Mechanical and Structural Characterization of POSS-Modified Polyamide 6

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ABSTRACT: This work investigated the mechanical behavior of POSS-modified polyamide 6 (PA6), containing PA6 chains terminated at one end with aminopropyl-heptaisobutyl POSS. Three systems with different POSS contents (5.4, 10.8, and 16.2 wt %), each characterized by a specific molecular mass, and the corresponding PA6 neat polymers were examined. The materials were first subjected to morphological and calorimetric analysis by wide-angle X-ray diffraction and differential scanning calorimetry, respectively. Tensile tests, performed on the samples in wet conditions, showed that stiffness, strength, and ductility were appreciably modified by the presence of POSS in the polymeric chains. The relationships among these effects and the microstructural characteristics of the systems also were analyzed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3409–3414, 2006

Key words: polyamides; nanocomposites; mechanical properties; differential scanning calorimetry (DSC); structure-property relations

INTRODUCTION

In the past few years polymer nanocomposites, that is, composites in which the filler has at least one dimension in the nanometer range, have attracted much interest for the development of high-performance plastic materials. In fact, it is well recognized that the behavior of composites largely depends on interfacial interactions, so that the smaller in size the components, the greater the contribution of interfacial interactions to the material properties. Substantial enhancement of mechanical, thermal and physicochemical properties has been achieved by incorporating nanofillers of different sizes and aspect ratios, such as layered silicates,[1] carbon nanotubes,[2] and polyhedral oligomeric silsequioxanes (POSS),[3] into various polymeric matrices. In particular, the dramatic improvement in thermooxidative resistance and reduction in flammability observed in some POSS-based nanocomposites has made these systems excellent candidates for high-temperature and fire-resistance applications.[4–6]

POSS compounds consist of an inorganic cage $(SiO_{1.5})_n$ ($n = 6, 8, 10\ldots$) bearing n organic substituents, which may be hydrocarbon residues or include one or more functional groups (see Fig. 1). By properly choosing such substituents, POSS molecules can be made compatible with polymers, into which they can be dispersed by blending. Even in this case, microphase separation can still occur, thus reducing the potential benefits associated with nanoscale dispersion. However, a distinct advantage of POSS over other nanofillers is that reactive functionalities can be easily introduced in POSS molecules, so POSS also can be incorporated into common polymers by copolymerization or grafting.

A number of POSS-containing copolymers including poly(methyl methacrylate),[4,7,8] polystyrene,[9,10] polyethylene,[5,11] polypropylene,[5,11] polysiloxane,[12] and epoxies[13,14] have been reported in the literature. It has been shown that microphase separation is less likely to occur in these systems than in physically blended POSS nanocomposites. The presence of POSS produces remarkable increases in decomposition and the glass-transition temperature. Dramatic modification of the viscoelastic behavior in the rubberlike plateau and an increase in the characteristic relaxation time at the terminal zone have been reported for many systems. Both effects have been ascribed to the retardation of segmental motions induced by the incorporation of massive POSS groups. Although several studies have appeared on POSS-based copolymers, only a few have addressed the effect of the incorporation of POSS on the mechanical properties of these materials. In the present work the mechanical behav-
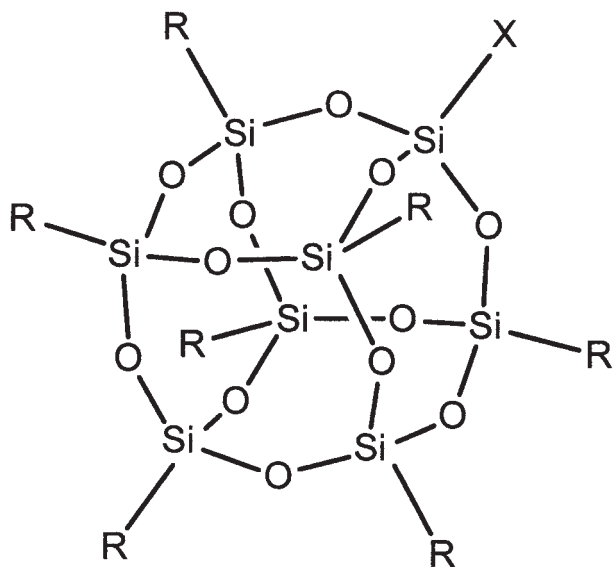
Figure 1 Structure of a POSS molecule bearing seven unreactive groups (R) and one reactive group (X).

ior of POSS-modified polyamide 6 (PA6) nanocomposites was investigated. The synthesis and molecular characterization of these systems were reported elsewhere.[15] Briefly, these materials were obtained by anionic polymerization of ε-caprolactam in the presence of a heptaisobutyl POSS-based activator (chain initiator) and thus consisted of PA6 chains carrying heptaisobutyl-POSS at one end. Three systems of different average molecular mass synthesized using different amounts of activator (0.6, 1.2, and 1.8 mol %) were investigated. Neat PA6 samples prepared using the same amounts of a POSS-free activator were also analyzed as reference materials.

EXPERIMENTAL

Materials

The materials investigated are listed in Table I. In the POSS-modified systems, 0.6, 1.2, and 1.8 mol % POSS activator corresponded to 5.4, 10.8, and 16.2 wt % POSS, respectively. The materials, synthesized as described elsewhere,[15] were subjected to viscometric analysis and then were compression-molded as films with a thickness from 50 to 150 μm, suitable for the preparation of specimens for the mechanical characterization.

Morphological analyses

The materials, in the form of compression-molded films, were subjected to both morphological and calorimetric analyses by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC), respectively.

WAXD patterns were recorded by a Philips PW1710 diffractometer, using Cukα radiation in the 2–50° 2θ range.

Calorimetric analysis was performed with a TA Instruments (New Castle, DE) DSC (model Q100). The samples were heated from 40°C to 250°C at 10°C/min under a nitrogen atmosphere in order to prevent oxidation. Heating scans were analyzed in the range of the melting temperature (T_m), and the heat of fusion (ΔH_f) was used to calculate the degree of crystallinity, defined as the ratio of ΔH_f to the heat of fusion of the purely crystalline forms of PA6 (ΔH_f°). Because ΔH_f° values of the two crystalline forms (α and γ forms) were nearly identical—241 J/g for the α form and 239 J/g for the γ form[16]—the average of the two, 240 J/g, was used to calculate the degree of crystallinity.

Uniaxial tensile tests

The tensile tests were carried out with an Instron (High Wycombe Bucks, UK) dynamometer (model 3366) on specimens prepared by cutting rectangular coupons 44 mm in length and 6 mm in width from the compression-molded films. All the tests were performed using a distance between the grips of 30 mm, at room temperature, and at a crosshead speed of 2 mm/min. Before testing, the specimens were conditioned in water at 30°C for 120 h. Their final water content, referred to as neat PA6, was 8–9 wt %. All properties were evaluated on an average of at least 6 specimens.

RESULTS AND DISCUSSION

Morphology

The molecular mass of the various materials was determined by viscometric analysis. The data shown in Table I indicate that for each molar fraction of activator used for the synthesis of the materials, the average

TABLE I
Viscosity-Average Molecular Mass (M_v) and DSC Data for POSS-Modified PA6-Based Systems and Neat Polymers

Activator (mol %)	POSS (wt %)	M_v[a]	T_m (°C)	x_c[b] (%)
0.6	0	48,000	214/218.7	19
	5.4	88,000	214.1	16
1.2	0	34,000	213/219	21
	10.8	60,000	213.6	16
1.8	0	22,000	211.6/218.6	22
	16.2	58,000	212.5	16

[a] M_v was determined in 95–97 wt % sulfuric acid at 20°C, using the equation[27] [η] = 0.51 × 10^{-3} $M_v$$^{0.74}$.
[b] x_c was calculated as the ratio $\Delta H_f/\Delta H_f$°, where ΔH_f° is the average of ΔH_f° (α) and ΔH_f° (γ), That is, 240 J/g.[16]
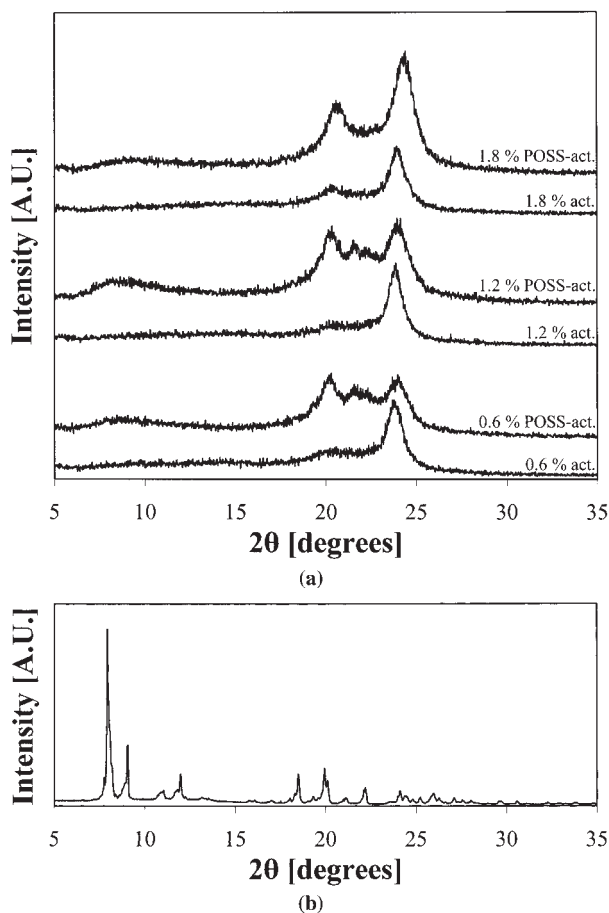
Figure 2 WAXD patterns of (a) samples of compression-molded films made from POSS-modified PA6-based systems and neat polymers synthesized using different molar fractions of activator (% is mol %; patterns shifted for clarity); (b) POSS activators.

not be clearly observed, and the α-form reflections were slightly shifted toward higher 2θ values. On the basis of the results obtained by Zheng et al.[18] and Waddon et al.,[19] who clearly showed evidence of crystallized POSS structures in POSS-modified semicrystalline polymers, the very broad peaks observed for POSS-modified systems at about $2\theta \approx 8°$, completely absent in the diffraction patterns of neat polymers, might be associated with the reflections originating from crystalline POSS [see Fig. 2(b)].

Figure 3 shows the DSC melting endotherms of POSS-modified systems and neat polymers synthesized using different molar fractions of activator, and Table I summarizes data from these scans. The scans showed that the neat polymers exhibited two distinct endothermic peaks, whereas the POSS-modified systems had a single peak, at the same temperature as the low-temperature peak of the corresponding neat polymer. In the neat polymers the temperature and the height of the low-temperature peak decreased slightly relative to the high-temperature peak, when increasing the molar fraction of the activators used for the synthesis, that is, with decreasing molecular mass, whereas the high-temperature peak was apparently unaffected by polymer molecular mass. In POSS-modified materials a shoulder prior to the endothermic peak could be clearly observed, and the intensity of this shoulder, in particular, was reduced by increasing POSS content until it practically disappeared in the system at 16.2 wt % POSS. In addition, in POSS-modified systems the peak temperature decreased slightly by increasing the POSS content. The DSC data presented in Table I show that with all three molar fractions of activator, the presence of POSS molecules
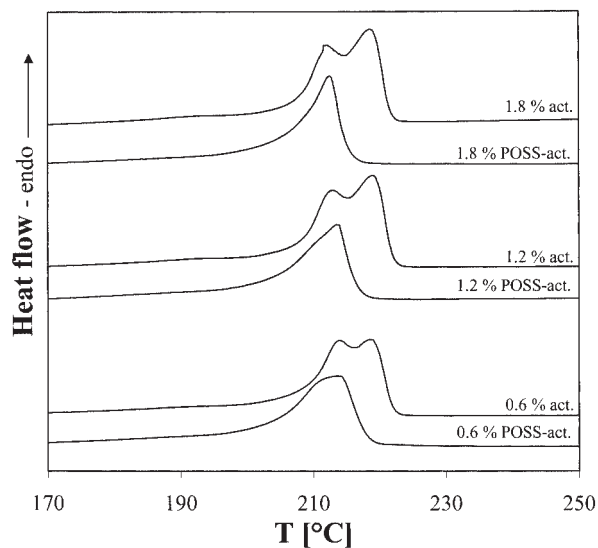
molecular mass of the POSS-modified system was remarkably higher than that of the corresponding neat polymer. In both POSS-modified systems and the neat polymers the viscosity-average molecular mass was reduced by increasing the molar fraction of activator.

The X-ray diffraction patterns of the POSS-modified systems and neat polymers are shown in Figure 2(a). WAXD analysis revealed that the presence of POSS in PA6 chains induced modifications of the polymeric crystal structure, which consisted of the progressive development of γ crystals coexisting with crystals of the α form. In particular, the WAXD patterns of the neat polymers showed two main peaks, at $2\theta \approx 20°$ and $24°$, which were attributed to the (002+202) and (200) crystallographic reflections of the α form.[17] For POSS-modified systems synthesized using 0.6 and 1.2 mol % activator, in addition to the α-form reflections, a peak could be observed at about $2\theta \approx 21.4°$, attributed to the (001) crystallographic reflection of the γ form.[17] For the POSS-modified system with 1.8 mol % activator, the peak corresponding to the γ form could

Figure 3 DSC traces of samples of compression-molded films made from POSS-modified PA6-based systems and neat polymers synthesized using different molar fractions of activator (% is mol %; scans shifted for clarity).
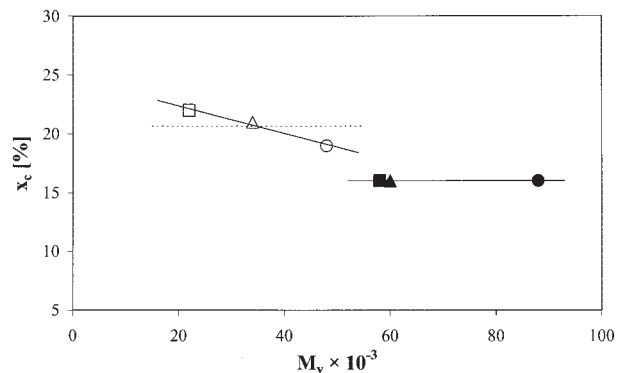
Figure 4 Degree of crystallinity versus viscosity-average molecular mass for POSS-modified systems (solid symbols) and neat polymers (open symbols) synthesized using 0.6 mol % (●), 1.2 mol % (▲), and 1.8 mol % (■) activator.

in the polymer chains caused a reduction in the degree of crystallinity that in POSS-modified PA6 had remained constant. The data, also plotted in Figure 4 as a function of polymer molecular mass, show that for neat PA6 the crystallinity content slightly decreased with increasing molecular mass. Despite this, basically two different degrees of crystallinity could be associated with the two (POSS-modified and -unmodified) systems. These results seemed to show that the lower degree of crystallinity in the POSS-modified PA6 systems than in the corresponding neat polymers could be ascribed to the presence of POSS molecules in the chains hindering the formation of ordered domains, compensating for the possible effects of molecular mass (in our samples a higher POSS content was associated with lower molecular mass).

In principle, the formation of either a small shoulder or a melting peak prior to the endothermic peak in PA6 may be associated with the presence of the γ crystalline form, or it may simply reflect changes in crystallite thickness and distribution of the α form.[17] The WAXD results helped in gaining an understanding of the thermal behavior of the various materials examined. Because in the WAXD patterns of the neat polymers only the α crystalline form could be detected, the low-temperature peak observed in the corresponding DSC thermograms was more likely to have been associated with the presence of imperfect α crystals, characterized by reduced thickness of the crystallite lamellae, rather than with the presence of a different crystalline form. On the basis of WAXD results, it was determined that the shoulder prior to the endothermic peak in POSS-modified systems with 5.4 and 10.8 wt % POSS could be associated with the presence of a γ crystalline form in addition to α crystals. The α crystals in the POSS-modified systems appeared similar to the imperfect α crystals observed in the corresponding neat PA6.

Stress–strain behavior

Typical stress–strain curves of the various materials investigated, shown in Figure 5, indicate that with all three molar fractions of activator used for the synthesis of the materials, the mechanical behavior of POSS-modified system was considerably different from that of the neat PA6. Data on elastic modulus, tensile strength, and elongation at break were obtained from the experimental stress–strain curves, which are summarized in Table II.

The results obtained for elastic modulus are shown in Figure 6 as a function of POSS content within the material. First, it can be observed that the neat PA6 samples were quite similar in elastic modulus, varying by less than a standard deviation. Further, the presence of POSS within PA6 resulted in decreased stiffness. This was clearly in contrast to the usual behavior of particulate composites containing rigid fillers of exhibiting reinforcement effects, and it can be justified only by the structural modifications of the polymer matrix. In fact, reinforcement effects in composite systems can be assessed only with reference to the modulus of the corresponding matrix, that was unknown and unmeasurable in the present study. The modulus of the polymeric matrices of the three POSS-modified systems was then evaluated by tentatively applying the analytical micromechanical model proposed by Kerner[20] to the experimental data. This model was developed for systems composed of rigid spherical particles embedded in a homogeneous matrix, whereas in the present study, the polymer matrices could not strictly be considered mechanically homogeneous because of the constitution of a soft amorphous component (in wet conditions the glass-transition temperature of PA6 was just below room temperature) containing crystalline (hard) domains. For polymers containing moderate concentrations of nearly spherical particles that are much more rigid than the polymer matrix, assuming uniform distribu-
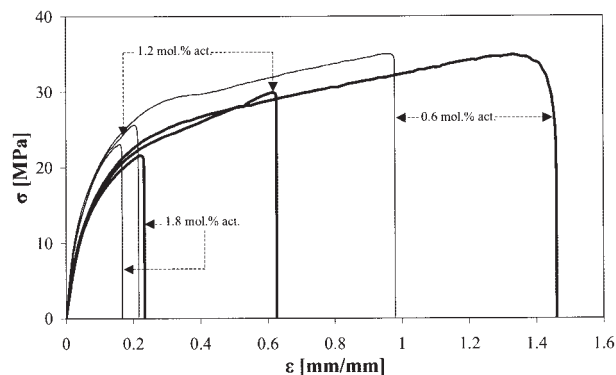

Figure 5 Typical stress–strain curves of POSS-modified PA6-based systems (▬) and neat polymers (—) synthesized using different molar fractions of activator.

TABLE II
Tensile Properties of the Various Materials

Activator (mol. %)	POSS (wt %)	E (MPa)	$\sigma_{\varepsilon\,=\,10\%}$ (MPa)	$\sigma_{\varepsilon\,=\,15\%}$ [MPa]	Elongation at break (%)
0.6	0	490 ± 61	20 ± 0.8	23 ± 0.8	60 ± 32
	5.4	290 ± 42	15 ± 0.7	19 ± 0.6	105 ± 41
1.2	0	430 ± 70	19 ± 1.2	23[a]	16 ± 5
	10.8	310 ± 28	17 ± 0.8	20 ± 1	40 ± 17
1.8	0	400 ± 53	20 ± 1	23[a]	13 ± 4
	16.2	325 ± 13	17 ± 0.4	19 ± 0.6	19 ± 4

[a] Average of only two values.

tion of the particles and good adhesion between filler and polymer, the Kerner equation is:

$$\frac{G}{G_1} = 1 + \frac{15(1 - \nu_1)}{8 - 10\nu_1} \cdot \frac{\Phi_2}{\Phi_1} \qquad (1)$$

where G and G_1 are the shear modulus of the composite and the matrix, respectively; ν_1 is the Poisson's ratio of the matrix; and Φ_2, and Φ_1 are the volume fraction of the filler and the matrix, respectively.

From the experimental values of the Young's modulus of POSS-modified PA6-based systems, by the application of eq. (1), the stiffness of the polymer matrix in each POSS-modified material is tentatively determined assuming for PA6 a density of 1.14 g/cm³ and a Poisson's ratio of 0.33 whereas for POSS molecules a density of 1.1 g/cm³. In particular, for each POSS-modified system, the experimentally determined mean Young's modulus of the composite and the two extreme values (the mean ± the experimental standard deviation) were used as inputs for the model. Therefore, the elastic modulus of the polymer matrix in each POSS-modified system, evaluated by the application of the model, can be expressed as a
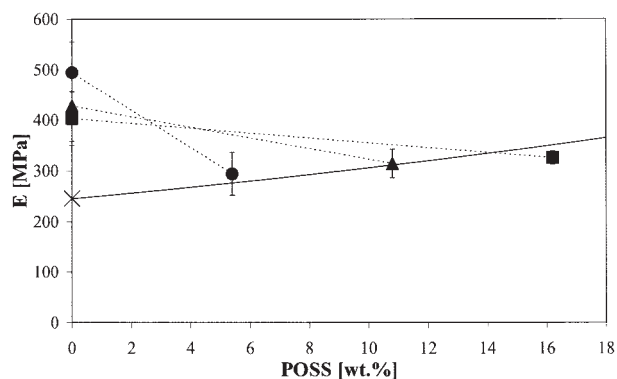

Figure 6 Young's modulus as a function of POSS content for the systems synthesized using 0.6 mol % (●), 1.2 mol % (▲), and 1.8 mol % (■) activator. The theoretical mean stiffness of the polymeric matrices of the POSS-modified systems (×) and the prediction of the modulus versus POSS content in POSS–PA6 composites according to the Kerner equation (see text) are also traced.

value corresponding to the mean experimental Young's modulus of the composite ± a specific variation in corresponding to the experimental standard deviation. The results were: 261 ± 37, 248 ± 22, and 228 ± 9 MPa for the matrix of the systems containing 5.4, 10.8, and 16.2 wt % POSS, respectively. Given the extent of the variations derived from the experimental standard deviation of the Young's modulus of the POSS-modified systems, the values were quite similar, indicating that the PA6 matrices of the different POSS-modified samples had approximately the same stiffness. This was expected given that each material had the same degree of crystallinity and that molecular mass alone can play only a secondary role. Thus, a unique value of elastic modulus could be associated to the matrices of the different nanocomposite. This value, averaged with those calculated from the model, also is reported in Figure 6. The higher elastic modulus of neat PA6 relative to those of the PA6 matrices in the nanocomposites, is explained by the higher degree of crystallinity. Therefore, the decreased stiffness promoted by the POSS molecules in the polymeric chains should be attributed mainly to changes in the degree of crystallinity, which overshadowed the intrinsic reinforcement action of the POSS particles.

The yielding and postyielding behavior of the materials investigated showed that the presence of POSS molecules in PA6 chains resulted in decreased strength but increased ductility, as shown by the increase in elongation at break. These results for wet samples tested at room temperature, that is, above the glass-transition temperature of the material, may be attributed to the decrease in the degree of crystallinity as well as to the differences between the crystallinity structures. In fact, it was reported in the literature that both degree and type of crystallinity determined the yielding and postyielding behavior in PA6. In particular, it was found that higher ductility and toughness were favored by lower crystallinity[21] and that the yielding mechanisms were basically governed by crystal slip processes peculiar to the particular form of the crystal, either α or γ.[22,23] Further, it was pointed out that the deformability of PA6 above the material glass-transition temperature was greatly affected by the

crystalline form and that, in particular, the γ form was more ductile than was the α form.[24] More recently, it was observed that PA6 samples predominantly containing the crystalline α form above the glass-transition temperature exhibited lower ductility but higher strength than those containing crystals mainly of the γ form.[25] Our results agree with these findings because the morphological analyses revealed that incorporation of a POSS molecule at the end of a polymer chain increased the development of the crystalline γ form and also decreased the overall degree of crystallinity, factors that both were detrimental to the material's strength but enhanced its ductility. Furthermore, in both the POSS-modified systems and the neat polymers, elongation at break decreased remarkably by increasing the molar fraction of the activators. This reduction might be correlated with the decrease in the polymer molecular mass, in agreement with the results obtained by Fornes et al.[26]

CONCLUSIONS

In the present work the microstructural characteristics and mechanical behavior of POSS-modified PA6 systems were analyzed and compared with those of the corresponding PA6 neat polymers. The morphological and calorimetric analyses revealed that the presence of POSS in the PA6 chains promoted modifications of the polymeric crystal structure, which consisted of the progressive development of γ crystals and a decrease in the overall degree of crystallinity. Mechanical testing, carried out above the material's glass-transition temperature, showed that the presence of POSS resulted in decreased stiffness relative to that in the PA6 neat polymers, which could be explained by the reduction in the degree of crystallinity. The yielding and postyielding behavior of the materials investigated showed that the presence of POSS molecules in PA6 chains produced decreased strength and increased ductility relative to those in the PA6 neat polymers. These effects can be attributed to both the decrease in the degree of crystallinity and the development of γ form, which was promoted by POSS modification.

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