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ESR Study of the Spin-labeled Poly(methyl methacrylate) Adsorbed on the Human Tooth and Hydroxyapatite

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The motion and the configurational behavior of the poly(methyl methacrylate) adsorbed on the surfaces of human tooth substances (dentin, enamel, and hydroxyapatite crystal) from a solution were clarified by using the electron-spin-resonance technique. The polymer molecules were more strictly bound by the surfaces of enamel and hydroxyapatite than the dentin. On both enamel and hydroxyapatite, the adsorbed molecules behaved in the same manner in their motion and configuration. However, the segments directly bound by each tooth substance had a much higher degree of motional freedom than those by the silica surface. These results were discussed in relation to the interaction between the polymer and the tooth, and in relation to the clinical adhesive aspects.

Electron spin resonance (ESR), coupled with a spin-labeling technique, has been successfully applied to the study of the adsorption behavior of several polymers.[1-4)]

The bound segments in the adsorbed polymers (train) are easily distinguishable from the segments in loops or tails on the basis of the difference in the ESR line shape, which corresponds to the difference in mobility among these segments. Thus, the ESR study is very useful in clarifying the detailed aspects of the interaction between a polymer and a solid surface.

On the other hand, restorative materials which consist of polyfunctional methacrylates and glass filler have often been used to fill the missing tooth produced by dental caries.[5,6)] However, the failure of the restorative materials to hold or secondary caries sometimes occur because of a lack of adhesiveness with tooth surface. In order to develop restorative materials which have a good adhesiveness with the tooth, it is necessary to obtain information on the adhesive mechanism between the materials and the tooth surface.

In our previous papers, the interaction between spin-labeled poly(methyl methacrylate) (PMMA) and a silica surface has been studied in detail by means of the ESR method.[3,4)] In this paper, the ESR study was performed in order to obtain information on the interaction between PMMA and the surfaces of three tooth substances, *i.e.*, dentin, enamel, and hydroxyapatite.

Experimental

A human tooth, dried at 60 °C for two weeks, was cut into two parts, the enamel and the dentin. Each part was then crushed with a ball mill to obtain a powder which could be used for the adsorption experiments. A sample of finely powdered hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, was purchased from the Seikagaku Kogyo Co., Ltd. The electron micrographs of these samples were obtained with a HITAC S-500 Scanning Electron Microscope. The diameters of these particles had a wide distribution in each case, 1—10 μm.

Spin-labeled PMMA was prepared by the method described in a previous paper.[3)] The sample used had a number-average molecular weight of 1.2×10^5 and a narrow mol wt distribution. The stereoregularity of the sample was highly isotactic.

The solid powder, 0.2 g, was added to 5 cm^3 of a CCl_4 polymer solution, after which the mixture was stirred for 4 h at 25±2 °C. The adsorbents were centrifuged after the adsorption equilibrium had been attained and separated from the supernatant solutions. The solids were rinsed with pure CCl_4 and 0.1 g of each sample was placed in a quartz sample tube. The ESR signals from the adsorbed polymer were measured on a JEOL JES FE 3-X spectrometer, applying a temperature control. On the other hand, the amount of adsorption was determined by means of ESR measurements of the changes in the polymer concentrations of the supernatant solution before and after the adsorption. The polymer concentration was calculated from the signal intensities of the polymer solution of a constant volume, approximately 0.1 cm^3, relative to those of the standard solutions. The other experimental methods have been described in previous papers.[3,4)]

Results and Discussion

The adsorption isotherms of PMMA on three kinds of tooth substances, *i.e.*, dentin, enamel, and hydroxyapatite, in CCl_4 at 25 °C are shown in Fig. 1. Each curve reaches a plateau at a low concentration of the polymer solution, with a slight increase at a higher concentration. This behavior is independent of the kinds of tooth substance. The saturated amount of adsorption, A_s, increased in the order of dentin (10 mg/g), enamel (30 mg/g), and hydroxyapatite (90 mg/g).

Let us now examine in detail the ESR spectra of the spin-labeled PMMA adsorbed on these tooth substances in the unsaturated stages. Figure 2 shows the ESR spectra of the PMMA adsorbed on hydroxyapatite crystals. These spectra can be assumed to be composed of three portions of the local chain, *i.e.*, train, short loop, and long loop.[4)] It should be noted that there is a significant change in the ESR line shapes with the degree of adsorption; this corresponds to the change in the conformation of PMMA

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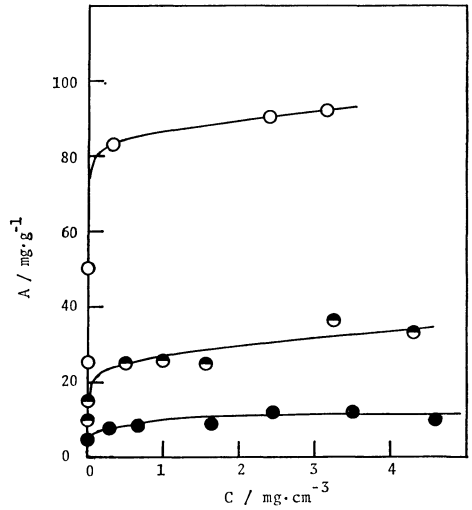

Fig. 1. The adsorption isotherms of PMMA on the tooth substances from CCl_4 dilute solution at 25 °C. ○: On hydroxyapatite, ◒: enamel, ●: dentin.

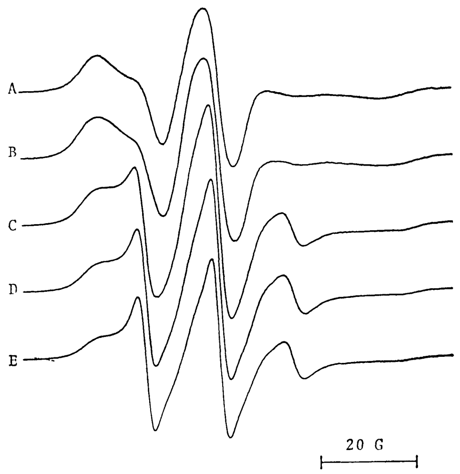

Fig. 2. The ESR spectra of the spin-labeled PMMA adsorbed on hydroxyapatite crystal at 25 °C. The relative amounts of adsorption (θ) are A: 0.3, B: 0.5, C: 0.8, D: 0.9, and E: 1.0, respectively. Here, 1 G is equal to 10^{-4} T.

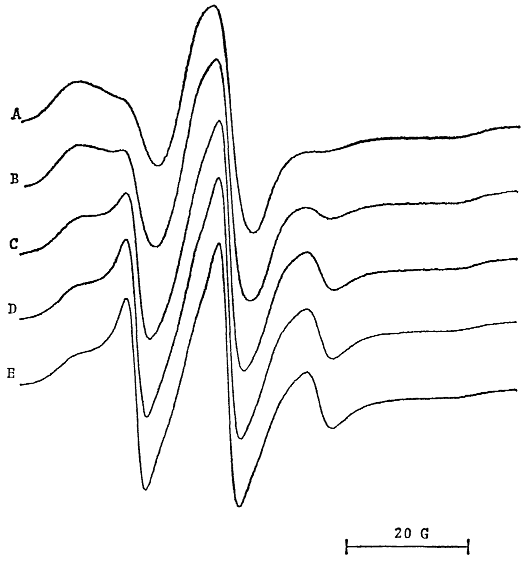

Fig. 3. The ESR spectra of the spin-labeled PMMA adsorbed on enamel at 25 °C. The relative amounts of adsorption (θ) are A: 0.3, B: 0.5, C: 0.8, D: 0.9, and E: 1.0, respectively.

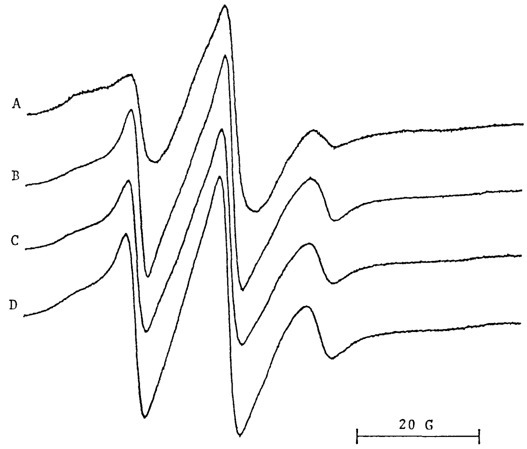

Fig. 4. The ESR spectra of the spin-labeled PMMA adsorbed on dentin at 25 °C. The relative amounts of adsorption (θ) are A: 0.2, B: 0.8, C: 0.9, and D: 1.0, respectively.

adsorbed on the hydroxyapatite surface. The adsorbed molecules initially tend to adsorb in a relatively flat conformation (train) and to become more looped as the saturation adsorption is approached. The spectral behavior of PMMA in the unsaturated stage was also qualitatively the same as in the cases of enamel and dentin, as is shown in Fig. 3 and 4 respectively. Moreover, there was no difference between the ESR spectrum of PMMA adsorbed on hydroxyapatite and that adsorbed on enamel, even at the saturated stage ($\theta \approx 1$). Here, θ is the amount of adsorption relative to the maximum amount of adsorption. On the other hand, a looser adsorption behavior was observed in the case of dentin, as is shown in Fig. 4. In order to clarify this difference, the fraction and the correlation time of the segments in the train conformation were calculated when $\theta = 1$. As has been mentioned above, these ESR spectra of the adsorbed PMMA can be assumed to be composed of three portions of the local chain. The fraction of each portion was evaluated by fitting the spectrum calculated from the superposition of appropriate three model spectra to the observed spectrum on a computer.[4] The correlation time, τ_c, of the bound segments is considered to be in the region of relatively slow motion from 10^{-7} to 10^{-9} s and can be calculated by the following equation, derived by Goldman *et al.*:[7]

$$\tau_c = a(1-S)^b,$$

where $S = A'_z/A_z$, A'_z is one-half the separation width of the hyperfine extrema (W) and where A_z corresponds to the rigid limit value (W_{max}). The parameters, a and b, are dependent on the rotational diffusion models and the intrinsic line-width in the spectrum. In this calculation, the values for the moderate jump diffusion model, $a = 1.10 \times 10^{-9}$ and $b = -1.01$,

Table 1. The correlation time, τ, and the fraction of bound segments of adsorbed PMMA

Sample	τ/s	Segment fraction
Hydroxyapatite	2.2×10^{-8}	0.55
Enamel	2.2×10^{-8}	0.54
Dentin	1.5×10^{-8}	0.44
Silica	$>10^{-6}$	0.48

were used. The results were summarized in the table, together with the data on silica reported previously.[4)] The fraction of bound segments decreased considerably, and the mobility increased significantly, in dentin compared with the values for hydroxyapatite and enamel. These results correspond to the difference in composition between dentin and enamel. The composition of dentin on a wet-weight basis is generally considered to be approximately 70% inorganic material, 18% organic material, and 12% water.[8)] The inorganic portion consists mainly of hydroxyapatite crystals, while the organic portion consists mainly of collagen. On the other hand, the composition of the enamel is 92—96% inorganic material, 1—2% organic material, and 3—4% water. Most of the inorganic material is hydroxyapatite here, also. Thus, the composition of the inorganic material (hydroxyapatite) decreases considerably in the dried dentin compared with that in the dried enamel used here. The carbonyl groups of PMMA are able to form a hydrogen bond with OH groups in the hydroxyapatite, and this interaction is considered to be a predominant force for the adsorption rather than other van der Waals interactions.[9)] Thus, a decrease in the amount of hydroxyapatite in dentin would cause a decrease in the fraction of bound segments and an increase in the mobility of the bound segments compared with the cases of enamel and hydroxyapatite. These conclusions derived from the ESR study are in agreement with the clinical results where polyfunctional methacrylates are found to be more adhesive to enamel than dentin.[10)–12)]

It should be noted that the motion of PMMA adsorbed on silica is significantly slower than those of PMMA adsorbed on hydroxyapatite, enamel, and dentin; *i.e.*, the correlation time of the bound segments is longer than 10^{-6} s for silica, while it is approximately 10^{-8} s for the tooth substances. Such a difference was also observed in the temperature dependence of the extreme separation width. The spectral change of PMMA adsorbed on enamel is shown in Fig. 5 at various temperatures. The value of W decreased gradually with a rise in the temperature. In contrast, the value remained constant over the wide temperature range of −120 to 70 °C in the case of the bound segments on silica, as has been described previously.[4)] These observations indicate that PMMA interacts with silica more strongly than with a tooth. This is interesting because composite resin, which is widely used as a restorative material for teeth, consists of polyfunctional methacrylates and silica powder.

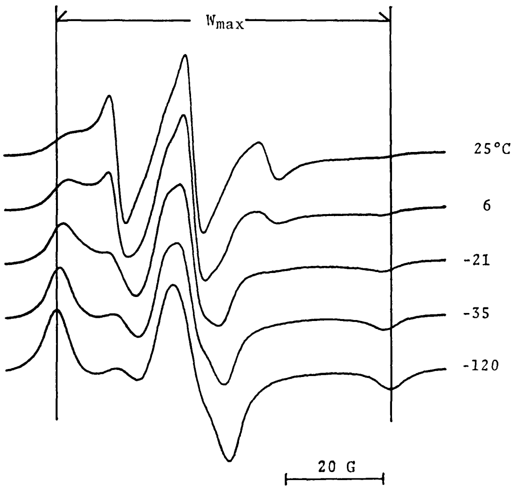

Fig. 5. The ESR spectral change of the spin-labeled PMMA adsorbed on enamel with temperature change. W_{max} is a rigid limit value in the extreme separation widths.

Thus, the ESR method, coupled with the spin-labeling technique, is very useful in studying the interaction between synthetic polymer and the tooth surface.

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