SUPERCRITICAL CO_2 PRE-CONDITIONING PROMOTES γ-CRYSTAL FORMATION IN AMORPHOUS SYNDIOTACTIC POLYSTYRENE FOR ENHANCING MECHANICAL PROPERTIES

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ABSTRACT

Being an engineering plastic attracting great attention, syndiotactic polystyrene (sPS) can form three different crystalline forms having the chains in the helical conformations, i.e., γ-, δ- and ε-form, as a consequence of suitable solvent treatment; and crystalline forms with all-trans planar zigzag conformation, i.e., α- and β-form, by melt crystallization. Among these forms, the helical chains in the γ-form are closely packed to generate a density of 1.10 g/cm^3, higher than other two helical crystalline δ- and ε-form (0.977 g/cm^3), the amorphous phase (1.05 g/cm^3), and two all-trans planar zigzag α-form (1.034 g/cm^3) and β-form (1.078 g/cm^3). Consequently, among those unstretched sPS films containing different crystalline forms and similar total crystallinity, the γ-form film displays the highest elastic modulus and glass transition temperature (T_g).[1] Therefore, an understanding of the modulation of γ-form crystallinity may be essential to modify the physical and mechanical properties by changing processing history.

The γ-form of sPS can be obtained by the solvent-induced crystallization of amorphous sPS. However, the γ-form generally transforms into the α-form at ~200 °C rapidly, and the solvent molecules remained in the amorphous phase can reduce the γ-α transition temperature, and even induce the formation of thermodynamically stable β-form from γ-form directly. It is worth noting that γ-form sPS with easily adjusted degree of crystallinity can be obtained from amorphous sPS by supercritical CO_2 ($scCO_2$) processing.[2]

The history of supercritical CO_2 conditioning changed significantly the thermal behavior and crystal phase transformation of sPS in further thermal treatment under ambient pressure. The results of differential scanning calorimetry scans and temperature-dependent Fourier transform infrared spectroscopy measurements show that in the amorphous sPS without conditioning polymer chains were preferred to cold-crystallize into crystalline α-form, while in the amorphous SPS after the conditioning polymer chains were preferred to arrange into crystalline γ-form by heating. Thus, mixed γ- and α-form was induced in the amorphous conditioned sPS, and the formation of α-form was totally suppressed in the conditioned sPS having only γ-form of small degree of crystallinity.

In conclusion, the history of $scCO_2$ conditioning changes significantly the crystallization behavior of sPS in further thermal treatment. The γ-form with high density and elastic modulus is preferred to form by heating the conditioned samples under ambient pressure. From the amorphous samples with different thermal histories, the coexistence of the γ- and α-forms has be reached conveniently with the aid of $scCO_2$. It has been suggested that the highest elastic modulus is observed for films presenting γ-form among unstretched sPS films, and for films presenting α-form among uniaxially oriented ones, respectively. Therefore, the samples with mixed γ- and α-form would be good objects for fundamental and application research of sPS materials.

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References

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