THERMAL AND MECHANICAL PROPERTIES OF POLYCAPROLACTONE-BASED COMPOSITES WITH DIATOMACEOUS EARTH AND HALLOYSITE NANOTUBES

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1. Introduction

The biodegradable polymers have been attracted interest for the design of green composites in recent decades to face the urgent environmental issues.
Polycaprolactone (PCL) is one of the most promising environmentally friendly polymers. Recent studies have reported that blending PCL with different types of fillers may affect its physic-chemical properties and crystallization rate.
Halloysite nanotubes (HNT) and diatomaceous earth (DE) have been recently investigated for the preparation of PCL-based composites with appealing performances[1],[2]. Both are naturally occurring materials with nanoscale dimensions and a structure that lend them also absorbent properties. Potentialities of such materials in polymer composites need to be further developed for environmental remediation applications[3].
For the study, binary blends of PCL with HNT and DE were prepared by melt mixing, starting from 5 w/t% of filler to the maximum miscible concentration to the polymer. The thermal and mechanical properties of the obtained composites were investigated. Thermogravimetric analysis, differential scanning calorimetry and dynamic mechanical analysis were employed for the research purposes.

2. Results and Discussion

Thermogravimetric analysis (TGA): The measurements were carried out by using the Q5000 IR instrument (TA Instruments) under nitrogen flow of 25 cm^3/min by heating the samples from 20° to 800 °C. with a rate of 1°C/min. The degradation temperature of the pristine materials and their composites were taken at the maximum of the first order derivative curves of mass percentage vs. temperature.
It was observed that concentration of HNTs up to 15 w/t% did not affect the thermal stability of PCL. The recorded T_{max} values show no significant variations compared to pristine PCL. Higher content of HNT, beyond these levels, leads to a significative decrease in the thermal stability of the PCL matrix, resulted in a lower onset decomposition temperature.
The addition of DE did not significatively affect the thermal stability of the composites, with a similar onset temperature for all of composites as the DE content increased.
Graphs of the residue vs filler concentration showed a good dispersion degree of the filler particles throughout the polymeric matrix.

Differential scanning calorimetry (DSC): The melting and crystallization behaviour testing of the composites and of pristine materials were carried out by using the differential scanning calorimeter TA Instrument DSC (2920 CE). Samples of approximately 5 mg were heated from 25°C to 80°C at a rate of 1 °C/min, under nitrogen atmosphere. The melting temperatures at the onset (T_{mi}), at the peak (T_{mp}) and the enthalpy of melting (ΔH_m) per gram of PCL in the composites were calculated.
The heating thermograms showed melting temperatures values constant for both PCL-based composites as compared to the neat PCL. The crystallinity degree (χ_c) of PCL did not change for blends with DE while significant variations were observed in PCL/HNT nanocomposites. The results showed that, up to the filler concentration of 15 wt%, χ_c increase, indicating that the well-dispersed HNT acted as nucleating agents in the PCL matrix. At higher concentrations, the crystallinity degree decreased, affected by the achievement of the percolation threshold of HNT and by the consequent decrease in molecular mobility of the PCL chains in the nanocomposites.

Dynamic mechanical analysis (DMA): Dynamic mechanical measurements were performed by using the DMA Q800 (TA Instruments). The temperature range was 30° to 80°C with a scan rate of 2°C/min, at an applied