

Chemical functionalization and dispersion of carbon nanofibers in waterborne polyurethane adhesives

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Carbon nanofibers (CNFs) are considered as ideal reinforcing fibers for polymer matrices in many technological applications due to their unique structure and properties: high aspect ratio, high Young's modulus, excellent mechanical strength and good thermal conductivity. They are excellent nanofillers in polyurethane matrices originating a new polymeric material, exhibiting the same chemical properties as organic polymers, whereas the rheological and thermal properties may be greatly improved.

However, the incorporation of carbon nanofibers to waterborne polyurethanes implies a great difficulty because of their tendency to form aggregates, which sometimes prevents an efficient dispersion [1]. This instability is related to: (i) the Van der Waals interactions between the nanofibers. (ii) the weak nanofiber-polymer interaction. (iii) the huge aspect ratio (length/diameter) in the carbon nanofibers [2]. In this sense, it is necessary to insert functional groups on the surface of the nanofibers, either to induce a repulsive force between the particles or to improve their interaction with the polymer, thus obtaining a stable dispersion [3,4]. Therefore, to improve the dispersion of nanofibers in the polymer, they must undergo a pre-oxidation, thus increasing the number of surface functional groups with oxygen, such as C=O, COOH, OH, NH₂, etc. and also raising the surface negative charge.

In this sense, several waterborne polyurethane adhesives (WBPU) containing carbon nanofibers were prepared by previous chemical functionalization. Thanks to the chemical treatment, the nanofibers oxidation is produced, the incompatibility between the polymer matrix and the nanofiber is improved and stability of the carbon nanofibers in the dispersion is achieved (Fig. 1).

From the primal polyurethane dispersion, four adhesives were prepared with a different amount of carbon nanofibers (0.10 wt%, 0.25 wt%, 0.50 wt% and 1 wt%). The kinetics of crystallisation was monitored by Differential Scanning Calorimetry (Fig. 2). The maximum of the curve obtained is considered as the crystallization time (t_c) of the polyurethane. Whereas the WBPU without carbon nanofibers reaches the highest crystallization rate of the soft segments at 13 minutes, the addition of the CNFs decelerates the crystallization of the polyurethane in a greater extent by increasing its content, until 21 minutes in case of WBPU/1%CNF. Therefore, although the addition of the carbon nanofibers does not affect the segmented structure of the WBPU, the kinetics of crystallization of the soft segments is decelerated [6], indicating the formation of a reinforced structure, being more noticeable as the content of the carbon nanofiber increases.

The rheological properties were determined using a controlled stress rheometer with a parallel plate shear system (Fig. 3). The addition of the carbon nanofibers produces a noticeable increase in both elastic and viscous moduli of the WBPU, indicating the existence of nanofiber-polyurethane interactions again. This increase is more pronounced as the content of the nanofiber increases [7], due to the existence of a great number of CNFs-polyurethane interactions.

Furthermore, the viscoelastic properties were determined by dynamic-mechanic analysis (DMA), using the two point bending system (single cantilever). According to Fig. 4, the polyurethane which shows the highest moduli values is the one it has the greatest contain in carbon nanofibers (1 wt%), indicating again the existence of polyurethane–CNFs interactions and suggesting a more enhanced structure, in agreement with DSC and plate–plate rheometry results.

References

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Figures

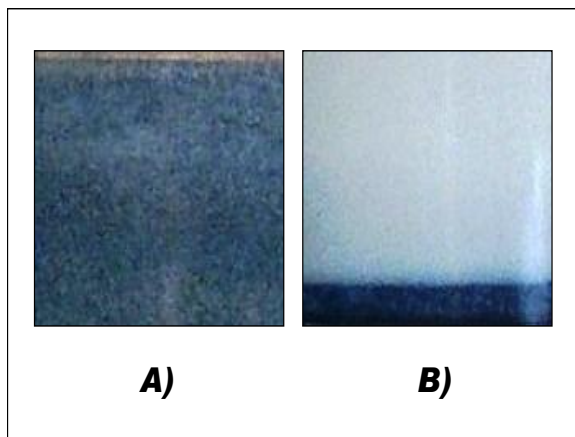


Fig. 1. Stability of the WBPU dispersion after the addition of carbon nanofibers:
 A) with chemical treatment of functionalization.
 B) without chemical treatment functionalization.

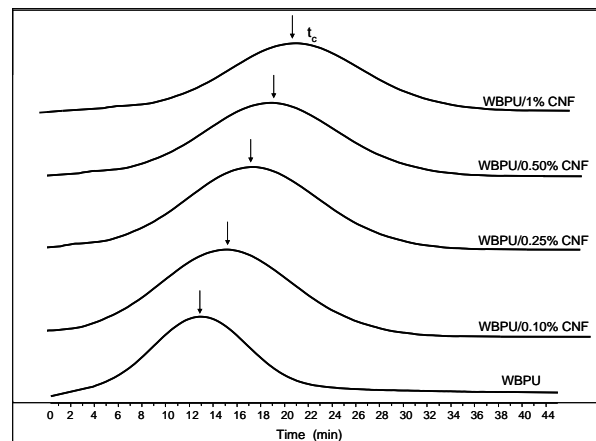


Fig. 2. DSC curves of kinetics of crystallization at 25°C of the WBPU with different content of carbon nanofibers.

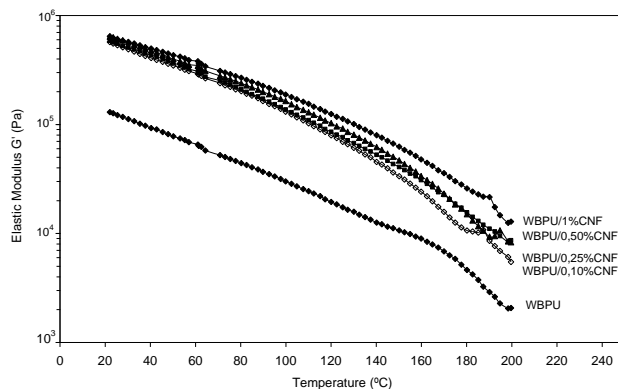


Fig. 3. Variation of the storage (G') modulus as a function of the temperature of the WBPU with different content of carbon nanofibers.

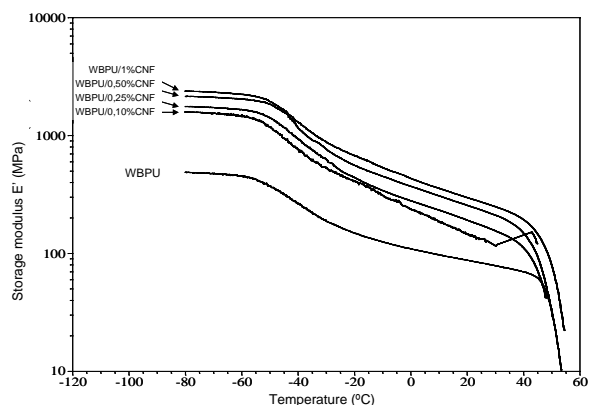


Fig. 4. Variation of the storage (E') modulus as a function of the temperature of the WBPU with different content of carbon nanofibers.

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