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Filler-Induced Structural Order and Mechanical Properties of Polystyrene-Silica Nanocomposites

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This study is concerned with the relationship between wide angle X-ray scattering (WAXS) analysis and physical properties of amorphous polystyrene (PS)-silica (SiO₂) composites. Nanoporous SiO₂ for the fillers was prepared by the hydrothermal reaction and the structures of the composites were examined by WAXS. In their WAXS patterns, two characteristic peaks, inner peak and outer peak, were observed at $q \approx 7 \text{ nm}^{-1}$ and 15 nm^{-1} corresponding to the intermolecular structure of PS chains and the intramolecular order of benzene rings, respectively. The ratio ($I_{in}/I_{out}=P$) in intensity of the inner peak (I_{in}) to outer peak (I_{out}) affords the structural parameter to well characterize the intermolecular and intramolecular structures of PS molecules and the P values are observed to change widely from 0.183 to 1.16 depending on the material compositions. The elongation at the break point increases monotonously with increasing P , whereas the yield strength and the Young's modulus decrease with P for $P=0.497$ or below but remain almost constant for larger P values. The elongation of 4.5% for (PS+MPS) / SiO₂ is enormously larger than those for PS and the other composites, in contrast to a slight decrease of the other two properties relative to those for PS. It is also revealed that a strong interaction works between the COO or COOH groups of maleic anhydride modified polystyrene (MPS) and the OH groups of SiO₂, which makes the PS polymer molecules to stack regularly on SiO₂ nanofillers, leading to control the physical properties of the composites.

Key Words: PS / MPS / SiO₂ / Nanocomposite / WAXS / Inner peak / Outer peak

1. INTRODUCTION

Polystyrene (PS) is one of the most widely used plastics with many excellent properties such as transparency, formability, rigidity for packages, sheets or films, molding, foaming and so on. However, PS is very brittle due to its high T_g and amorphous structure. For improving these poor properties, high impact polystyrene (HIPS) or polyacrylonitrile-polystyrene copolymer with butadiene particles (ABS, AS, etc) has been developed, however the lack of transparency is largely disadvantages for many applications.

Recently, increasing attention has been focused on the highly functional materials based on nanometer-sized building units such as nanoparticles and nanotubes.¹⁾ A variety of layered, hexagonal or cubic nanostructured inorganic solids templated by surfactant assemblies and their deorganized or ion-exchanged porous ones have been extensively synthesized to provide a fundamental class of materials for nanotechnological devices and systems.^{2,3)} One of the most important applications of nanomaterials is directed to the filler-reinforced polymer composites. Clay minerals have been

applied for the polymer composites in which the delaminated silicate plates as a reinforcing material are uniformly dispersed in a matrix of nylon 6,⁴⁾ polypropylene⁵⁾ or other engineering polymers. These polymer/clay nanocomposites are classified into a new family of engineering plastics in respect of their higher strength, higher modulus, higher heat distortion temperature, and lower gas permeability.⁶⁾

In previous studies about WAXS observation of PS⁷⁻¹¹⁾, it was shown that the two characteristic peaks were observed at $q=7.5 \text{ nm}^{-1}$ (inner peak) and 10.0 nm^{-1} (outer peak) corresponding to the intermolecular distances of PS chains and benzene rings interaction, respectively. The intensity of inner peak was increased by drawing or heating, whereas the intensity of outer peak was a little changed and therefore the ratio ($=I_{in}/I_{out}$) in intensity of inner to outer peak was correlated primarily with the intermolecular structure of PS. According to these reasons the inner peak was named as "polymer peak". In this study, the nanocomposites composed of nanoporous SiO₂ and PS or PS/MPS (maleic anhydride modified PS) were prepared to examine their structures by WAXS method and it

was first revealed that the characteristic WAXS patterns are strongly related to the physical properties of these composites.

2. EXPERIMENTAL

2.1 Preparation of Mesostructured Silica

Two kinds of hexagonal mesoporous silica were synthesized by the templating method using cationic surfactant in a manner of Kresge et al.¹²⁾ Fused silica, cetyltrimethyl ammonium chloride (CTAC), NaOH, and H₂O were mixed at a molar ratio of 1/0.45/0.25/67, and then reacted at 140 °C for 48 hours under the hydrothermal condition. The resulting precipitate was washed with pure water three times and then dried in air oven to yield CTAC-complexed hexagonal mesophase silica (SiO₂(St)), followed by the calcination at 500 °C for 7 hours to obtain hexagonal-structured mesoporous silica (SiO₂).

2.2 Preparation of Polymer-Nanofiller Composite Films

Atactic-polystyrene (PS;US310) from Idemitsu Petro Chemical, and modified polystyrene with maleic anhydride of 12.5 mol% (MPS) from Sigma-Aldrich Japan for introducing the polar group to PS were used for preparing the composite materials. PS and a 95:5 (wt/wt) mixture of PS and MPS for the matrix polymers were dissolved in toluene in the polymer mixtures. The latter will be abbreviated as PS+MPS. The silica/polymer nanocomposites were prepared as follows. A given amount of SiO₂(St) or SiO₂ was ultrasonically dispersed in toluene and then each dispersion was mixed with PS or (PS+MPS) at a polymer concentration of 20 wt% in each solution. Filler dispersed polymer solution was apparently transparent due to the perfect dispersion of nanofillers in polymer solution and casted on a glass plate and then the solvent was evaporated to form a transparent thin film of 200 μm thick.

2.3 Characterization of Fillers and Nanocomposites

The nanofillers and obtained composite films were characterized by the following analytical methods. XRD measurements were conducted on a Shimadzu XD-D1 diffractometer with Cu Kα radiation at a scanning rate of 2 degree/min. Scanning electron microscopic (SEM) images were observed by a Hitachi H-4100M. Energy dispersive X-ray (EDX) microanalysis was carried out on a HORIBA EMAX-5770. Thermogravimetric and differential thermal analyses (TG/DTA) were observed by a SEIKO TG/DTA320U with a heating rate of 10 °C/min in air. Fourier transform infrared (FT-IR) spectra were measured by the KBr pellet method using a Nippon Bunko FT/IR-300. The film was

cut into specimens 5 mm wide and 30 mm long for the tensile test. The physical properties are obtained by the methods of JIS K-7113.

3. RESULTS

3.1 Characterization of Fillers

The silica fillers, SiO₂ and SiO₂(St), used here were primarily examined by X-ray diffraction to characterize their hexagonal structures. The BET measurement of SiO₂ gave a very large value of $1.18 \times 10^3 \text{ m}^2/\text{g}$ for the specific surface area and 3 nm for the pore diameter, as shown in Fig. 1. The particle sizes of SiO₂ and SiO₂(St) were less than 100 nm by SEM observation (Fig. 2).

3.2 WAXS Analysis of PS- and (PS+MPS)-Nanofiller Composites

According to a structure model for PS proposed by Mitchell and Windle,¹¹⁾ the structure of PS is separated essentially into the intermolecular structure (named 'superchain') and the intramolecular or intermolecular stacking of benzene rings, as schematically shown in Fig. 3.¹³⁾ The former (long range structures) and the latter (short range structures) can be correlated to two characteristic peaks typically observed at around $q = 7 \text{ nm}^{-1}$ (inner peak) and 15 nm^{-1} (outer peak), respectively, in the WAXS pattern of PS. Each peak is characterized in detail by three parameters, the scattering

Fig. 1. Pore size distribution curve for SiO₂ nanofiller.

Fig. 2. SEM images of the SiO₂ and SiO₂(St) nanofillers used.

vector ($=q$) defined as the following Eq.(1), scattering intensity ($=I$) and half width ($=H_{1/2}$).¹⁴ Here, the q -value means the first order approximation of the intermolecular distance of PS or intramolecular distance of benzene rings, I the probability of the molecules with same q , and $H_{1/2}$ the dispersion of intermolecular distance of PS or the intramolecular distance of benzene rings.¹⁵

$$q = 4\pi / \lambda \sin(2\theta/2) \quad (1)$$

These parameters were evaluated from the WAXS patterns of the present composites systems shown in Fig. 4. From the results of evaluations summarized in Table I, II and Figs. 5 and 6 we can see quite opposite tendencies in WAXS parameters between the PS and the PS+MPS based composites. For the

Fig. 3 PS intermolecular and intramolecular structure proposed by Michell et al.¹³⁾

Fig. 4 WAXS charts of matrix polymers and their composites with silica fillers for the (A) PS and (B) PS+MPS systems. The inner and outer peaks are indicated by arrows.

Table I WAXS parameters of polymers and their nanocomposites.

polymer/filler	Inner halo			Outer halo		
	q_{in} (/nm)	I_{in} a.u.	$H_{1/2in}$ rad.	q_{out} (/nm)	I_{out} a.u.	$H_{1/2out}$ rad.
PS/-	7.2	60	0.071	13.7	160	0.123
PS/SiO ₂	7.11	31	0.038	16.8	87	0.195
PS/SiO ₂ (St)	6.65	29	0.041	16.3	99	0.174
(PS+MPS)/-	(6.96) ^{a)}	(19) ^{a)}	(0.017) ^{a)}	15.3	104	0.183
(PS+MPS)/SiO ₂	8.07	246	0.071	13.6	212	0.127
(PS+MPS)/SiO ₂ (St)	8.01	83	0.057	13.1	167	0.118

The q is scattering vector and defined as following eq., and I and $H_{1/2}$ means the intensity and the half wide of XRD peak.

$$q (/nm) = 4\pi / \lambda \times \sin \theta$$

a) the inner halo peak is very weak to characterize the WAXS parameters as shown in Figure 4.

Table II Parameter P and physical properties of polymers and the composites.

polymer/filler	$P (=I_{in}/I_{out})$	S (MPa)	E (GPa)	ε (%)
PS/-	0.375	1.43	1.47	3.13
PS/SiO ₂	0.356	2.11	1.15	2.75
PS/SiO ₂ (St)	0.293	1.76	1.44	2.15
(PS+MPS)/-	0.183	2.55	1.54	2.51
(PS+MPS)/SiO ₂	1.16	1.35	0.55	4.5
(PS+MPS)/SiO ₂ (St)	0.497	1.18	0.72	2.63

S , yield strength; E , initial modulus; ε , elongation at break point.

Fig. 5 Relationship between scattering vectors q_{in} inner peak for polymers and the compositions of the composites. Non means polymer only and SiO₂ and SiO₂(St) show the fillers used in composites.

Fig. 6 Relationship between scattering vectors q_{out} of outer peak for polymers and the compositions of the composites. Non means polymer only and SiO₂ and SiO₂(St) show the fillers used in composites.

the outer peaks are smaller and broader than those for PS matrix. In more detail, the q_{in} , I_{in} and I_{out} values for these composites are smaller than those for PS alone, whereas the q_{out} and H_{out} values for the formers are larger than those for PS alone. These findings indicate that on mixing with SiO_2 or $\text{SiO}_2(\text{St})$ fillers the intermolecular distances of PS molecules become larger and the intermolecular polymer structures become less regular. This means that there is no strong interaction between PS molecules and fillers in the PS/ SiO_2 and PS/ $\text{SiO}_2(\text{St})$ composites, which leads to an increase of the intermolecular distances of PS because the fillers are independently dispersed among the polymer chains. For the (PS+MPS)/ SiO_2 and (PS+MPS)/ $\text{SiO}_2(\text{St})$ composites, on the other hand, it is observed that the inner and the outer peaks are larger and narrower than those of (PS+MPS) matrix. The q_{in} , I_{in} and I_{out} values for both composites are much larger than those for (PS+MPS) matrix, whereas q_{out} , H_{in} and H_{out} values for the formers are smaller than those for the latter. These observations indicate that both the SiO_2 and $\text{SiO}_2(\text{St})$ fillers mixed with PS+MPS matrix act to decrease the intermolecular distances of polymer chains and increase the regularity of the intermolecular polymer structures, in marked contrast to the MPS-free systems.

For further discussion about the structural properties of the present materials, we introduce the parameter P defined as Eq.(2).

$$P = I_{in}/I_{out} \quad (2)$$

For example, it is known that the intensity of inner peak ($=I_{in}$) for PS films is significantly increased by drawing or annealing, but the intensity of outer peak ($=I_{out}$) is decreased or little affected by these treatment, according to the changes of intermolecular and intramolecular structures of PS¹¹⁾. Thus the parameter P can be taken as an effective measure to evaluate primarily the degree of order or disorder of the intermolecular in PS-based systems.

In the filler-free systems, the P value for (PS+MPS) is decreased to 0.183 relative to the P value of 0.37 for PS, because the bulky maleic anhydride groups in MPS would disturb PS intermolecular structure and increase the average distances between of PS molecules. In marked contrast, the P values for the (PS+MPS)/ SiO_2 and (PS+MPS)/ $\text{SiO}_2(\text{St})$ composites systems are largely increased to 1.160 and 0.497 much more than those for PS or (PS+MPS) matrix, respectively. This is because the numbers of PS molecules assembled at same q values are distinctly increased through the strong interaction between COO- or COOH groups of

MPS in the matrix polymer and OH groups on the surface of SiO_2 or $\text{SiO}_2(\text{St})$, although the overall fraction of the maleic anhydride modified polymer (MPS) in the matrix polymer is as small as 5 wt%.

In the previous study¹¹⁾, a definite increase in intensity of inner peak was observed for drawing or heating PS film, but the P values remained at 0.4-0.5 or below. Therefore it is worth remarking that the marvelously large P values more than 1.0 is observed in the present study. It is also remarked that the P values for the $\text{SiO}_2(\text{St})$ composites are much less than those for the SiO_2 ones. This is because the external and the cylindrical internal surface of $\text{SiO}_2(\text{St})$ particles are mostly covered with the surfactant molecules, leading to a significant decrease in direct interfacial interaction between matrix polymer molecules and silica particle surface.

On the basis of the above observations, we can propose the formation mechanism of the present composites based on the interaction between polymer and fillers, as schematically shown in Fig. 7. In the (PS+MPS)/ SiO_2 composites with large P values, polymer molecules are attracted to the surfaces of SiO_2 nanofillers through the hydrogen bond or electrostatic interaction, which induces epitaxial assembling of polymer chains on SiO_2 . Usuki also reported a similar finding that a stacking structure of several layers of SEBS polymer molecules formed on the surface of fillers in SEBS/ SiO_2 nanocomposite was observed by TEM method.¹⁶⁾

In short, the present data reveal that the strong interaction between COO- or COOH groups of MPS and surface OH groups of SiO_2 or $\text{SiO}_2(\text{St})$ in the mixed polymer composites

Fig. 7 Schematic mechanism for generation of the composites consisting of polymer and SiO_2 nano-fillers. PS or MPS molecules are described as flexible tube shapes and SiO_2 nanofiller shown as rectangular shapes with OH groups on the surface. The polymer molecules are attracted to the SiO_2 nanofillers through the hydrogen bond or electrostatic interaction and further assembled on the SiO_2 by their intermolecular hydrophobic forces.

must be the key factor to make the PS polymer chains to assemble epitaxially and stack regularly on the surface of SiO₂ nanofillers.

3.3 Mechanical Properties of PS- and (PS+MPS)- Nanofiller Composites

The mechanically hard and brittle properties of PS are sometimes disadvantageous in practical applications. Amorphous polymers molecules with high T_g such as PS cannot move freely at room temperature lower than T_g and it is easy to break down because of generation and propagation of microvoids in PS.¹⁷⁾

The mechanical properties of the present composites are summarized in Table II and Fig. 8. Interestingly, the mechanical properties of these composites demonstrate a uniform dependence on P values independently of their compositions. The elongation (ε) at the break point shows a tendency to simply increase with increasing P , whereas the yield strength (σ) and the Young's modulus (E) decrease linearly at the range of P less than 0.497 and remain almost constant at larger P values. It is worth remarking that the ε value of 4.5% for (PS+MPS)/SiO₂ is enormously larger than those for PS or the others, in contrast to a slight decrease of its σ and E values relative to those for PS. The large elongation of the (PS+MPS)/SiO₂ composite is expected highly effective for improving the brittleness of PS. In this composite, the strong interaction between polymers and fillers would induce a significant decrease in intermolecular distances and an increase in regularity of intermolecular structures of PS, which serves to reduce the concentration of microvoids generated in the material leading to improvement of the mechanical property of PS.

Fig. 8 Relationships between structural parameter $P(=I_{in}/I_{out})$ and mechanical properties, yield strength (S), initial modulus (E) and elongation at break point (ε). The solid and half-solid symbols are for the filler-free PS and MPS systems, respectively. The open symbols are for the other composite systems.

4. CONCLUSIONS

- 1) It is demonstrated that the structural properties of PS, PS+MPS, and their composites with SiO₂ or SiO₂(St) can be well characterized in terms of X-ray parameters defined on the basis of two characteristic peaks observed in their WAXS patterns.
- 2) The strong interactions between COO- or COOH groups of polymer and OH groups on fillers make the polymer chains to be attracted and epitaxially assembled on the fillers in (PS+MPS)/SiO₂ composite, whereas the PS/SiO₂ composite without such strong interaction causes no significant change in intermolecular structure of polymer chains.
- 3) The ratio ($=P$) of inner halo intensity (I_{in}) to outer halo intensity (I_{out}) in WAXS is of great importance as a characteristic structural parameter which well characterizes the intermolecular structures of PS strongly dependent on the interaction between polymer and nanofillers.
- 4) It is found that the elongation, yield strength, and Young's modulus of PS and PS/nanofiller composites can be closely related to their P values as a structural parameter.
- 5) The mechanical property analysis based on the P parameter reveals that the composite of PS, MPS, and mesoporous SiO₂ fillers is highly effective for improving the brittleness of PS mainly through the increase in elongation.

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