joints as a function of carbon nanotubes content. 32 min and 72 h after joint formation. Locus of failure by visual inspection of failed joint surfaces: A1 = adhesive failure to the leather; A2 = adhesive failure to the SBR rubber; S2 = rubber exfoliation.

Finally, addition of CNTs produced an increase in electrical conductivity of the polyurethane matrix,[3,5,6,9,10] especially from a certain value considered electrical percolation (Figure 5), where CNTs must be approximated to form the electrical conductive network.[5,13,14]

The obtained results agree with the following electrical-rheological percolation mechanism (Figure 6). At low concentrations of nanotubes (a), the properties are dominated by the polymer itself. By increasing the concentration of nanotubes (b), the rheological percolation threshold could be reached: the CNTs begin to interact with polymer and the viscosity of the polyurethane is increased. After a further increase of the amount of nanotubes

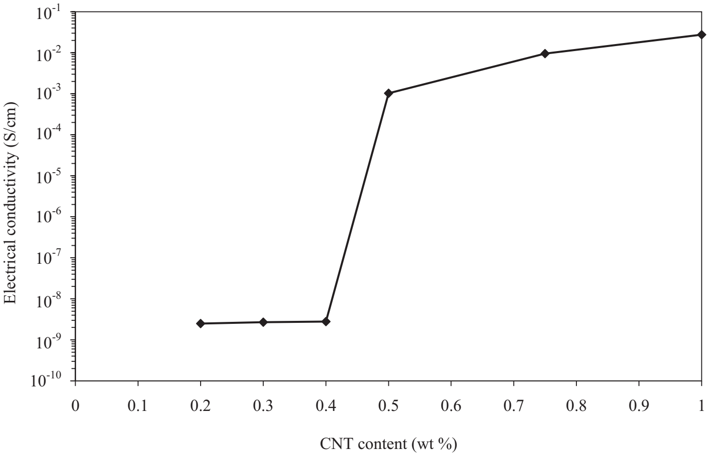

Figure 5.
Electrical conductivity values of the polyurethanes as a function of carbon nanotubes content.

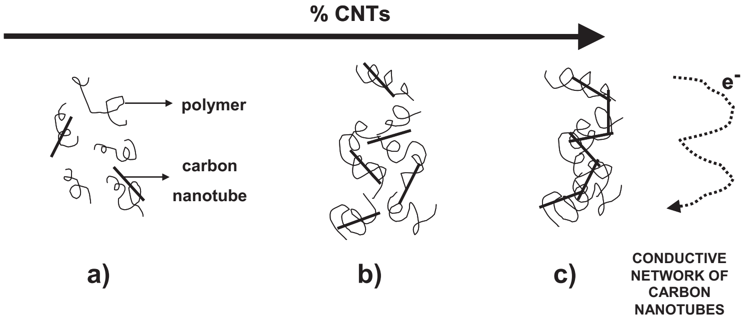

Figure 6.
Scheme of the effect of the carbon nanotubes on the polymer chains (a) taking into account rheological percolation threshold (b) and electrical percolation threshold (c) resulting in a nanotube conductive network.

(c), the electrical percolation threshold is reached, where CNTs must be approximated to form the conductive network thanks to the tunnelling effect of electrons.[15] These limits depend on several parameters, such us: structure and properties of the polymer, electrical and mechanical properties of the carbon nanotubes, nanotube/polymer interactions, aspect ratio (L/D) of the nanofiller, homogeneous and stable dispersion of the nanofillers in the polymer, nanotube orientation, etc.[14,15]

Conclusion

The addition of carbon nanotubes to waterborne polyurethane adhesives influences its rheological, thermal, viscoelastic and adhesive properties. The obtained results indicated the formation of an enhanced structure with CNT-polyurethane interactions which produced a decrease of polymer chains movement. A noticeable increase in the electrical conductivity is produced specially above the electrical percolation threshold.

Acknowledgements: This research was supported by the Institute for Small and Medium Industry of the Generalitat Valenciana (IMPIVA) of Spain through its R&D Program for Technologic Institutes (Project IMDEEA/2012/129). Thanks to NANOCYL (Sambreville, Belgium) and INSOCO (Alicante, Spain) for providing carbon nanotubes and polyurethane dispersion, respectively.

[1] S. Ijima, *Nature*, **1991**, *354*, 56.
[2] T. W. Ebbesen, *Annu. Rev. Mater. Sci.* **1994**, *24*, 235.
[3] M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolos, G. Bister, A. Fonseca, *Nano Lett.* **2004**, *4*, 353.
[4] F. Jiang, G. Hu, S. Wu, Y. Wei, L. Zhang, *Polym. & Polym. Compos.* **2008**, *16*, 471.
[5] M. Chapartegui, N. Markaide, S. Florez, C. Elizetxea, M. Fernandez, A. Santamaría, *Compos. Sci. Technol.* **2010**, *70*, 879.
[6] H. Ha, S. C. Kim, *Macromol. Res.* **2010**, *18*, 647.
[7] F. Buffa, G. A. Abraham, B. P. Grady, D. Resasco, *J. Polym. Sci. Part B: Polym. Phys.* **2007**, *45*, 490.
[8] M. Fernandez, M. Landa, M. E. Muñoz, A. Santamaría, *Macromol. Mater. Eng.* **2010**, *295*, 1031.
[9] F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, K. I. Winey, *Macromolecules*, **2004**, *37*, 9048.
[10] A. K. Kota, B. H. Cipriano, M. K. Duesterberg, A. L. Gershon, D. Powell, S. R. Raghavan, H. A. Bruck, *Macromolecules*, **2007**, *40*, 7400.
[11] M. M. Rahman, E. Y. Kim, K. T. Lim, W. K. Lee, *J. Adhes Sci Technol.* **2009**, *23*, 839.
[12] Standard UNE-EN 1530 7: 2007. Adhesives for leather and footwear materials. Upper-sole joints. Minimum strength requirements.
[13] F. Du, J. E. Fischer, K. I. Winey, *Phys. Rev. B*, **2005**, *72*, 121404.
[14] A. Behnam, J. Guo, A. Ural, *J. Appl. Phys.* **2007**, *102*, 044313.
[15] N. G. Sahoo, S. Rana, J. W. Cho, L. Li, S. H. Siew, *Prog. Polym. Sci.* **2010**, *35*, 837.