Study on Mechanical Properties of Polystyrene/Polyphenylsilsesquioxane *In Situ* Blend

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SYNOPSIS

Impact strength and dynamic mechanical analysis of polystyrene/polyphenylsilsesquioxane (PS/PPSQ) *in situ* blend was studied. Toughness, thermal stability, and storage modulus of the brittle PS matrix could be improved by addition of some much more brittle PPSQ particles when the percentage of PPSQ in this blend was not more than 5%. The toughening mechanism about the deformation of the PPSQ particles, which is due to good adhesion between the dispersed PPSQ particles and the continuous PS matrix and some particle-induced crazes or yielding zones, was discussed. PPSQ has the better effect on the modification of PS than its prepolymer with low molecular weight. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Rubber reinforced plastics (i.e., plastics toughened by inclusion of rubber particles in brittle polymer matrix) constitute an important class of commercial polymers. The best known members of the class are high impact polystyrene and acrylonitrile-butadiene-styrene terpolymer. Basically, there are two-phase systems in which rubber particles, a few micrometers or less in size, are dispersed in a rigid polymer matrix. The currently accepted view of the mechanism of rubber toughening is that impact energy is absorbed by crazing and shear yielding in the glassy matrix, both of which are induced by the presence of rubber particles.[1]

Quite recently, a new concept of impact toughening has been put forth by Kurauchi and Ohta[2] through the studies on plastic blends composed of a ductile matrix and dispersed brittle particles. They proposed the "cold drawing concept," that impact energy is absorbed by a large plastic deformation of the brittle particles dispersed in a

ductile matrix. Inoue et al.[3] studied nine kinds of systems, poly carbonate (PC)/polymethyl methacrylate (PMMA), PC/acrylonitrile-co-styrene (AS), PC/polyphenylene sulphide (PPS), polybutylene terephthalate (PBT)/AS, PBT/PMMA, nylon/PMMA, nylon/polystyrene (PS), polyvinyl chloride/PS, and polyether ether ketone/AS. Only three pairs of them, PC/AS, PC/PMMA, and PBT/AS, were toughened.[3] In the literature,[4] some mechanical models were reviewed that had been used to interpret the toughening mechanism of these systems consisting of brittle particles and ductile matrix. Because some new materials that have good toughness and good mechanical strength, rigidness, and thermal stability can be obtained by this method, much attention has been paid to these toughening systems.

Since 1984, we studied the synthesis, solution property, characterization of structure, thermal stability, and decomposition of polyphenylsilsisquioxane (PPSQ).[5–10] PPSQ, a ladderlike polymer, has excellent properties of withstanding high temperature and solubility in many solvents. In our present study, a new type of toughened plastics containing a brittle matrix (PS) and much more brittle particles (PPSQ) was prepared. Some mechanical properties of this blend were investigated and its toughening mechanism is also discussed.

Table I   Compositions of Specimens

No.	Compositions of Specimens (Weight Ratio)
0	100% PS
1	1% PPSQ, 99% PS
3	3% PPSQ, 97% PS
5	5% PPSQ, 95% PS
Y5	5% prepolymer of PPSQ, 95% PS
Y10	10% prepolymer of PPSQ, 90% PS
Y20	20% prepolymer of PPSQ, 80% PS

EXPERIMENTAL

Preparation of specimens

PPSQ (M_w = 1.72 × 10^4) or its prepolymer (M_w = 1.98 × 10^3) synthesized by us was completely dissolved in styrene monomer containing the initiating agent azobisisobutyronitrile. PS and all blends of PS and PPSQ in a range of compositions (shown in Table I) were obtained after the addition polymerization of styrene. PS and PS/PPSQ *in situ* blend were manufactured with a lathe into rectangular bars for impact tests and dynamic mechanical analysis. The dimension of specimens for tests was 60 × 6 × 4 mm.

Mechanical tests

An unnotched impact test was performed using 1 J (10 kg cm) capacity Charpy Impact Tester (Veb Werkstoffprufmaschien, Zeipzig) at a room temperature of 28°C. Relative humidity was 63%. The unsupported span was 40 mm. Impact strength was calculated by the following formulae:

$$a_k = A/F$$

where a_k is impact strength in kJ/m^2, A is impact energy in kJ used for fracture of specimen, and F is cross-section area of specimen in m^2.

Dynamic mechanical analysis (DMA) was evaluated by the use of Du Pont DMA 982/1090B. The experiments were carried out from −120 to 130°C at a rate of 5°C/min. Low temperature was attained by slow cooling with liquid nitrogen. The heater was automatically started, and the data were recorded on a computer. The storage modulus and damping, which is in proportion to loss modulus, can be obtained by this measurement.
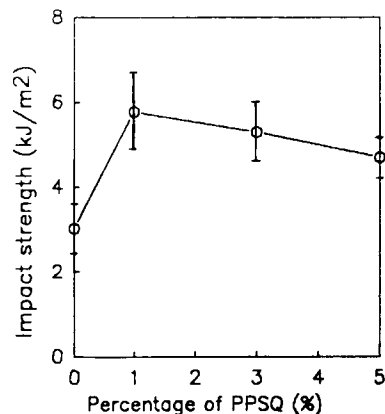

Figure 1   Impact strength of PS/PPSQ *in situ* blend vs. the percentage of PPSQ.

Electron microscopy

The fracture surfaces of specimens after the impact test were observed with scanning electron microscopy (SEM) (Model S-530, Hitachi Co., Japan).

RESULTS AND DISCUSSION

Toughening mechanism of PS/PPSQ *in situ* blend

Average impact strength and scatterbands of PS and its blends at different compositions are shown in Figures 1 and 2. The number of experiments for each group of samples is more than five. From Figure 1, it is obvious that the impact strength of the pure PS is less than those of PS/PPSQ when the blends contain a small amount of PPSQ (<5%). Especially, the impact strength of sample 1, in which the percentage of PPSQ is 1%, is almost two times as much as that of the pure PS. The values decrease on fur-
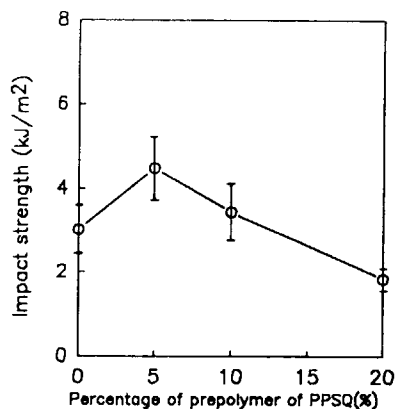

Figure 2   Impact strength of PS/prepolymer of PPSQ *in situ* blend vs. the percentage of prepolymer of PPSQ.
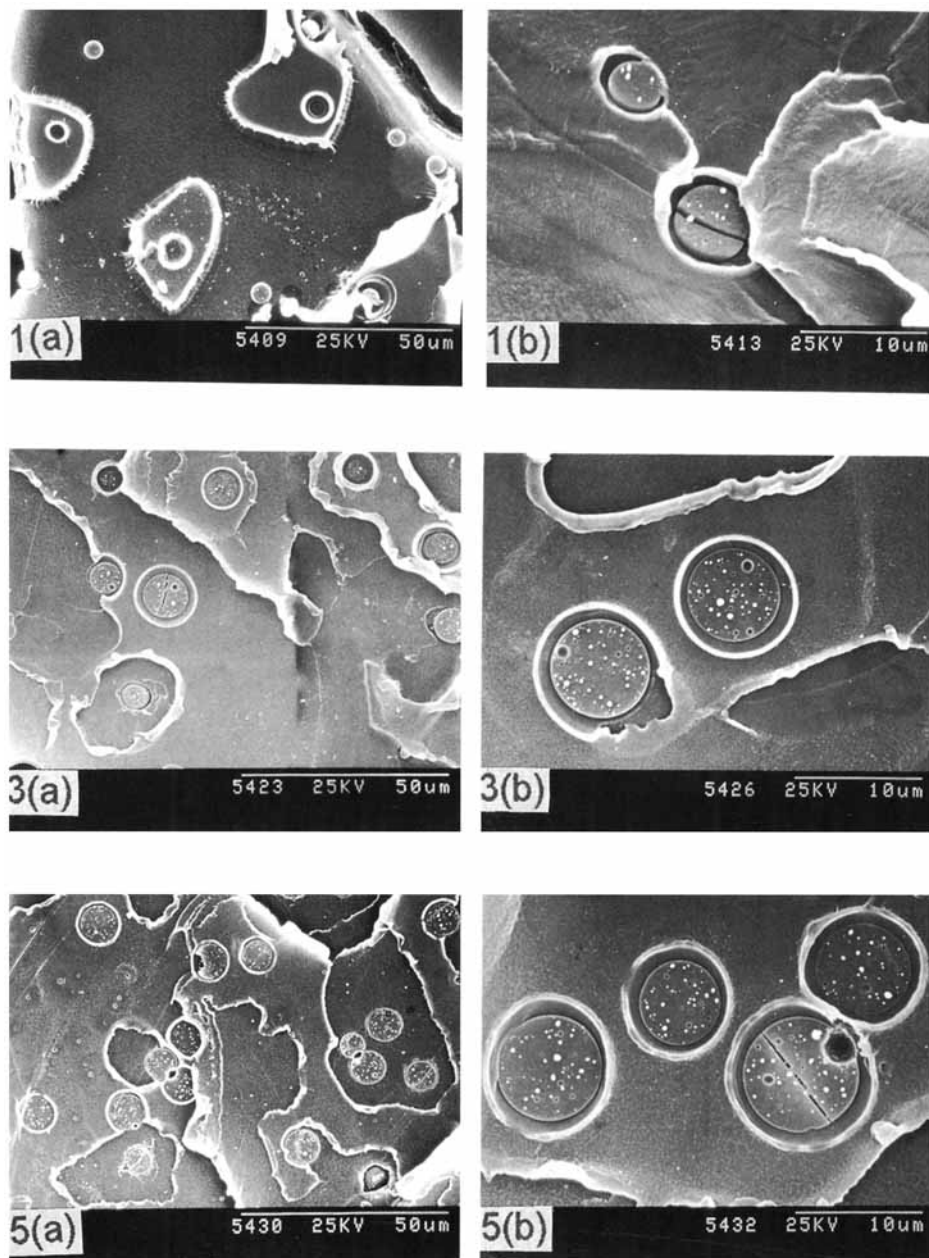
Figure 3   SEM micrographs of fracture surfaces of samples 1 (1(a) and 1(b)), 3 (3(a) and 3(b)), and 5 (5(a) and 5(b)) after impact strength test. (Magnification size of micrographs (b) are larger that those of (a)).

ther increases of the amount of PPSQ when the percentage of PPSQ is more than 1%. The same conclusion can also be obtained from Figure 2. Although the percentage of prepolymer of PPSQ increases to 20%, the impact strength of this blend is less than that of PS. Both PS and PPSQ are brittle at room temperature, and PPSQ is much more brittle than PS.[11,12] Therefore, in the PS/PPSQ *in situ* blend, addition of PPSQ to PS raises the impact strength

of PS and the values of some blends exceed that of PS. In other words, the brittle PS matrix can be toughened by inclusion of the much more brittle PPSQ particles.

To study the toughening mechanism of this PS/PPSQ blend system, we observed fracture surfaces of specimens after impact tests by SEM (Figs. 3 and 4). There are two phases in all blends: the continuous phase, in which PS is the major component and
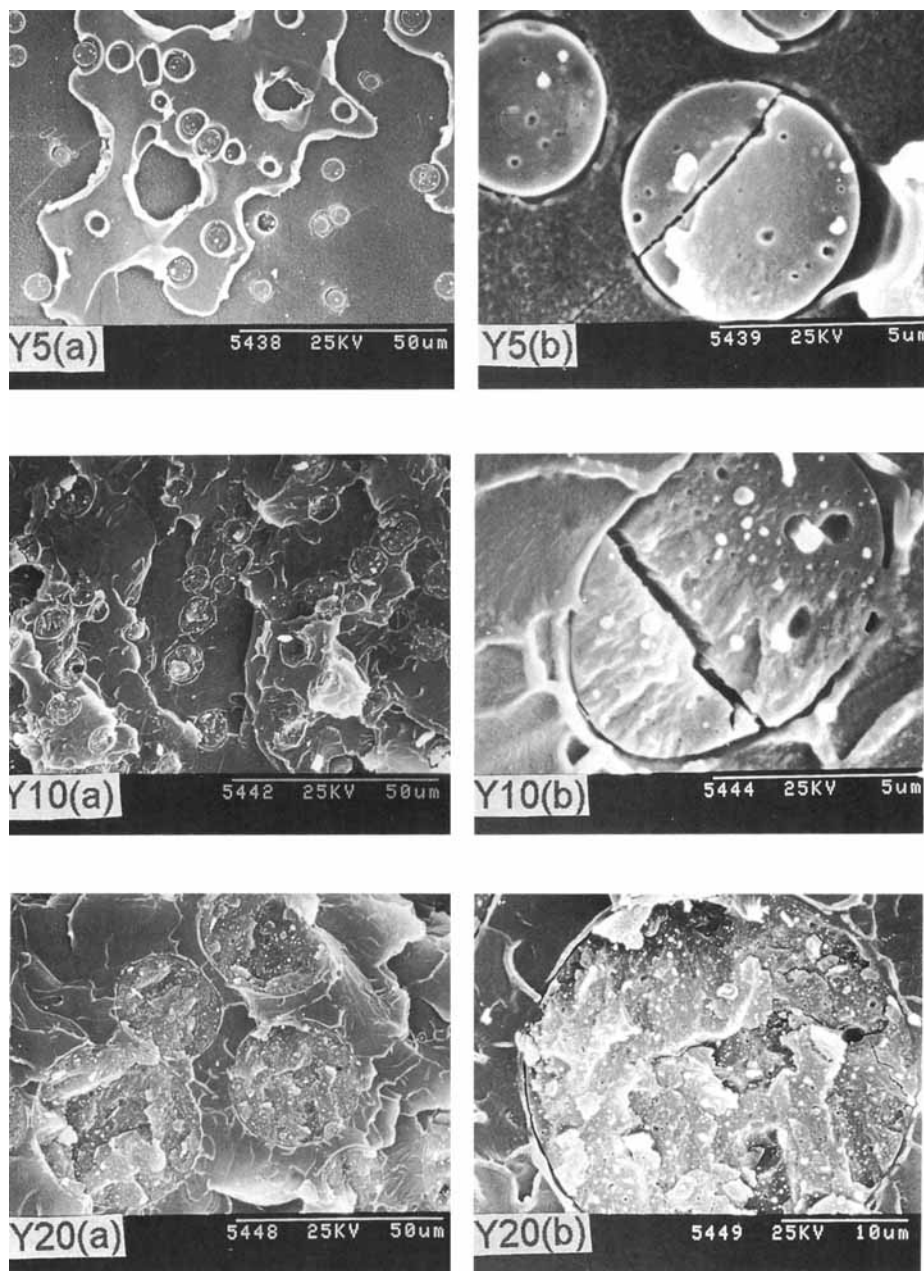
Figure 4   SEM micrographs of fracture surfaces of samples Y5 (Y5(a) and Y5(b)), Y10 (Y10(a) and Y10(b)), and Y20 (Y20(a) and Y20(b)) after impact strength test. (Magnification size of micrographs (b) are larger than those of (a)).

PPSQ is the minor component, and the dispersed phase, which contains many PPSQ molecules and a few PS molecules (data not shown) because PPSQ had been completely dissolved in a styrene monomer before its addition polymerization. The coexistence of PPSQ and PS in both the continuous phase and dispersed phase results in better adhesion between PS matrix and PPSQ particles. Therefore, the brittle particles could deform as the matrix deformed, and

there is not any detachment of the dispersed PPSQ particles from the continuous PS matrix (Figs. 3 and 4).

The phenomenon of some cracks across the dispersed particles observed from Figures 3 (1(b), 3(a) and 5(b)) and 4 (Y5(b) and Y10(b)) demonstrates the large deformation of PPSQ particles in the process of fracture. The deformation of brittle particles can absorb some impact energy and improve the im-

pact strength of the PS/PPSQ blend.[2] From Figures 3 (1(a), 3(a) and 5(a)) and 4 (Y5(a)), the fracture surfaces of PS/PPSQ specimens with a small amount of PPSQ or its prepolymer reveal the presence of some short crazes or white yielding zones that occur around or in a short distance from the brittle PPSQ particles. These crazes or yielding zones were caused by the large deformation of the continuous PS matrix because the dispersed particles provide some points of stress concentration due to the difference between the elastic moduli of the dispersoid and the matrix, and there is good adhesion between the two phases.

This result is another explanation for the improvement of impact strength of the PS/PPSQ in situ blend. It is also found that the size of PPSQ particles plays an important role on the toughness of its modified PS system. With an increase of the content of prepolymer of PPSQ, the size of dispersed particles becomes larger and the number of particle-induced crazes or yielding zones near the particles decreases (Fig. 4). Large brittle particles seem to be inefficient for improvement of impact strength.[13] Consequently, if the percentage of prepolymer of PPSQ in the blend is more than 10% and the size of particle is larger than 5 μm (Fig. 4), impact strength of this blend reduces rapidly.

DMA

DMA curves of PS and its blends (Fig. 5) show that the storage modulus of the PS/PPSQ blend at the glassy state is higher than that of PS and that the values become larger with an increase of the content of PPSQ. The percentage of PPSQ in this blend is so small that there is only one distinct glass transition observable (Fig. 5). Glass-transition temperatures (T_g) were determined from the damping peak temperature. T_g of samples 0 (PS), 1, 3, and 5 are
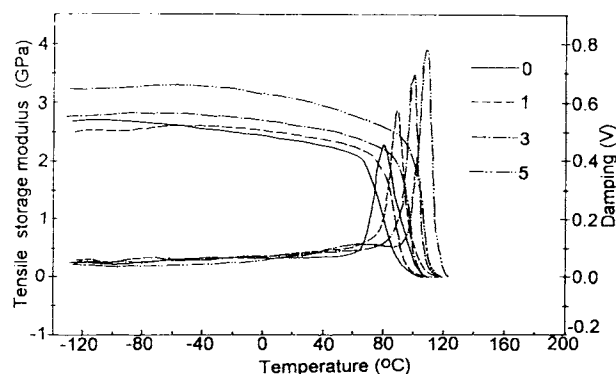

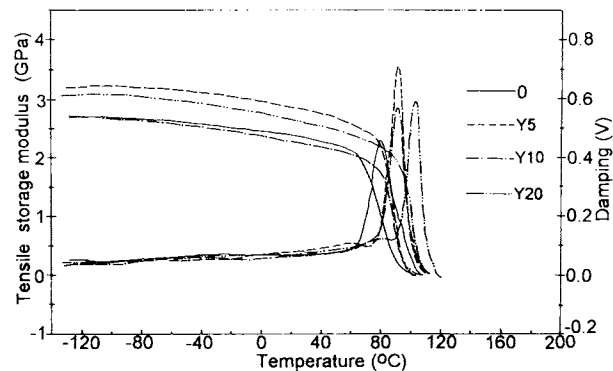**Figure 5**   DMA curves of PS/PPSQ in situ blends.

Figure 6   DMA curves of PS/prepolymer of PPSQ in situ blends.

80, 90, 100, and 108°C, respectively. It is easily noted that the glass-transition temperatures of these blends increase with the percentage of PPSQ. From Figure 6, tensile storage modulus of sample Y5 is the greatest among samples Y5, Y10, and Y20. Although the percentage of prepolymer of PPSQ is as high as 20%, there is only one prominent damping peak caused by PS glass transition (Fig. 6). T_g of samples 0, Y5, Y10, and Y20 are 80, 86, 86, and 92°C, respectively. Although prepolymer of PPSQ has little influence on the T_g of this blend (Fig. 6), T_g of PS/prepolymer of PPSQ also shifts to higher temperature as the amount of prepolymer of PPSQ increases, except sample Y10. The dynamic mechanic property of Y5 is better than that of Y10. The storage modulus of 5 and Y5 is the highest among all specimens from −120°C to 75°C, and the T_g of sample Y5 is lower than that of sample 5. PS modified by PPSQ has the better dynamic mechanical property than the corresponding blend system modified by prepolymer of PPSQ.

Therefore, not only can the brittle PS matrix be toughened by addition of the much more brittle PPSQ particles but also the thermal stability and storage modulus of PS can be improved when PS/PPSQ in situ blend contains a small amount of PPSQ. PPSQ with higher molecular weight has the better effect on the modification of PS.

CONCLUSIONS

Toughness, thermal stability, and storage modulus of a brittle PS matrix could be improved by addition of some much more brittle PPSQ particles when the percentage of PPSQ is not more than 5%. The possible toughening mechanism is the deformation of brittle particles and many particle-induced crazes or yielding zones. PPSQ with higher molecular

weight has a better effect on the modification of PS than its prepolymer.

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