

THERMOPLASTIC POLYURETHANE FIBERS FILLED WITH MULTI-WALLED CARBON NANOTUBES: RELATIONSHIPS AMONG FIBER DRAW RATIO, FILLER CONTENT AND PERFORMANCES OF EPOXY BASED ITEMS

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Abstract

The research is aimed to investigate the influence of draw ratio of thermoplastic polyurethane based fibers filled with multiwalled carbon nanotubes on the final properties of epoxy based products reinforced by the same. In more details, extruded compounds were melt spun using a spinning line to make nanocomposite fibers with two draw ratios properly named as low and high draw ratio fibers and with nanotube loadings equal to 0.2, 1, 3 and 5 wt%.

These latter, opportunely analyzed especially in terms of tenacity and viscoelastic behavior, were subsequently employed to reinforce a bi-functional epoxy resin. At this regard, with the help of a mold designed ad hoc, preliminary investigations have been performed on samples derived from plaques of a typical epoxy resin: Diglycidyl ether of bisphenol-A, in which a certain number of fibers were disposed parallel.

The influences of fiber draw ratio and their filler content on performances of produced epoxy composites were assessed by tensile, flexural and three-point bending dynamic tests.

1 Introduction

Thermoplastic Polyurethanes (TPUs) are linear segmented block copolymers consisting of hard and soft segments [1,2]. The glassy semicrystalline hard segments are made from diisocyanate and short chain extender molecules (i.e. diol or diamine) while the rubbery soft segments consist of long flexible polyether or polyester chains which interconnect two hard segments. In particular, the hard segments act as crosslinks in a vulcanized rubbers, while the soft segments form an elastomer matrix which accounts for the elastic properties of TPUs. Typically, hard and soft species are not miscible in each other, often leading to a partially phase separated structure. In particular, depending on the hard segments/soft segments mutual content, the morphology of the hard domains changes from isolated domains to interconnected domains [3]. Thus, a wide variety of properties can be achieved by varying the molecular weight of the hard and soft segments, their ratio, and chemical type [4-6].

In light of the above considerations, TPUs are known for having several interesting properties such as high toughness, flexibility, elasticity, high abrasion resistance, tear strength and excellent shock absorption. Moreover, these resins can be processed from the molten state using conventional thermoplastic processing technologies while recovering their rubber-like properties upon solidification. Current applications of TPUs range from ski boots and footwear to gaskets, coatings, flexible tubing, hoses, and seals.

Nevertheless, pure thermoplastic polyurethanes demonstrate low stiffness and poor resistance to heat which make their applications limited [7,8]. In other words, also in this case, the increasing use of plastics even for extreme applications leaves enough space to the research to try improvements.

In this frame, it is widely established that the addition of fillers into polymeric matrices may enhance desired properties of these latter. In fact, a huge number of experimental evidences are available about improvements physico-chemical and mechanical properties of TPU matrices gained by adding very low amounts of carbon nanotubes [9-11], layered silicates [12-17] or other specific fillers [18-21].

In particular, carbon nanotubes have received significant attention showing an extraordinary ability to enhance mechanical performances, thermal behaviour and electrical conductivity of polymers at very low concentrations ($\leq 5\text{wt}\%$).

Usually, carbon nanotubes offer low density, excellent electronic and mechanical strength, high electrical and thermal conductivity and thermal stability. As a consequence, a number of potential benefits are expected when these fillers are employed as reinforcing agents in nanocomposites as long as an optimal dispersion of the filler is ensured. For example, for some specific applications it may be interesting to dispose or align the filler particles only in certain areas of the polymer matrix, avoiding waste of nano filler in the bulk of the same.

In general, especially in case of melt compounding, it is well known that these requirements are not always easy to achieve and segregation (flocculation) phenomena are often very likely unless additional additives such as surfactants are used or an opportunely functionalization of the filler is considered.

Recently, new approaches as self-assembling of nano-filler in organic structures similar to those of block copolymer have already shown interesting results.

An alternative way could be the production of composite fibers to be used, in turn, as reinforcement of other polymer matrices.

In line with this trend, aim of this research is to assess the influence of draw ratio of fibers filled with multiwalled carbon nanotubes on final properties of epoxy based products reinforced by the same. In more details a thermoplastic polyurethane resin was modified by inclusion in the melt state of up to 5 wt% of multi wall carbon nanotubes, using a twin screw lab extruder. All extruded and pelletized materials were melt spun using a spinning line to make nanocomposite fibers with draw ratios ranging from 20 to 100 and with nanotube loadings equal to 0.2, 1, 3 and 5 wt%.

These nanocomposite fibers were subsequently employed to reinforce a bi-functional epoxy resin. At this regard, with the help of a mold designed ad hoc, preliminary investigations have been performed on samples derived from plaques of a typical epoxy resin: Diglycidyl ether of bisphenol-A, in which a certain number of fibers were disposed according specific directions.

The reinforcement effect of fiber with low and high draw ratio and varying filler content on performances of produced epoxy composites was assessed by flexural and three-point bending dynamic tests.

2 Materials and testing methods

2.1 Materials

The polymer used as the matrix was a film grade thermoplastic polyurethane (TPU) elastomer ELASTOLLAN 1185A (density 1.12 g/cm³, T_g=-42 °C) supplied from Elastogran GmbH, Germany. The polymer is constituted of 1,4-butanediol and diphenylmethane 4,4'-diisocyanate hard segment and poly(tetramethylene oxide) soft segment.

Multiwalled carbon nanotubes (MWNTs) purchased from Shenzhen Nanotechport Co. Ltd, China, with length approximately equal to 15 μm, external diameter ranging from 10 to 30 nm, aspect ratio in the range 500-1500 and specific surface area of 55-65 m²/g were used as fillers.

A commercial bicomponent system (EC57/W282), supplied by Camattini. (Collecchio, Parma, Italy), consisting of a Diglycidyl ether of bisphenol A (DGEBA)-based low molecular weight epoxy resin (EC57: epoxy-equivalent 172–182 g/equiv) and a hardener (W282) was selected as a thermosetting matrix to be reinforced with the nanocomposite TPU fibers.

2.2 Melt compounding procedure and composite preparation

The matrix, carbon nanotubes and relative compounds were dried in a vacuum oven at 90°C overnight before each step of processing.

All composites were obtained by mixing polyurethane and carbon nanotubes in a HAAKE twin screw extruder using a screw speed of 90 rpm with the care of supplying a constant flow of nitrogen in the hopper and applying an almost flat temperature profile from the hopper to the die at 200 °C.

Compounds with MWNT mass concentration of 0.2, 1, 3 and 5 wt% were prepared and used to obtain composite fibers with different draw ratio, approximately ranging from 20 to 100, by a DSM Xplore melt spinning line.

Preliminary epoxy based coupons were obtained by placing parallel composite fibers in a specific mold cavity in which the thermosetting resin / hardener (mix ratio 100:32) formulation was subsequently poured and then applying an appropriate curing protocol recommended by the supplier of the resin: temperature ramp at a speed of 3 °/ min up to 100 °C followed by a 2 hours isothermal step.

2.3 Characterization techniques

All the obtained fibers were investigated by mechanical tests carried out in static and dynamic way as reported below.

Tensile tests were performed by using an Alpha Technologies Tensometer (Mod. 2020). All tensile experiments were carried out at ambient temperature at a strain rate of 36 mm/min. Load cell: 10 N, gauge length: 15 mm. For each sample at least ten specimens were analysed.

Dynamic-mechanical measurements were done by a DMA Tritec 2000 operating in tensile mode (TM) at a constant frequency of 1 Hz, over the temperature range -80÷50 °C.

Heating each sample at a rate of 4°/min, viscoelastic parameters such as dynamic moduli (E' and E'') and their ratio (tanδ) were monitored as a function of the temperature.

Epoxy-composite fiber coupons were analyzed by morphological observations and mechanical tests performed in flexural mode in both dynamic and static way.

In details, the morphology of surfaces obtained by cryogenic fracture of coupons in the direction transverse to the reinforcing fibers has been carried out by a field emission scanning microscope Quanta 200 ESEM FEG from FEI equipped with a Schottky field emission gun (FEG) for optimal spatial resolution.

Dynamic flexural tests were performed using the same instrument used for fiber analysis using a scanning rate of 5 °C/min over the temperature range 25÷140 °C at a constant frequency of 1 Hz.

Static flexural evaluations were made by using the cited tensometer according to the ASTM D790 Standard Method using a load cell of 5 kN.

3 Results and discussion

Tensile measurements have indicated that, generally, the presence of carbon nanotubes induces an increase of the matrix stiffness at the expense of the mechanical parameters of fibers at break: effect increasing with the filler content.

With regard to the dynamic characterization, the comparison of the neat TPU fibers with the ones containing 1, 3 and 5% by weight of carbon nanotubes and having the same draw ratio have confirmed an improvement of the storage modulus of composite spun fibers with respect to the neat matrix based ones on the whole considered temperature range. This behavior, only slightly manifested in presence of the minimum amount of carbon nanotubes, has appeared more pronounced all over the examined range of temperatures for higher filler contents.

On the other hand, the inclusion of carbon nanotubes induces a reduction of the damping ability of the fibers, usually explained by the onset in composite formulations of major constraints on the macromolecular mobility of the matrix chains.

With regard to the coupons, electron micrographs of cryo-fractured sections in the transverse direction with respect to the position of the fibers (see Fig 1) showed a satisfactory fiber / matrix adhesion: necessary condition to ensure an adequate transfer of stress at the interphase in the composite system.

Regarding dynamic-mechanical properties of coupons, three point bending tests, performed along fiber direction, have shown that the addition of composite fibers induces a significant reduction of both the stiffness and the glass transition temperature of the matrix as indicated by the shift toward lower temperatures of the damping signal $\tan \delta$. This effect, even if partially expected, given the elastomeric nature of TPU, in some cases it appeared surprising in terms of amount, taking into account the modest content of the elastomeric phase generally included (<1% by volume). This behavior, for the same number of included fibers, appeared to be partially recovered by increasing the filler content of composite fibers or their drawing ratio.

Finally, static flexural tests of coupons have confirmed the trend of the module with a recovery of the geometric characteristics of the specimen, after removal of the applied load, for epoxy specimens reinforced composite TPU fibers with respect to those ones based on pure epoxy resin and processed in the same conditions (Fig. 2).

4 Conclusion

Fibers of neat thermoplastic polyurethane or containing up to 5% by weight of carbon nanotubes (MWNTs) were prepared by melt spinning with different draw ratio and used as a reinforcement of a bicomponent epoxy resin. The analysis of mechanical properties of the as-spun fibers showed a stiffening of the fibers increasing with the content of included nanotubes, at the expense of performance at break of the same. The draw ratio of the latter, while having a positive influence on their tensile modulus, on the other hand it appeared to have a less marked effect on the parameters at break (strength and elongation).

With regard to the dynamic-mechanical properties, the results obtained so far have confirmed the increase of storage modulus of the fibers with both the filler content and the draw ratio of the fibers, but as expected they have shown a certain reduction of the mechanical damping ability of the composite fibers with respect to pure TPU ones.

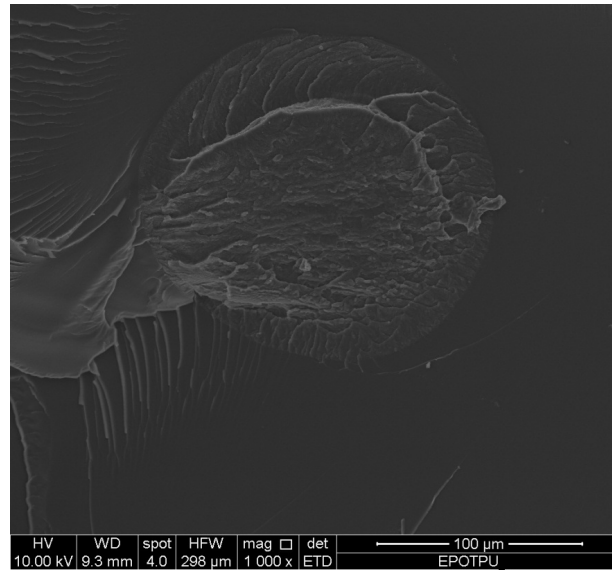


Figure 1. Scanning Electron Micrograph of a coupon section fractured transversely to the position of reinforcing composite TPU fibers

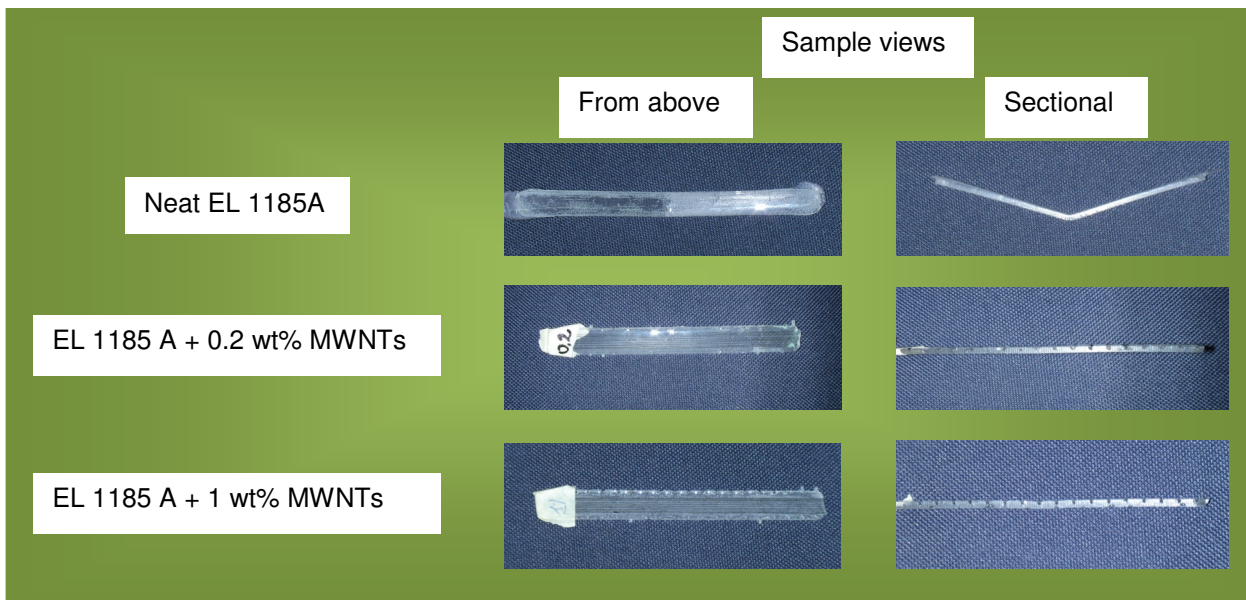


Figure 2. Geometric features of epoxy based coupons subjected to flexural load and released

The characterization of preliminary epoxy based coupons reinforced by TPU / MWNTs composite fibers in terms of morphological issue and flexural properties showed a satisfactory fiber-matrix adhesion at the interface but also a clear softening of the matrix mainly ascribed to the elastomeric nature of the thermoplastic polyurethanes. It is clear that, if it is necessary to maintain a certain level of rigidity of the composite system, it will be necessary to take into account the simultaneous use of additional reinforcing filler, maybe distributed in the bulk of the matrix.

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