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Polymer Blends of a Polysilane with Polystyrene and Polypropylene

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ABSTRACT: Polymer blends were made from the polysilane copolymer "polysilastyrene" [poly(dimethylsilylene-*co*-phenylmethylsilylene), PSS] at 0.2, 1.0, and 5.0% concentration in polystyrene and also in polypropylene. Excellent dispersions up to 5% PSS were obtained with polystyrene, but with polypropylene some segregation of PSS was observed, especially above 1%. Blending of PSS with polystyrene decreased surface resistance, increased hardness, and provided some protection from degradation by sunlight. Similar but smaller effects were observed for PSS–polypropylene blends. The commercial polysilane copolymer PSS-120 was characterized by NMR, UV, GPC, WAXD, DSC, surface resistance, and hardness measurements.

In recent years the polysilane polymers have been intensively studied, because of both their unusual electronic properties[1] and their actual and potential technological applications.[1,2] However, few studies of polysilanes as engineering materials have been published. In particular, there seem to be no studies of properties of polymer blends containing polysilanes or of the miscibility of polysilanes with more conventional polymers.

Here we report a study of molecular composites containing the commercial polysilane polysilastyrene[3] (PSS-120) from Nippon Soda Co. with both polystyrene and polypropylene. Improvements of polymer properties are often found in polymer blends.[4] The object of these experiments was to see if blending with PSS could improve the properties[4] of conventional polymers by reducing surface charge buildup or increasing their resistance to scratching. The effectiveness of PSS in protecting the polymers against degradation by sunlight was also investigated.

Polysilastyrene (PSS) is a copolymer containing Me_2Si and PhSiMe groups in the polymer chain.[3] Before the blends were investigated, experiments were done to characterize the commercial PSS.

Experimental Section

Polymers. Polysilastyrene, PSS-120, was obtained from Nippon Soda, lot no. PSS-120(60). Polystyrene, Esbrite 500A, lot no. 7111521, was from Showa Denko K.K. This polymer was radical polymerized and atactic. DSC showed T_g = 90 °C but no melting point was detected. The initial flow point by capillary rheometry was ~135 °C.

Polypropylene, Shoallomer MA710, lot no. 251996-6, was also from Showa Denko. This material was polymerized by Ziegler catalysis and was isotactic with 96.5% mm triad configurations by ^{13}C NMR. X-ray analysis indicated 46.1% crystallinity (36.1% monoclinic, α; 10% hexagonal, β). Other properties of these polymers are summarized in Table 1.

Characterization of Polysilastyrene PSS-120. The NMR spectra of polysilastyrene PSS-120 were determined on 10% by weight solutions in C_6D_6 in 10-mm sample tubes. ^1H and ^{13}C NMR spectra were determined using a JEOL FX-200 spectrometer (^1H resonance at 200 MHz and ^{13}C resonance at 50 MHz). The ^{29}Si spectrum was studied using a Bruker AMX-400 spectrometer (^{29}Si resonance at 79 MHz). The INEPT polarization transfer method was used, with the variables τ and Δ chosen for a coupling constant $^3J_{H\text{-}S}$ = 6.8 Hz. Pulse sequence lengths were 80–100 ms with total pulse delays of 4–8 s. Resolution was 1.7 Hz (0.04 ppm). The ultraviolet spectrum was determined in THF solution using a Hitachi 3210 UV spectrometer.

Table 1. Characteristics of Polyolefin Resins Used in This Study

	resin type	
	polystyrene Esbrite 500A	polypropylene Shoallomer MA710
wt av mol wt (M_w, GPC)	19.8 × 10^4	17.9 × 10^4
no. av mol wt (M_n, GPC)	6.8 × 10^4	2.2 × 10^4
polydispersity index (GPC)	2.9	8.2
density (g/cm^3)	1.0	0.9
melt index (g/10 min)	13.0	25.0
flexural modulus (kg/cm^2)	2.1 × 10^4	1.6 × 10^4
notched Izod impact strength (kg·cm/cm^2)	9.0	1.7

GPC measurement of polysilastyrene PSS-120 was performed in freshly distilled THF at a flow rate of 1 mL/min on a Waters single-pump liquid chromatograph attached to two Shodex GPC K-80M columns fitted with a 254-nm UV absorbance detector and a refractive index detector. Molecular weight is relative to polystyrene standards. The thermal study of PSS-120 was carried out on a Perkin-Elmer differential scanning calorimeter at scan rate of 10 °C/min over the temperature range from −50 to +200 °C under a nitrogen atmosphere.

The X-ray equipment used to examine polysilastyrene PSS-120 consisted of an X-ray source, a computer-controlled diffractometer, and an array detector. The X-ray source, a Rigaku RAD RC 18-kW rotating-anode generator, utilized a copper target ($\lambda_{K\alpha}$ = 1.541 Å) fitted with a graphite monochromator. The scintillation counter consisted of a NaI crystal and a photomultiplier.

Polymer Blends. Polysilastyrene PSS-120 (0.1, 0.5, and 2.5 g) was blended with 50 g of the polystyrene or polypropylene for 5 min at a rotation speed of 30 rpm using a Duisburg Plasti-Corder kneading machine. The blending temperature was 180 °C for polystyrene and 200 °C for polypropylene.

Surface Resistivity Measurements.[5] Surface resistivities of polysilastyrene, polystyrene, polypropylene, polysilastyrene–polystyrene blends, and polysilastyrene–polypropylene blends were examined with a Yokogawa Hewlett-Packard 4329 high-resistance meter at 23 °C and 50% humidity.

A flat-plate test sample of polysilastyrene with comparatively high density was made by gradual evaporation of solvent from a THF solution. The flat-plate test samples of the polystyrene and polysilastyrene–polystyrene blend compositions were molded with a heat press at 60 kg/cm^2 and 200 °C for 1 min. Similar samples of the polypropylene and polysilastyrene–polypropylene blend compositions were molded with the heat press at 60 kg/cm^2 and 190 °C for 3 min. These moldings follow a standard procedure (JIS K6871).

Scratch Resistance. Surface resistance to scratching was measured using calibrated pencils in a standard pencil hardness test (JIS K5400).[6] A load of 100 g was applied to pencils of successively greater hardness, held vertically above a flat-plate test sample and drawn across the surface using a Shintokagaku

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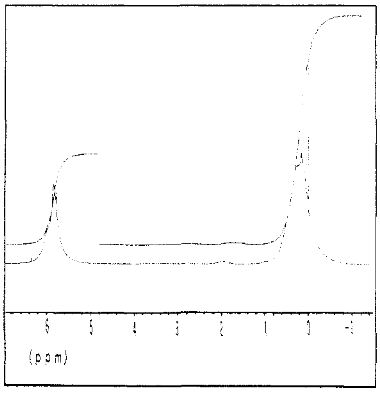


Figure 1. ^{1}H NMR spectrum of polysilastyrene, 10% in C_6D_6.

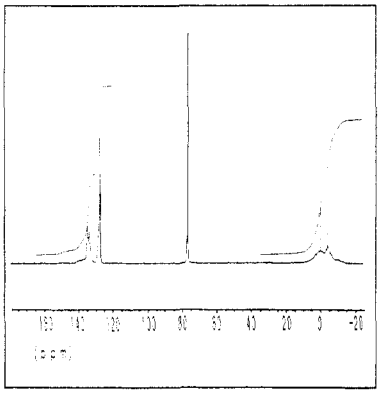


Figure 2. ^{13}C NMR spectrum of polysilastyrene, 10% in C_6D_6.

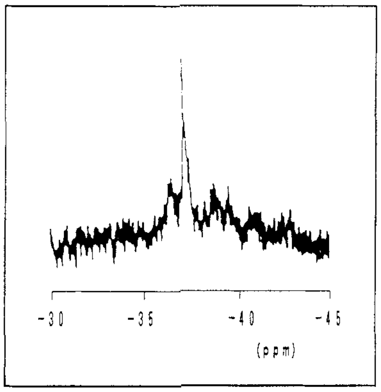


Figure 3. ^{29}Si NMR spectrum of polysilastyrene, 10% in C_6D_6.

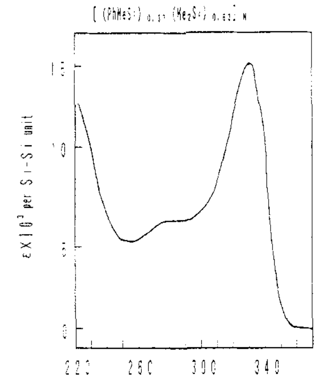


Figure 4. Ultraviolet absorption spectrum of polysilastyrene, in THF, 0.0045 wt % (5×10^{-4} mol L^{-1}).

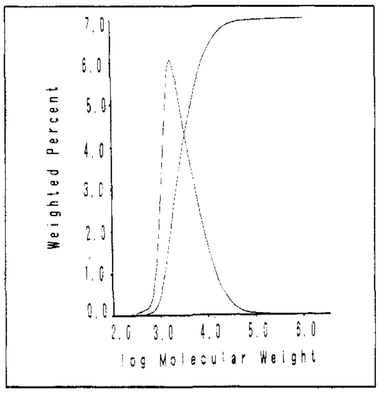


Figure 5. Gel permeation chromatogram of polysilastyrene, THF solvent.

scratch tester, Heidon-14, at 50 mm/min. The pencil hardness at which scratching of the surface first took place was evaluated visually.

Tensile Strength. Samples of the various polymers and blends were examined using a Toyo Baldwin Co., Ltd., UTM-II-500 tensile test machine and a stretching rate of 50 mm/min. Properties determined were tensile strength at yield, tensile strength at break, elongation at break, and tensile modulus.[7] Samples were studied before and after exposure to Tokyo sunlight for 6 months, June 1, 1992 to December 1, 1992. Each of the results shown in Tables 3 and 4 is an average of eight separate determinations; variation of the eight results were all within 10% of the average value.

Electron Microscopy.[8] Cross-section surfaces of the polymer blends were studied from the secondary electron images using a scanning electron microscope (JEOL JSM-T330A). Silicon atoms were located from the silicon X-rays using an energy-dispersive X-ray microanalyzer (JEOL-JED-2000). Magnification was 500×, using an electron beam of 15 kV. The polymer samples, 1 mm in thickness, were broken immediately after molding and cooling under liquid nitrogen and then coated with a 10-nm gold film on the broken section for imaging.

Results and Discussion

Characterization of PSS-120. Poly(dimethylsilylene-*co*-phenylmethylsilylene), "polysilastyrene", was first studied more than a decade ago, and the general properties of this copolymer are well known.[3] The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of PSS-120 are shown in Figures 1–3; the spectra agree well with those reported earlier. The ultraviolet spectrum, shown in Figure 4, is also similar to the published spectrum.

In the ^{1}H NMR spectrum only two broad peaks were found, near 5.8 ppm (phenyl protons) and 0.2 ppm (methyl protons). Integration of the areas under those peaks gives the CH_3/C_6H_5 ratio and hence the composition of the copolymer. For the PSS-120 used in this study, the composition was $(Me_2Si)_{0.63n}(MeSiPh)_{0.37n}$.

Earlier experiments have shown that polysilastyrene prepared by cocondensation of Me_2SiCl_2 and $PhMeSiCl_2$ under the usual conditions (sodium, toluene diluent, 110 °C) is quite blocklike.[3c] The ^{29}Si NMR of PSS-120 in Figure 3 is similar to that for blocklike PSS and quite different from that for the partially ordered polymer $(PhMeSi–SiMe_2)_n$. The strong singlet at −37.4 ppm is characteristic for Me_2Si moieties, further indicating that PSS-120 is blocklike with significant runs of $(Me_2Si)_n$ units. The blocklike nature of the polysilane may be important for its miscibility with other polymers.

The PSS-120 had a monomodal molecular weight distribution by GPC (Figure 5): $M_w = 27000$, $M_n = 14000$, $M_w/M_n = 1.9$, based on polystyrene standards. Thermal analysis of the sample from −50 to +200 °C gave a weak melting endotherm at 55–75 °C; no glass transition was observed. The wide-angle X-ray diffraction pattern, shown in Figure 6, indicates that the polymer is mainly amorphous, although with some long-range order as indicated by the broad weak peak at $2\theta = 9°$. Surface resistivity and hardness of PSS had not been reported earlier; the surface resistivity was rather low, 10^{11} ohm cm, and the pencil hardness was quite high, 12.1, on the Vickers hardness scale.

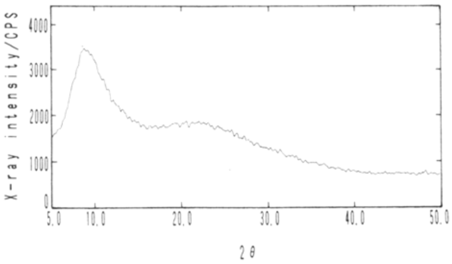
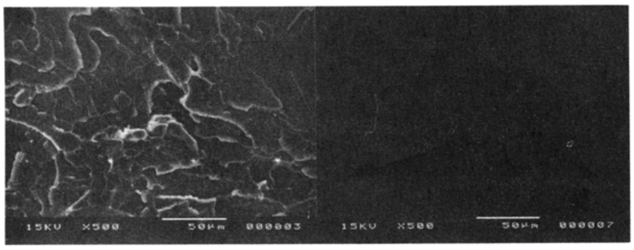
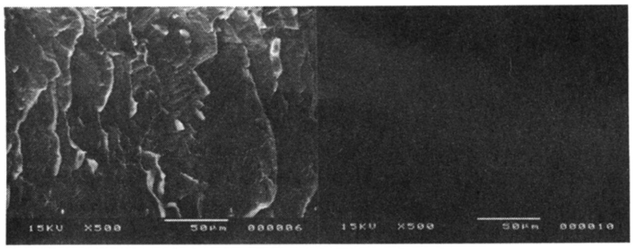


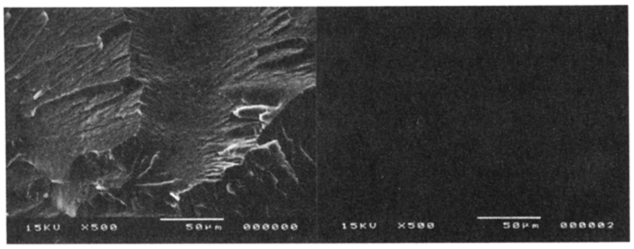
Figure 6. X-ray diffraction pattern of a film of polysilastyrene.



0.2wt% of polysilastyrene



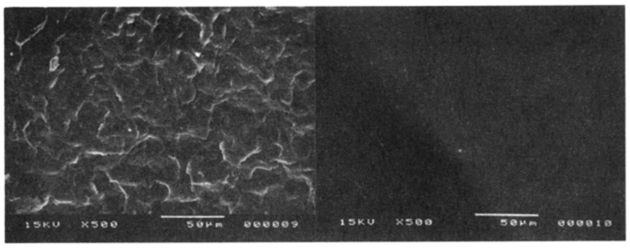
1.0wt% of polysilastyrene



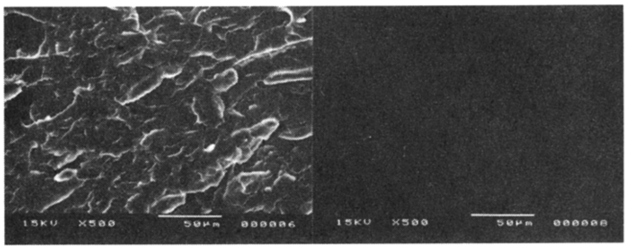
5.0wt% of polysilastyrene

Figure 7. Scanning electron microscopy of blends of polysilastyrene with polystyrene: left half, secondary electron image; right half, silicon image from energy-dispersive X-ray microanalyzer.

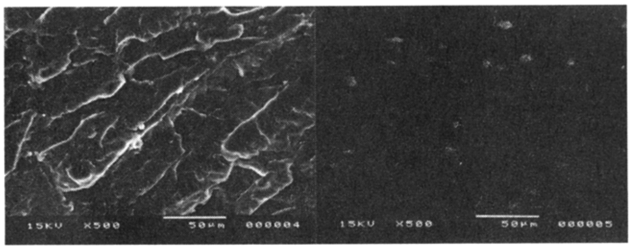
Properties of Polymer Blends. To study the effectiveness of the dispersion of PSS in the polystyrene and polypropylene, fractured polymer samples were examined by scanning electron microscopy. Secondary electron imaging was also used to locate the position of the silicon atoms. Results are shown in Figures 7 and 8. With polysilastyrene, dispersion of PSS is excellent even at 5% concentration. The SEM Photographs do not show particles of PSS from the secondary electron image, and energy-dispersive X-ray measurements reveal that the silicon atoms are well dispersed. For polypropylene, however, here is evidence for defective dispersion. Particles of PSS can be seen in the secondary electron images at 1% and especially at the 5% concentration, and clustering of silicons, indicating phase separation, is clearly evident from the energy-dispersive X-ray measurements.



0.2wt% of polysilastyrene



1.0wt% of polysilastyrene



5.0wt% of polysilastyrene

Figure 8. Scanning electron microscopy of blends of polysilastyrene with polypropylene: left half, secondary electron image; right half, silicon image from energy-dispersive X-ray microanalyzer.

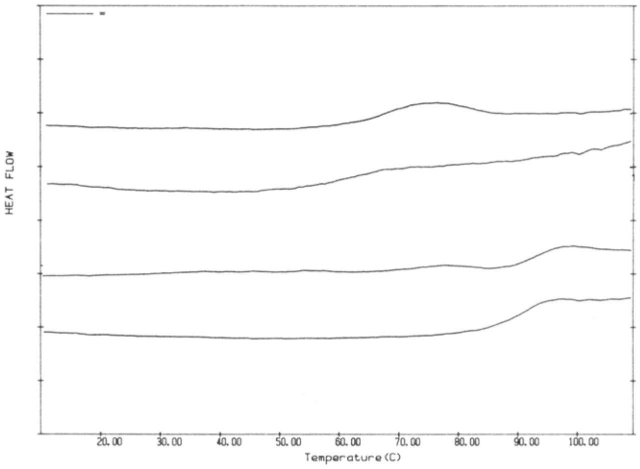


Figure 9. Differential scanning calorimetry curves from 20 to 110 °C. (1) Pure PSS showing melt transition at 55–75 °C. (2) 5% PSS in polypropylene; the PSS melt transition is evident. (3) Pure polystyrene, showing T_g at ~90 °C. (4) 5% PSS in polystyrene; the PSS melt transition is now observable.

The dispersion of PSS in the two polymers was also investigated by DSC. The results between 20 and 110 °C are shown in Figure 9. The topmost curve is the DSC for pure PSS, showing the weak melting transition with onset at ~55 °C, peaking at 73 °C. The second curve shows the DSC for 5% PSS in polypropylene; the melt transition for PSS is still evident, weaker of course because of dilution. (Polypropylene itself shows no transitions whatsoever from 20 to 110 °C.) Thus the PSS must be present as a separate phase. The third curve is that for pure polystyrene, showing the T_g at ~90 °C. In the bottom curve is the DSC for 5% PSS in polystyrene; it is essentially identical to that for pure polystyrene. The melting transition of PSS has disappeared, consistent with formation of a true molecular dispersion.

The surface resistivity and pencil hardness for the PSS–polystyrene and PSS–polypropylene blends are shown in Table 2. Blending with PSS improves these properties for both polymers, lowering the surface resistivity and increasing the hardness, but the effects are more pronounced with polystyrene than with polypropylene.

Table 2. Surface Resistivity and Hardness of Polymer Blends

	polysilastyrene–polystyrene blend (wt ratio)				polysilastyrene–polypropylene blend (wt ratio)			
	0/100	0.2/100	1.0/100	5.0/100	0/100	0.2/100	1.0/100	5.0/100
surface resistivity (ohm cm)	10^{17}	10^{17}	10^{14}	10^{13}	10^{17}	10^{17}	10^{16}	10^{16}
pencil scratch test (Vickers hardness)	<6.2	<6.2	6.8	6.8	8.0	8.0	8.4	8.4

Table 3. Effect of Sunlight Exposure on the Tensile Properties of Polysilastyrene–Polypropylene Blends

	PSS–polypropylene blend ratio							
	0/100		0.2/100		1.0/100		5.0/100	
	no exposure	6-month exposure	no exposure	6-month exposure	no exposure	6-month exposure	no exposure	6-month exposure
tensile strength at yield (kg/cm^2)	372	357	376	368	381	374	358	352
tensile strength at break (kg/cm^2)	369	353	363	355	374	368	354	349
elongation at break (%)	700	80	820	350	730	373	576	389
tensile modulus (kg/cm^2)	1.3×10^4	1.1×10^4	1.4×10^4	1.3×10^4	1.5×10^4	1.4×10^4	1.5×10^4	1.4×10^4

Table 4. Effect of Sunlight Exposure on the Tensile Properties of Polysilastyrene–Polystyrene Blends

	PSS–polystyrene blend ratio							
	0/100		0.2/100		1.0/100		5.0/100	
	no exposure	6-month exposure	no exposure	6-month exposure	no exposure	6-month exposure	no exposure	6-month exposure
tensile strength at yield (kg/cm^2)	204	195	197	192	203	200	202	201
tensile strength at break (kg/cm^2)	145	137	140	136	136	135	136	134
elongation at break (%)	38	6	54	35	26	22	25	22
tensile modulus (kg/cm^2)	2.1×10^4	1.8×10^4	2.1×10^4	2.0×10^4	2.1×10^4	2.1×10^4	2.1×10^4	2.1×10^4

The tensile strength measurements for the PSS–polystyrene blends are given in Table 3, and those for the PSS–polypropylene in Table 4. No UV stabilizer was included with the polymer samples. As seen from the data, the addition of PSS has little effect on the tensile properties of the blends when they are not exposed to sunlight. The tensile strengths at the yield and break points for the polymers, alone or blended, were not altered by exposure to sunlight. However, for the pure polymers sunlight exposure reduced the elongation at break markedly and the tensile modulus slightly. Blending of PSS with polystyrene greatly increased the elongation at break after light exposure and, at concentrations of 1.0 and 5.0%, increased the tensile modulus after sunlight exposure to the original value. The protective effect of the PSS against light degradation is quite evident.

For PSS with polypropylene (Table 3), it is instructive to examine first the elongation at break in the unexposed samples. The elongation increased for 0.2% PSS but then decreased in the 5.0% blend. The increase could be accounted for by a plasticizing effect of the PSS, which contains some molecules of low molecular weight. At high concentrations of PSS, immiscibility and phase separation may be responsible for the lower elongation.

After exposure to sunlight, the tensile modulus of polypropylene decreases and the elongation at break is greatly reduced. PSS has a protective effect against photodegradation, increasing both of these values. The sunlight protection appears to increase slightly with increasing amounts of PSS in the blend.

Conclusions

The results of this study show that polysilastyrene can be blended with either polystyrene or polypropylene. Admixture of small amounts. ~1%, of PSS to form a molecular composite improves the surface conductivity, hardness, and resistance to UV degradation of both polymers. The beneficial effects are however greater for polystyrene than for polypropylene. This may reflect the fact that the molecular dispersion of PSS in polystyrene is much more effective than in polypropylene, perhaps because of interactions between the phenyl substituents in both of these materials.[9] Blending of polysilane with conventional polymers appears to be a promising method for improving polymer properties; further experiments with other polysilanes and host polymers seem warranted.

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