Influence of annealing-induced phase separation on the shape memory effect of graphene-based thermoplastic polyurethane nanocomposites

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Shape memory polymers (SMPs) is an emerging class of smart materials, which are of special interest due to their ability to return to their original shape after being subjected to an external stimulus, such as mechanical stress, electric or magnetic fields, temperature, among others [1]. Among the shape memory polymers, thermoplastic polyurethane (TPU) stands out for its easy processability and versatility, which raises its range of final shapes and applications, including membranes, medical implants, smart stents and artificial muscles [2].
TPU is a multiblock copolymer and its morphology is composed by rigid and elastomeric immiscible segments highly dependent on thermodynamic parameters, leading to a phase separation and forming domains[3]. The elastomeric segment (soft domain) is associated with a polyol or a long chain diol, while the hard domain refers to the intercalation of a diisocyanate and a chain extender. However, the low stiffness, tensile strength, thermal and electrical conductivity are still some of TPU limitations. In addition, the use of temperature as the main type of stimulus for the returning into the original shape narrows its application. In this scenario, the incorporation of nanomaterials is widely explored in the literature in order to obtain composites with superior final properties.
In this study, 0.1 wt.% of graphene nanoplatelets (GNP) and multilayers graphene oxide (mGO) are incorporated into TPU by polymer solution casting, and a contribution on the phase separation of these domains is observed. This phenomenon is even more pronounced when these graphene-based nanocomposites are submitted to annealing at 110 ºC for 24 hours, suggesting a good interaction between the fillers with both soft and hard domains. To elucidate the relationship between the hard and soft phase separation and the shape memory properties, the samples were characterized within a rheometer, by selecting well defined thermal cycles. As consequence, after annealing, both nanocomposites (TPU+GNP and TPU+mGO) presented better performance in SME regarding the increase on shape recovery ratio (Rrec) in more than 3%. All nanocomposites maintained a high strain during SME programming, even higher than that presented by pure TPU, before and after annealing, indicating a direct influence of the graphene-based nanostructures on the shape memory effect.

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