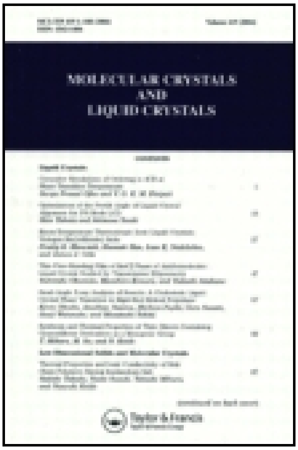

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Effect of Heat Treatment on Phase Behaviour and Molecular Dynamics of Mineral-Filled PPS

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Version of record first published: 24 Sep 2006

To cite this article: Jan Jurga, Marek Nowicki, Karol Bula, Bronisław Susła & Sadek Saleh Rejeibi (2000): Effect of Heat Treatment on Phase Behaviour and Molecular Dynamics of Mineral-Filled PPS, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 354:1, 43-48

To link to this article: http://dx.doi.org/10.1080/10587250008023600

Mol. Cryst. and Liq. Cryst., 2000, Vol. 354, pp. 43-48
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Printed in Malaysia

Effect of Heat Treatment on Phase Behaviour and Molecular Dynamics of Mineral-Filled PPS

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Investigation concerning the structure and molecular dynamics of a nanocomposite made up of poly(p-phenylene sulfide) and silicon dioxide (SiO_2) has been conducted by means of atomic force microscopy (AFM) and nuclear magnetic resonance (NMR). AFM and NMR studies of samples PPS in the neat and composite forms show that during annealing the fragmentation of big agglomerates of PPS take place. Between agglomerates and smaller aggregates there exist repulsion forces which are probably the source of fragmentation in the polymer network. The work has also proved that inside agglomerates and smaller aggregates of PPS dipolar magnetic interaction exist, whereas the electrostatic one occurs between them.

Keywords: composite of PPS; molecular structure; atomic force microscopy; nuclear magnetic resonance

INTRODUCTION

Invaluable information about the morphology, nanoscale structure and chain order in polymers can be obtained from atomic force microscopy (AFM). This technique, besides other spectroscopic and microscopic methods is a good tool in the characterization of polymers. In general, the molecular structure and morphology of the topmost surface layers (several nanometers thick) differ from those of the bulk polymer. Therefore, comprehensive surface analysis is needed to correlate the surface structure with the physical and chemical properties of the tested composite material.

The aim of this work is to investigate nanoscale structure as well as molecular dynamics of poly(p-phenylene sulfide) (PPS) and its composites. Earlier results obtained by AFM measurements indicated that PPS in the solid state should be characterized by a significant interagglomerate free volume [1]. Presumably, this might be one of the factors allowing the insertion of relatively great amounts of the filler into the polymer. Application of spectroscopic methods for this purposive research would provide information concerning the mechanism of filling with powder fillers on a molecular level.

EXPERIMENTAL

Pristine PPS (RYTON PPS V-1) of Phillips Petroleum Company, and composites made of RYTON PPS V-1 and synthesized SiO_2 were mixed in the ratio of 1 to 5. The size of SiO_2 particles was in the range of 30 to 700 nm [2]. SiO_2 particles size in this range is compatible with the dimensions of interagglomerate free volume of virgin PPS [1]. Injection molding in the case of "cold mold" (at 50 ^{O}C) on ENGEL ES 80/20 HLS machine for PPS and its composites was performed. Samples prepared for testing were divided into two groups. The first group of these samples was subjected to AFM and NMR investigations. The remaining ones were annealed at 150^{0}C for 1 hour and then tested by the same techniques. For comparison of results, injection molded pristine PPS samples were also investigated.

STM/AFM (OMICRON) equipment has been used at room temperature to study the topography of polymers. Atomic force microscope images at constant force mode were applied. For AFM observation the sample was placed on a single tube piezoelectric translator by using the tips of silicon nitride (Si_3N_4) fixed under a cantilever. Maximum area available to scan was 5000x5000 nm^2 and typical images consisted of 256x256 dots/line. The scanning rate was within range of few Hz's per line. The STM/AFM resolution was 0.01 nm in the z-direction and 0.05 nm on the surface plane.

Temperature spin-lattice relaxation times measurements for PPS/SiO_2 composites were carried out with a pulse NMR spectrometer operating at 30 MHz for protons [3]. The measurements were performed within the temperature range from -100 to +10^{0}C. The sample temperature was maintained by blowing liquid nitrogen. The relaxation times T_1 were measured by means of $\pi/2$-τ-$\pi/2$ according to conventional method. The duration of $\pi/2$ pulse was 2 μs and the dead time of spectrometer was 10 μs.

RESULTS

Results of AFM studies at constant force mode of injection molded PPS/SiO_2 composites are presented in Figures 1 and 2. Extremely different results for those of pristine PPS and its composites have been detected. Below the glass transition temperature of PPS (T_g = 92 ^{0}C) for samples molded at 50 ^{0}C the crystallinity is very low [1,4]. The AFM image shows very long agglomerates of average width in the range 100 nm. Heat treatment at 150 ^{0}C for 1 hour increases the crystallinity of PPS and simultaneously divides the long agglomerates to small aggregates [1] which are being connected with very narrow bands (see Figure 1).

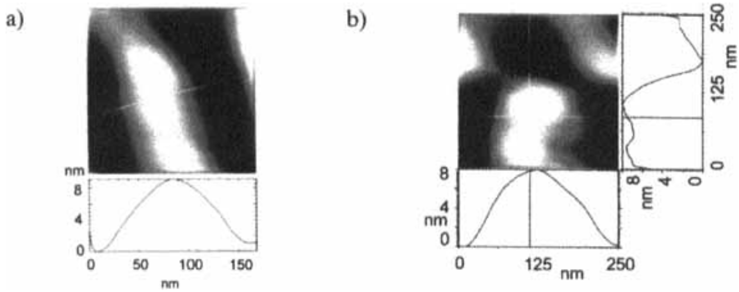

FIGURE 1 The AFM image of pristine PPS injected to, a) cold mold (50 ^{0}C), b) annealed at 150 ^{0}C after injection to the cold mold.

Between aggregates holes of 8 nm deep are observed. The average diameter of the aggregates is about 150 nm and approximately 8 nm high. The width of the bands is about 20 nm (see Figure 1b).

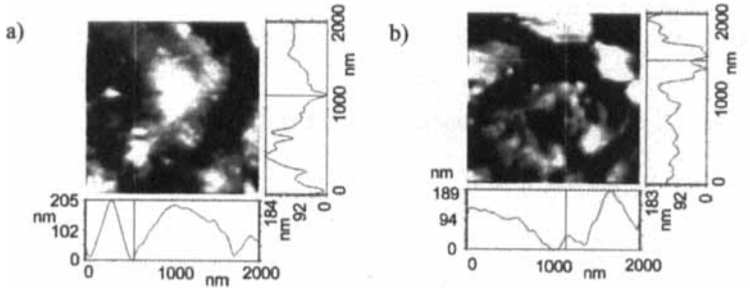

FIGURE 2 The AFM image of PPS/SiO_2 composite injected to: a) cold mold, b) annealed at 150 ^{0}C after injection to the cold mold.

AFM data collected from PPS/SiO_2 composites presented in Figure 2a have much bigger agglomerates in comparison with virgin PPS. The average diameter of these agglomerates is 800 nm. Annealing at 150 ^{0}C for 1-hour is also applied for this composite. The change in the surface morphology is observed in the same manner as observed in pristine PPS (see Figure 1b). The size of the PPS/SiO_2 composites after annealing is twofold larger in comparison with PPS without filler (see Figure 2b).

The temperature proton spin-lattice relaxation time dependence in the case of PPS and its composites with SiO_2 after injection and heat treatment (annealing) are presented in Figure 3. The temperature dependence of relaxation time T_1 of virgin PPS is similar to those discovered earlier in commercial grades of RYTON PPS R-4 and PPS R-6 obtained after annealing [5]. In both cases the recoveries of magnetization were exponential. The introduction of mineral filler to pristine PPS changes the recovery of magnetisation in non-exponential manner. In the last case of PPS composites the temperature dependence of relaxation time show a very sharp increase followed by a minimum.

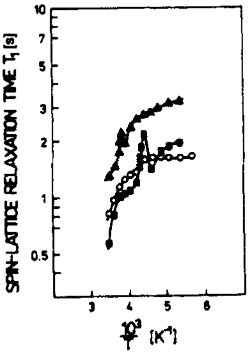

FIGURE 3 Temperature dependence of spin-lattice relaxation time T_1 for: pristine PPS - O, PPS/SiO_2 composite without annealing - ■, PPS/SiO_2 composite annealed at 150°C for 1 hour - ▲.

DISCUSSION

Results of surface morphology of pristine PPS and its composites are interpreted as an interfacial strain effect in the polymer network. There are probably weak sections of morphological structure of the polymer where the internal stress exists. Therefore it is suggested that introducing silicone dioxide filler to the polymer network increase the distance between aggregates. This leads to a limited exchange in energy of protons between the neighbouring aggregates. Distances between agglomerates and aggregates are far compared with the distance in which dipolar interactions take place. For this reason it is assumed that non-exponential recoveries of magnetisation in mineral filled PPS is connected with the interaction between nuclear spins inside some particles. Therefore the nature of interactions between aggregates or agglomerates system are different from the interaction inside them. It is assumed that these systems interact due to electrostatic charges located on polymer chains, which cause mutual repulsion. In this polymer there exist paramagnetic centres located on oligomers, which are probably the source of these interactions [6]. These centres were also observed in injection moldings of pristine PPS by electron paramagnetic resonance (EPR) [7].

CONCLUSIONS

Exponential recovery of magnetisation for pristine PPS suggests that the exchange of spin energy between aggregates is rapid as a result of a good contact between different phases of the polymer. Introduction of filler to the polymer changes the interaction mechanism. Inside the agglomerates and also aggregates there exists dipol-dipol interaction mechanism. This interaction is opposite to electrostatic interaction between these systems. The contact between different composite polymer phases is weak and therefore non-exponential recovery of magnetisation is observed. This means that the molecular reorientation of protons is independent in each of the phases.

AFM and NMR studies of unfilled and mineral-filled PPS show that fragmentation during anealing in both cases has the same nature. Between agglomerates and smaller aggregates there exist repulsion forces which are probably the source of fragmentation in the polymer network.

Acknowledgments

Authors are grateful to Professor A. Krysztafkiewicz from Department of Chemical Technology at Poznan University of Technology for providing the synthesised silicon dioxide. This work was partially supported by the PUT research program No DPB 62-129.

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