PROCESS-PROPERTIES RELATIONSHIPS OF THERMOPLASTIC POLYURETHANE BASED MATERIALS FILLED WITH CARBON NANOTUBES

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1 Introduction

In the last decades, the development of new polymer based materials through modification of commercial resins by introduction of fillers has gained an ever increasing interest [1,2]. Nowadays, it is well established that nanoparticles offer significant advantages over micro-sized fillers, including a greater surface area to mass ratio, low percolation threshold, and often very high aspect ratio.

In this context, an outstanding attention has been dedicated to the incorporation of carbon nanotubes (CNTs) in polymer matrices and to the fabrication of nanostructured materials with high performances [3,4]. At this regard, a uniform dispersion of carbon nanotubes in the host matrix and a good interfacial adhesion are necessary to ensure satisfactory properties of products.

Thermoplastic polyurethanes are segmented multiblock copolymers constituted by repeating units of hard and soft segments [5,6]. Because of these structural aspects, many researchers are interested to highlight industrial potentialities of this class of polymers especially due to their peculiarity to combine thermoplastic performances and processability with elastomeric properties.

In this work, multi walled carbon nanotubes were melt compounded with a film grade thermoplastic polyurethane.

Extruded nanocomposites, once pelletized and opportunely dried, were further processed by film extrusion technology to prepare single-layer films and coextruded three layers LDPE/TPU/LDPE films with plain and carbon nanotubes filled TPU. In order to enhance our know-how about TPU nanocomposite processing and optimization, the effect of working conditions on morphology, mechanical and dynamic mechanical properties of nanostructured films were systematically investigated.

2 Experimental

2.1 Materials

The polymer used as the matrix was a film grade thermoplastic polyurethane (TPU) elastomer ELASTOLLAN 1185A (density 1.12 g/cm^3, T_g=-42 °C) supplied from Elastogran GmbH, Germany. The polymer is constituted of 1,4-butanediol and diphenylmethane 4,4'-diisocianate hard segment and poly(tetramethylene oxide) soft segment.

Multiwalled carbon nanotubes (MWNTs) purchased from Shenzen Nanotechport Co. Ltd, China, with length 5-15 µm, external diameter: 20-30 nm, aspect ratio: 50-250 and specific surface area: 55-65 m^2/g were used as fillers.

2.2 Melt compounding procedure

Thermoplastic polyurethane (TPU) nanocomposites containing up to 3% by weight of carbon nanotubes (CNTs) were obtained by melt mixing in a HAAKE twin screw extruder (Mod. Ptw 24/40, L/D = 40) by setting a flat temperature profile at 200 °C along the screws to the die and using a screw speed of 90 rpm, with the care of supplying a constant flow of nitrogen in the hopper during the process.

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

2.3 Film production procedure

The comparison of two different processing techniques was made by performing film extrusion on a) cast film apparatus with flat die geometry and chill roll cooling system and b) film blowing technique by making use of a tubular die geometry with air cooling and draw up nip rolls.
In both cases, the material was dried in vacuum at 70 °C for 12 hours prior to any use.
If not properly dried, the material did not allow any stable process and samples presented irregular shape and surface.
Products were always characterized by a very high stickiness which determined the difficulty of film collection on a winding roll. In the case of blown film, it was even impossible to open the tubular after the cooling.
The problem was overcome as follows: for the cast film the winding up was performed by coupling in line a continuous paper ribbon whereas the problem of film blowing production has been approached by making use of a co-extrusion system.
In particular a three layers extrusion line was used in order to insulate the sticky polyurethane layer between two slipping layers of low density polyethylene (LDPE). After cooling and collecting on a winding roll, the polyurethane film samples were easily separated from the LDPE layers.
The co-extrusion apparatus is composed by three identical single screw extruders (D = 12 mm, L/D = 24), a tubular co-extrusion spiral mandrel die with a diameter of 40 mm, a blow up and winding unit. The extrusion speed was set at 25 rpm for the two LDPE extruders and 50 rpm for the PU extruder. The thicknesses of each LDPE layer was thus almost half respect to the PU layer.

2.4 Characterization techniques

The morphology of the nanocomposite films was studied by using a transmission electron microscope (FEI Tecnai G2 Spirit TWIN) equipped with an emission source LaB_6. Film samples, previously incorporated into a cyanoacrylate resin, were cut with a diamond blade. The nominal thickness of the samples was 200 nm.
Capillary shear evaluations were carried out using an Advanced Capillary Rheometer (model RH10) having a barrel diameter of 16 mm, a capillary die (D = 1mm – L/D = 16) and with a pressure transducer positioned in front of the die entry. Measurements were conducted at 200°C.
Tensile tests were performed by using an Alpha Technologies Tensometer Mod. 2020 on rectangular specimens. Experiments were carried out at room temperature.
Dynamic-mechanical measurement were done by a DMA Tritec 2000 in tensile mode at a constant frequency of 1 Hz, over the temperature range -40÷ 140 °C. The viscoelastic behaviour of TPU systems was investigated in terms of dynamic moduli and damping ability by heating each film sample at a rate of 2°/min.

3 Results and discussion

The processability of the neat matrix and its compounds with CNTs ranged from weak to fairly good in the case of cast film production.
In particular, the increase of CNT load was followed by a reduction of adhesiveness of the film and a more stable process.
The film blowing process, as expected, was strongly related to the processability of the LDPE which normally yields a very stable film blowing process. However it has to be said that some surface instabilities were detected at the PU – LDPE interface, probably due to the interfacial effect between the two incompatible polymers.
These effects, also related to the rheological behavior of the two resins, determined poor processability for the pure PU and the compounds with the lower CNT content. The process stability was pretty good for the other compositions (0.5 and 1 % by weight).
The results confirmed the correlation between processing conditions and properties of nanostructured systems.
In particular, some morphological observations reported in Fig. 1 show that a satisfactory level of dispersion of carbon nanotubes was achieved at least in the case of the cast filming procedure.
Similar TEM observations are not yet available for samples produced by film blowing. In this case, unfortunately, the thickness of the thin film has greatly complicated the preparation of samples for examination under a microscope.
The inclusion of nanofiller leads to an increase of rheological parameters as demonstrated in terms of

dynamic and steady-state shear viscosity (see, for example, Fig. 2).

Regarding the tensile behaviour, the comparison between performances of pure TPU films respect to those containing carbon nanotubes, has generally shown a significant effect of the filler content on the tensile elastic modulus of samples. This effect, as expected, seems to be influenced by film production technique. Ultimate mechanical properties, instead, showed an increase of the strain hardening phenomena by increasing the filler loadings with a significant reduction of the strain at break.

Due to the problems occurred during the film production, it was not possible to analyze blown films of TPU and nanocomposite system containing 0.2 wt% of carbon nanotubes.

The mechanical parameters of film measured in machine direction are collected in Table 1.

In particular, it appears that increasing the filler content implies changes in tensile properties depending on the process used to obtain the film. The samples obtained by flat cast film show an increase in the stiffness and tensile strength with increasing content of nanotubes at the expense of elongation at break that is reduced by more than 40% in the presence of maximum concentration of filler herein considered, with respect to the pure matrix.

For films produced by film blowing, however, the effect of the content of nanotubes on the tensile strength and elongation at break of the films appears not relevant while increasing the concentration of the filler from 0.5 to 1.0% implies a halving of the stiffness.

These effects can be due to the different level of dispersion and orientation of the nanotubes obtained with the two used film techniques, which also differ in cooling system. In particular, the cast film production is usually characterized by a higher cooling speed than the blown one.

This consideration will be supported at the conclusion of the above mentioned morphological analysis.

Finally, in spite of the low contents of carbon nanotubes herein considered, dynamic-mechanical evaluations have indicated relevant influences especially in terms of elastic modulus for nanostructured films with respect to neat TPU ones.

In details, Table 2 shows the elastic behavior of the films produced in terms of values of the storage modulus in the glassy and rubbery regions, highlighting in gray parameters characterizing films obtained by blowing.

Again, as expected, the viscoelastic behavior depends on the process technology used to prepare film sample and, therefore, mainly on the level of dispersion of the nanotubes obtained as well as on the possible influence of the nanotubes on the level of crystallinity of the phases constituting the host matrix.

As for the static properties, with the same content of carbon nanotubes, performance of cast films are better than the blown ones.

4 Conclusion

Melt blended thermoplastic polyrethane/multi walled carbon nanotubes compounds have been studied in terms of processability, flow behavior and physical properties. Films were prepared by cast film extrusion and by blown film coextrusion procedure. Processing conditions were related to mechanical performances and morphological aspects of the films.

Further analyses are in progress in order to correlate the effect of the two different processing techniques to mechanical and viscoelastic behaviour of the investigated nanocomposite systems.

SAMPLES (NTC content)	**E [MPa]**	**ε_{br}[%]**	**σ_{max}[MPa]**
Film casting			
EL 1185A	**7.2±1.1**	**791±22**	**24.4±2.2**
0.2 wt%	11.6±0.6	502±43	32.3±1.9
0.5 wt%	13.7±1.4	491±27	34.7±1.2
1 wt%	14.6±0.4	461±31	26.6±1.5
Film blowing			
0.5 wt%	23 ± 4.1	527 ±	10.4 ± 1.7
1 wt%	11 ± 1.7	608 ±	11.9 ± 1.1

Table 1. Tensile parameters of TPU/CNTs film samples.

Film Sample	E’ @ -80°C (MPa)	E’ @ 40°C (MPa)
EL 1185A	974	14.8
0.2 wt% CNTs	1787	21.3
0.5 wt% CNTs	1887	22.4
1 wt% CNTs	2156	20.6
0.5 wt% CNTs	1172	22.1
1 wt% CNTs	1722	24.3

Table 2. Storage modulus of TPU/CNTs films evaluated in the storage and glassy viscoelastic region.

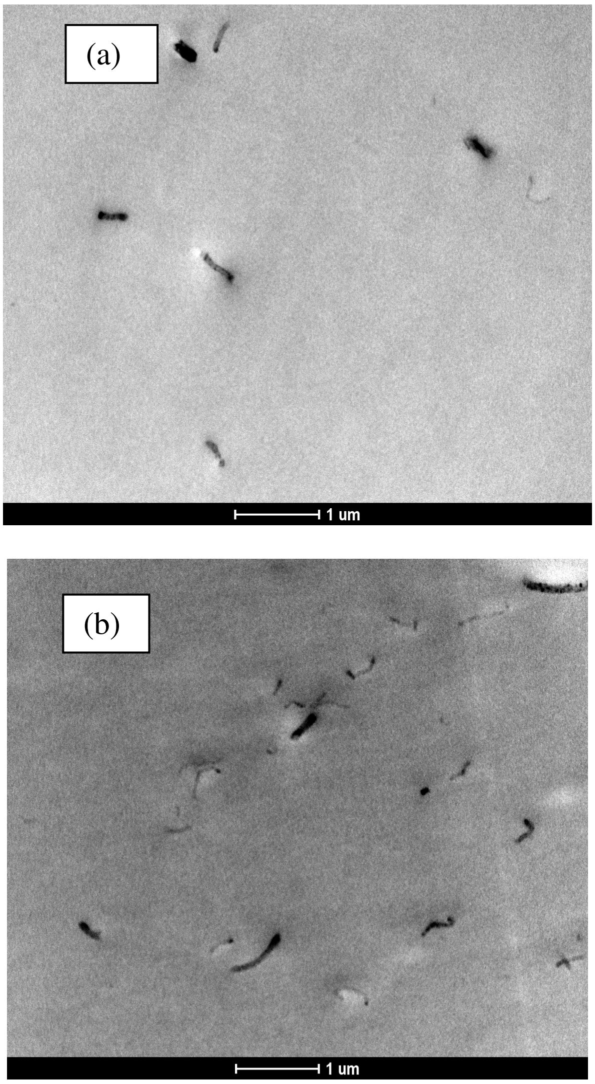

Fig. 1. TEM images of cast film samples of TPU based nanocomposites filled with (a) 0.2 wt% and (b) 1.0 wt% carbon nanotubes.

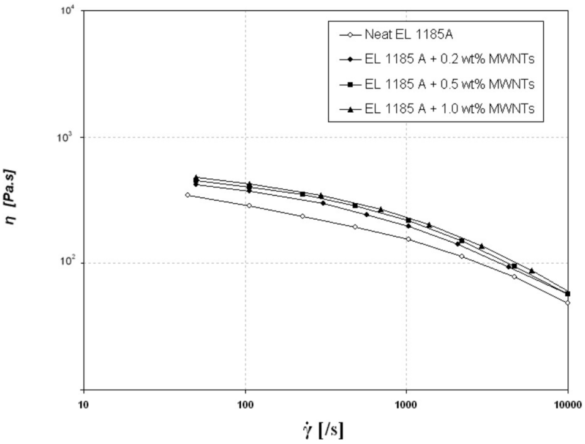

Fig. 2. Capillary steady shear viscosity of TPU/MWNTs melt blended composites at various filler loadings, as a function of shear rate at 200 °C.

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