Spin Probe Study of Composite Materials

INTRODUCTION

The spin label technique is at present widely employed as a useful method in the fields of biological physics or physical chemistry.[1-9] The spin probe method is one of the branches of the technique and is conducted to dissolve a stable paramagnetic probe in the sample.[10-12] From ESR spectra analysis of the probe, one is able to obtain the information about the motion of the probe, which reflects the state of surrounding matrix. Rabold examined the structure of various polymers by the method.[11] He mixed the probe with polymer by a mechanical way and measured the spectra at various temperatures from −196° to 160°C.

The combination of polymer with the solid surface is an important problem on the property of composite materials such as GFRP, which is made from glass fiber and polymer. For example, silane coupling agents are used for the purpose of the improvement of adhesion between polymer and glass.

Jenkel et al. found that specially oriented layers were formed in the interface when polymer was solidified on aluminum foil and named them "transcrystal."[13] Kwei et al. found that the modulus of elasticity of the transcrystal layer in polyethylene was twice that of the inner layer.[14]

In this way, polymers are thought to form special structures in the interface with inorganic matters. If this is the case, the spin probe method must be an effective technique to examine the problem. In this paper, we report the effect of silica and alumina on the structure of polymers when they were dispersed in poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), and polystyrene (PST) using the spin probe method. As probe, 2,2,6,6-tetramethyl-4-piperidone nitrogen oxide was chosen from various N-oxides because of the simplicity of the structure and the ease of synthesis.

EXPERIMENTAL

The probe, 2,2,6,6-tetramethyl-4-piperidone nitrogen oxide, was synthesized by the method of Hall[15] and Murayama et al.[16]

Anal. Calcd for $C_9H_{16}NO_2$: C = 63.53; H = 9.60; N = 8.25. Found: C = 63.56; H = 9.76; N = 7.89.

Silica (Mallinckrodt) is 100-mesh powder and analytical reagent; alumina (Merk) is neutral (Type T) for thin-layer chromatography. PMMA (supplied by Toray, D.P. = 1000) and PST (Mitsubishi, D.P. = 1000) were dissolved in benzene. PVA (Wako, D.P. = 2000) was dissolved in water. The probe was then dissolved in these solutions in such a way that the weight ratio of the probe to polymers is 1:5000. Silica and alumina were mixed with these solutions and stirred sufficiently for dispersion. The mixtures of solid with benzene solution and with aqueous solution were spread on mercury and a glass plate, respectively. Films of these composite materials were cast by evaporation of the solvents at room temperature and were cut into small pieces for charging in Pyrex sample tubes. The samples composed of polymer and probe without solids were prepared by the same method.

The spectra of nonheat-treated samples were measured in the presence of air. Then, the samples were evacuated for 3 hr at room temperature, sealed at 10^{-4} mm Hg, and heat treated at 100°C for 1 hr.

ESR spectra were recorded at room temperature on a Japan Electron Optics Laboratory Model JES-3BS.X Spectrometer (X-band) with 100 kHz field modulation. The width of modulation was 1.2G.

RESULTS AND DISCUSSION

Figure 1 shows the ESR spectra of the probe in various polymers in which solids were not dispersed. The peak-to-peak separation width of two side peaks in the spectrum of PVA is 70G (Fig. 1A). The value must be twice that of apparent Azz and means that the probe is rigidly
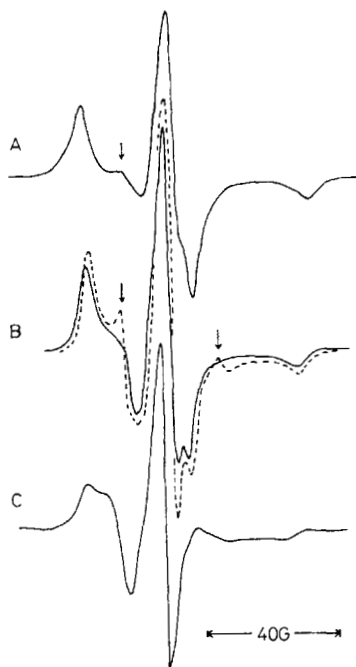
Fig. 1. ESR spectra of the spin probe in polymers: (A) PVA; (B) PMMA; (C) PST. Dotted line in (B) is the spectrum measured after heat treatment for 3 hr.

fixed in the polymer.[3,4] A small peak indicated by an arrow means that the absorption of the mobile probe superposes on that of the immobile one. However, a similar spectrum is obtainable when N-oxide rotates around the Z-axis of the N—O group and Axx was averaged with Ayy.[2] Therefore, uncertainty remains in this assignment. In the case of PMMA, the probe is more mo-
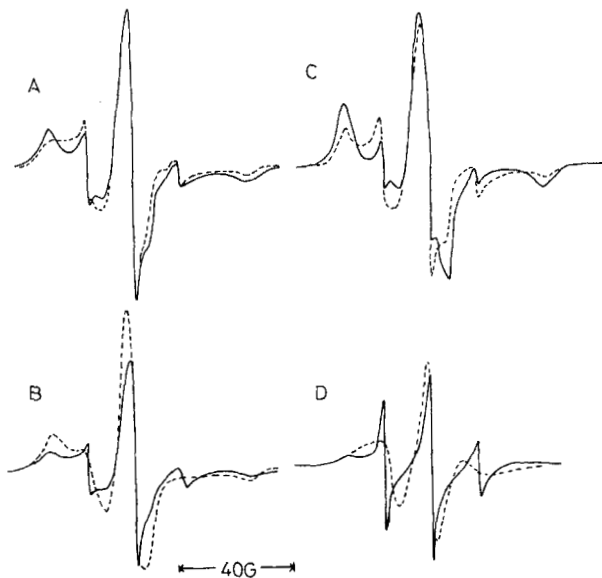

Fig. 2. ESR spectra of the spin probe in PVA–solid system: (A) PVA–silica 20%; (B) PVA–silica 200%; (C) PVA–alumina 20%; (D) PVA–alumina 200%. Spectra of Samples measured after heat treatment are shown as dotted lines.
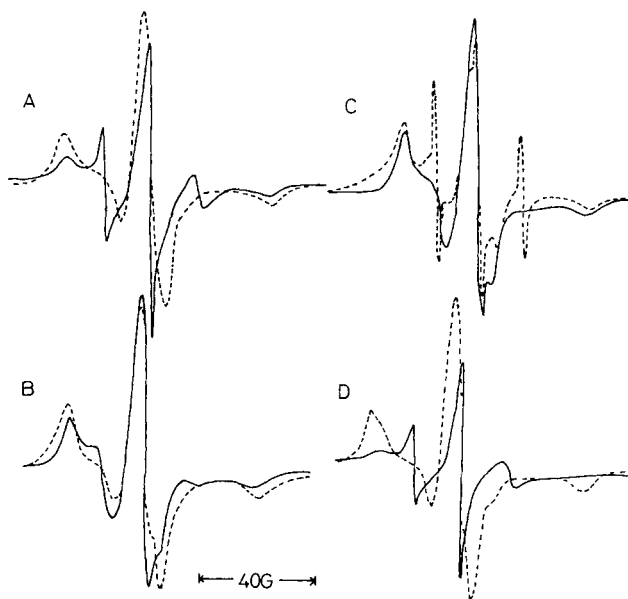
Fig. 3. ESR spectra of the spin probe in PMMA-solid system: (A) PMMA-silica 20%; (B) PMMA-silica 200%; (C) PMMA-alumina 20%; (D) PMMA-alumina 200%.   Spectra of samples measured after heat treatment are shown as dotted lines.

bile than that in PVA as can be understood from the separation width of 65G (Fig. 1B).   New peaks indicated by arrows appeared clearly when the sample was heat treated at 100°C for 3 hr, shown as dotted line.   The existence of two different states of the probe is evident in this case, and the mobile probe was increased by heat treatment.   The spectra of PVA and PST, on the contrary, did not change by heat treatment.   The separation width of PST is 61G (Fig. 1C),
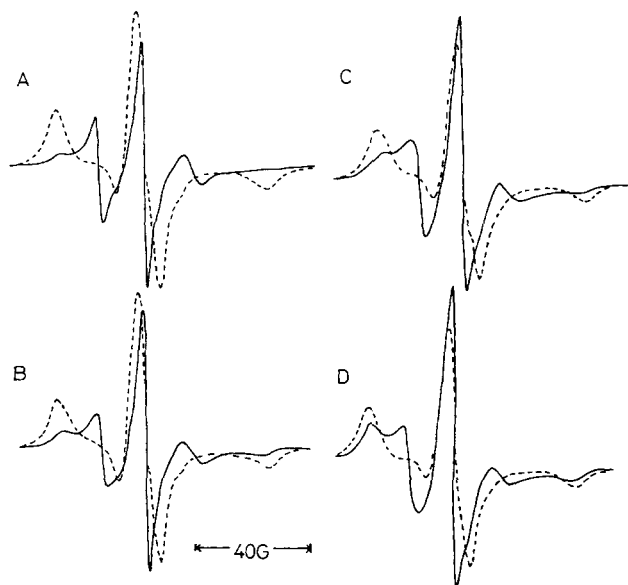

Fig. 4. ESR spectra of the spin probe in PST-solid system: (A) PST-silica 20%; (B) PST-silica 200%; (C) PST-alumina 20%; (D) PST-alumina 200%.   Spectra of samples measured after heat treatment are shown as dotted lines.

which means that the probe is most mobile in these three polymers. Furthermore, the peak of the mobile probe was found also in the high field side.

A sharp absorption spectrum separated by 33G emerged from the spectrum of PVA in which 20 wt-% of silica was dispersed (denoted hereinafter as PVA–silica 20%, Fig. 2A). The intensity ratio of this sharp spectrum to the original broad one increased in the spectrum of PVA–silica 200%. Heat treatment at 100°C affected reversely these two samples, that is to say, the mobile probe which shows a sharp spectrum increased in PVA–silica 20%, in contrast to PVA–silica 200%. The sharp spectrum also appeared in the PVA–alumina system, but concentration dependence differs from that of PVS– silica. For example, the spectrum of PVA–alumina 200% is composed only of the absorption of the mobile probe and was broadened by heat treatment as a result of hindering of motion (Fig. 2D). In conclusion, the dispersion of solids into PVA transforms some parts of the immobile probe to the mobile one. PVA is known as a highly crystalline polymer. Therefore, it is conceivable that the structure of polymer was broken by the dispersion of solids.

Similar results was obtained in the PMMA–alumina system (Figs. 3C, 3D). The effect of heat treatment was remarkable in this case. However, PMMA–silica 20% was an exception; here, the mobile probe was decreased by the treatment (Fig. 3A).

The results of the PST–solids system is very different from those of the above-mentioned samples (Fig. 4). At the stage of preparation of films, the mobile probe increased, compared with the spectrum of Fig. 1C, but the probe changed to the immobile one in all these samples by heat treatment.

Considering all the above-mentioned results, one is able to conclude that the dispersion of solids destroys the structure of polymer and produces newly the mobile probe or increases that which coexists with the immobile one. The degree of increase of the mobile probe varies from sample to sample. The irregularity is possibly related to the condition of preparation of composite materials such as the way of vaporization or thickness of the film.

The spectra of the mobile probes are very similar to each other. That is to say, the separation width of the lines of the low and high field sides is 32–33G, and the ratio of peak-to-peak height of each three lines is also similar. The spectrum of the probe dissolved in benzene was composed of sharp three lines, and the separation width of each side peaks was 28G. Compared with this value, the mobile probe in polymer composites seems to be considerably freely rotating. The fact that similar mobile probes exists in each sample suggests the existence of a hole or free volume in which the probe is occluded. The hole or free volume must be produced by dispersion of solids. If they are mainly in the interface between solid and polymer, it is conceivable that the spectrum of the mobile probe is extremely strengthened in 200% of solids samples. Therefore, experimental data suggest that they are produced in the bulk of polymers.

Next, the effect of heat treatment was considered. Heat treatment generally increases the crystallinity of polymer, as is known for PVA. If this is the case also in PVA–solid systems, the mobile probe must be decreased or unchanged because the polymer becomes rigid as a result of increased crystallinity. However, the reverse is true of PVA–silica 20% and PVA–alumina 20%. Therefore, it is conceivable that the solids interfere with the contraction of heated polymer during the cooling process, and the hole or free volume is produced by the stress of contraction. The proportion of solid to polymer is thought to influence strongly the stress in this case.

For the analysis of the property of composite materials, it is necessary to keep in mind the position of the probe which has polar C=O and N—O groups in the molecule. It has a possibility to be adsorbed on the solid surface with the polar groups in nonpolar polymer such as PST and be immobilized. The effect of the adsorption is omitted as to the samples before heat treatment because the mobile probe was increased by the dispersion of solids. However, heat treatment increased the mobile probe in some cases, notably in the PST–solid system. Therefore, it is difficult to decide in this case whether the probe is immobilized by the adsorption or formation of rigid layer such as transcrystal. The study on this point is being continued at present.

As apparent from the above results and discussion, the spin probe method was revealed to be an effective technique for the investigation of composite materials made of polymer and inorganic substances.

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