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# REACTION COMPOSITES FROM POLYFUNCTIONAL MACROMOLECULES AND INORGANIC SOLIDS

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## ABSTRACT

For special applications of composite materials, particularly for biomedical uses, the interface between polymer and solid should have a less ordered molecular architecture in order to confer the mobility needed for reactions of ions and low molecular weight agents. Therefore, composites were obtained by controlled reaction of macromolecules, mainly polyepoxides derived from polybutadiene, with glass ceramics which are biocompatible and bioactive. Direct linking of the reacting components by covalent bonds has been demonstrated by IR and NMR spectroscopy using model reactions with silica and other oxides.

## 1. INTRODUCTION

The study of composite materials is important from both fundamental and applied points of view. The formation of macromolecular structures on inorganic solids, such as metals, oxides, and ceramics, which are used as functional interfaces (e.g., for construction elements in microelectronics or as membrane models for use in immunochemistry, in molecular biology, or in biomedical uses) requires detailed investigations of interactions and reaction mechanisms of heterophase reactions. While the good understanding of homogeneous reactions allows effective control of reactions on a technical scale, such a state of the art has not yet been realized in heterophase systems. Apart from the lack of an adequate reaction theory, methods for characterizing the molecular structure in the interfaces are not yet developed sufficiently, so that, in most cases, one cannot distinguish between (a) reaction composites or even molecular composites that are really connected by covalent or ionic bonds and (b) adhesion composites which are held together by only physical interaction forces.

The formation of reaction composites can be considered as a heterogeneous polymer-analogous reaction (HPAR). This paper deals with how HPAR's are carried out, how the degrees of reaction is determined, and how the nature of interfacial bonding might be characterized. Optimization of the composite properties is focused predominantly on biomedical uses.

## 2. THEORETICAL AND PRACTICAL OBJECTIVES

The following methods are suitable for reactive linking of polymers to inorgainc solids:

(1) Sorption of monomers onto solids which have chain or bond structures, such as silicates, phosphates, or borates (inorganic polymers), continued by polymerization via various methods of activation.
(2) Reactions of polyfunctional macromolecules in solution with solids. These are HPAR's in the strict sense. Functional groups might be: CO, OH, $CO_2H$, $CO_2R$, epoxy, NHR, etc. In suitable cases, postreactions by thermal activation may follow, in order to increase the polymer-analogous degree of reaction or for desired optimization of the properties (ratio of hydrophilicity to hydrophobicity).
(3) Induced precipitation of oxide hydrates or salts, respectively, from solutions or colloidal solutions by polyfunctional macromolecules. If suitable, postreactions according to (2) might follow.

Successful work has been done according to (1) where the monomer orientation depends on fluids such as water. By the Langmuir-Blodget technique, monolayers and multilayers were obtained and used as membrane models for investigating special problems in molecular biology [1, 2]. This way is, in principle, also suitable for solid interfaces.

One disadvantage of this technique is the drastic increase of viscosity when the oriented monomers polymerize, and the flexibility of the layers is lost completely. To achieve materials with a specific ratio of hydrophobic and hydrophilic properties, as well as biocompatibility or blood compatibility, we have carried out the direct reaction of polyfunctional macromolecules with inorganic solids, such as bioceramics or model oxides. Apart from some other macromolecules, the most successful results were obtained by using polyepoxides based on polybutadiene. As inorganic solids, we have used glass ceramics containing silicate and special silicate-free bioceramics, mainly consisting of hydroxyapatite, the dominant component of human bones [3]. For elucidation of the degree of reaction and the nature of bond formation between the interfaces, we have conducted model reactions with various types of silica, $Al_2O_3$, and $Fe_2O_3$, in order to improve our understanding of the very complex behavior of our products [4].

From the theoretical point of view, the degree of reaction of a HPAR depends on: 1) the nature and the degree of interactions between the polymer and the solid interfaces (these are, donor-acceptor centers, dispersion and Coulomb interactions, areas of interfaces, charge of interfaces, solvents, thickness of water layer, etc.) and 2) reaction conditions (pretreatment of the solids, temperature, polymer concentration, time of reaction, etc.).

Whether the orientation of macromolecules on solids leads to monolayers or multilayers, caused by their sequential organization facilitated by their conformational mobility, depends on the concentration, temperature, and time of reaction in thermodynamically good solvents. In principle, which of these two borderline cases might be realized depends on the Gibbs-Helmholtz equation, as visualized schematically in Fig. 1.

For our practical aim, the development of a hard-tissue substitute (i.e., a bone cement), the time dependence of which can be modeled on the biomedical use, a multilayer would be desirable, in which the strength properties of the implant materials can be varied by further network-forming reactions.

## 3. EXPERIMENTAL

The following silica gels and other solids were used for elucidation of model reactions: Aerosil-300 ($A_{BET} = 267$ m$^2$/g), Suprasil ($A_{BET} = 150$ m$^2$/g), $Al_2O_3$-C ($A_{BET} = 84$ m$^2$/g), and $\alpha$-$Fe_2O_3$ ($A_{BET} = 4.5$ m$^2$/g), where $A_{BET}$ is the BET surface area.

Polyepoxides derived from various types of low molecular weight polybutadiene were used. Sconamoll Type 32/80 (VEB Chemische Werke Buna/Schkopau, GDR), $\bar{M}_n$ 5600, 50% 1,2-structure, 20% *cis*-1,4-structure, 30% *trans*-1,4-structure. In some cases we have used: Polyoel 110 (Chemische Werke Hüls AG, FRG), $\bar{M}_n$ about 2000, 72% *cis*-1,4-structure, 27% *trans*-

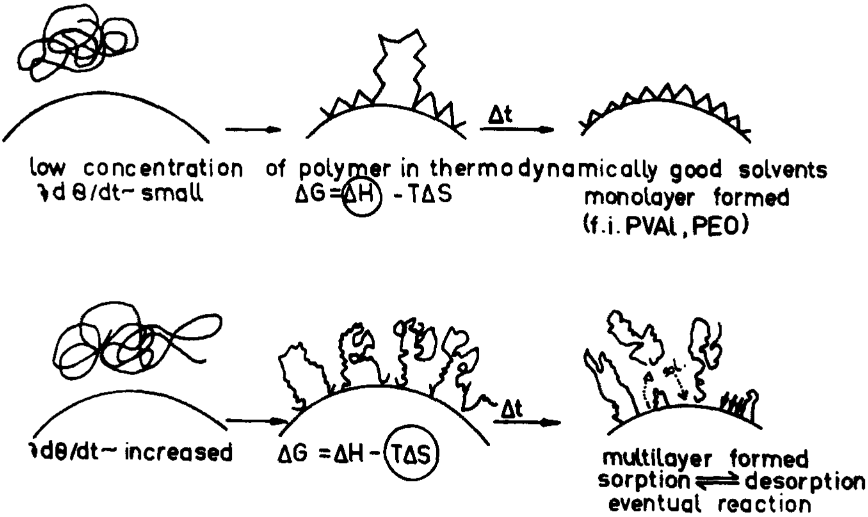


FIG. 1. Schematic picture of controlled synthesis of monolayer and multilayer formation by different routes of HPAR.

1,4-structure. The formation of polyepoxides was carried out either with preformed peracids or by generation *in situ* from carboxylic acids and $H_2O_2$, as described in detail in Ref. 5. The epoxide content was between 10 and 60%, expressed by the abbreviations PBDE 10, PBDE 12, PBDE 16, PBDE 35, and PBDE 60, respectively.

In all the work, the inorganic solids were dried for 24 h at 150°C under vacuum and then dispersed into a solution of 10 wt% PBDE in benzene by ultrasonic agitation. After removing the solvent by evaporation under nitrogen, the probe was kept for about 3 h under vacuum at 60°C.

Unreacted PBDE was removed by extraction with benzene, and the degree of reaction (DR) was estimated as follows:

$$\mathrm{DR} = \frac{\text{mass of bonded PBDE}}{\text{mass of inorganic solid}} \tag{1}$$

A home-built thermogravimetric balance [6] with a heating rate of 5 K/min was used as a second method for the estimation of DR. The methods showed good agreement.

When normal glass, such as Heliovar (VEB Jenaer Glaswerk Schott u. Gen., GDR) or silicate-containing bioactive glass ceramics, was used for the formation of the reaction composite, the solid surface was so reactive that the reaction took place at or above room temperature without pretreatment. For special applications, silicate-free bioceramics were used consisting of various compositions of oxides within the limiting concentrations: $Na_2O$ 10-25 wt%, CaO 8-26 wt%, $Al_2O_3$ 3-21 wt%, and $P_2O_5$ 43-58 wt%. Depending on the glass formation procedure [3], the ceramics consisted mainly of calcium hydroxyapatite, or fluoroapatite when $CaF_2$ was added. Most of these bioactive glass ceramics required activation by pretreatment with phosphoric acid (50 wt%) at various temperatures for 12-24 h.

The reaction composite formation can be performed with the pretreated solids and PBDE from solution or without solvents. In some cases, PBDE 60 was allowed to react with fatty acids, so that some of the epoxide groups were converted and others remained for the reaction with the solid interfaces. The activation of glass ceramics, the partial reaction of polyepoxides with fatty acids, and the formation procedure of reaction composites must be optimized in such way that the reaction mass can be molded and the time of curing maintained between 5 and 15 min.

Molecular weight distributions of the polymers and the extracted PBDE were determined by GPC. A commercial Knauer gel chromatograph FR-30, equipped with silica gel columns, was used. The eluent was tetrahydrofuran (THF), the temperature 40°C, and the flow rate 1 mL/min.

Characterizations of composites by IR spectroscopy were performed with a UR-20 spectrometer (VEB Carl Zeiss Jena, GDR). Mostly, the normal KBr disk technique (approximately 1.5 mg/200 mg KBr) was used. A newly developed IR technique was used [7] for investigating the interaction of PBDE 30 with highly dispersed $SiO_2$ under absolutely dry conditions. For this purpose, 30-50 mg highly dispersed $SiO_2$ ($A_{\mathrm{BET}} = 280\ \mathrm{m^2/g}$) was pressed into 20-mm disks at 3000 $\mathrm{kg/cm^2}$. The disks were dehydrated at 973 K under high vacuum and then submerged for 14-158 h in a solution of PBDE 30 in $CCl_4$ at 293 K. To avoid disturbing the total absorption of the "*in situ*" reaction during spectrum scanning, the sample was taken out of the solution.

$^{13}$C-NMR spectroscopic measurements of solids were performed with a home-built spectrometer of the Department of Physics, Friedrich-Schiller University of Jena. The working frequency was about 15 MHz. The cross-polarization technique was combined with magic-angle spinning (MAS) to minimize the band width. The rotation frequency was 2 kHz. Adamanthane was used as reference material; its band width was found to be less than 5 Hz. The spectra were measured with a pulse delay of about 25 ms, the cross-polarization time was 2 ms, and the decoupling time was 40 ms. We used a $^1$H-Solid-NMR spectrometer at 270 MHz, constructed by the Department of Physics, Friedrich-Schiller University of Jena, for characterization of hydroxyl groups at the solid interfaces.

Structural elucidation and the epoxy content of the epoxydized polybutadienes were obtained by both $^1$H- and $^{13}$C-NMR spectroscopy with a KRH 100 R/$^{13}$C-FT 100-MHz spectrometer (Center of Scientific Instrumentation of the Academy of Science, GDR). The working frequency for $^{13}$C spectroscopy was 25 MHz. All samples were measured in $CDCl_3$, and the chemical shifts were related to TMS.

## 4. RESULTS AND DISCUSSION

In clinical practice there is considerable need for bioceramic materials for artificial limb or moldable hard-tissue substitutes. However, the presently available materials have some disadvantages [8-11].

As described in Section 3, reaction composites were synthetized from pretreated bioglass ceramics, PBDE 35 and PBDE 60, prereacted with fatty acids. The resulting mechanical properties can be varied from rubberlike elastic to fully cured, partly brittle materials [3, 4]. We have tried to visualize the rather complex structure of the interfacial region schematically in Fig. 2.

In comparison with adhesion composites, we expect the following advantages, particularly for biomedical uses:

(1) HPAR leads to composites containing X—O—C bonds (X means Si, P, etc.), which should show improved phase homogeneity.
(2) Unreacted epoxy groups will react with OH groups of the solid interface and the polymer as well, so that a diffuse network should be obtained within a multilayer zone.
(3) A relatively flexible network should be formed in spite of covalent bonding due to mobility of chain segments and site interchange of hydrophobic lipid sequences.
(4) Similarities to animal cell membranes (phospholipids) and to polyhydroxy sequences in plant cell membranes (polysaccharides) should allow reversible interactions within the network zone with water (human lymph) and, therefore, ion transport ($H^+$, $Na^+$, $K^+$, $Ca^{2+}$) can take place as one important requirement of biocompatibility.
(5) The advantages according to (4) might be further improved when, e.g., antibiotics or polyelectrolytes are involved in the composite-

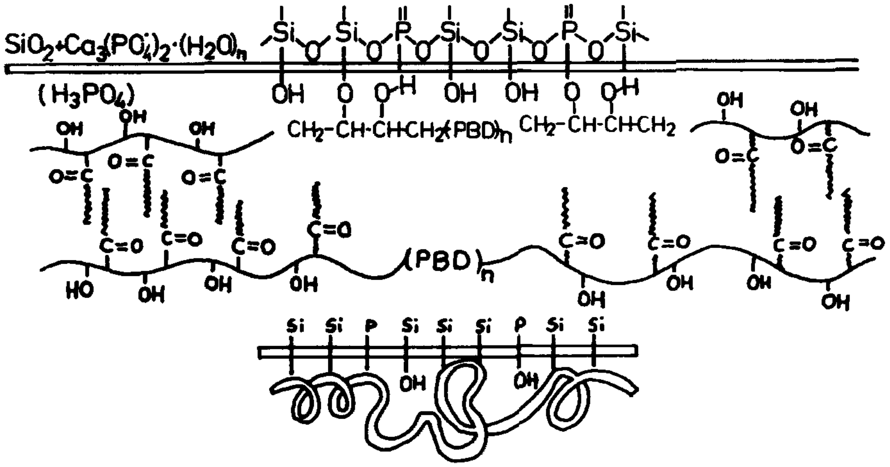


FIG. 2. Schematic representation of the molecular structure of reaction composites obtained by HPAR.

forming procedure. Suitability tests of the materials with cell cultures and implant tests on animals are under way in cooperation with various medical institutions. These results will be reported in forthcoming papers.

In contrast to the incomplete understanding of biosurfaces, we obtained some insight into the mechanism of reaction composite formation by physicochemical investigation of simplified model systems. These findings involve some brief results for α-$Fe_2O_3$ as a model for polymer-bonded magnetic materials.

Figures 3-5 show the degree of reaction (see Section 3), which represents the irreversible bonding of various solid to PBDE. As expected, DR depends on both the surface area of the oxides and the content of epoxy groups in PBDE. Apart from the surface area, we are assuming that the greater number of SiOH groups on Aerosil-300 compared with the very low amounts of FeOH groups on α-$Fe_2O_3$ plays a main role in that different reactivity.

Figure 6 shows the GPC curves of PBDE 35 and of extracted polymers which were not irreversibly bonded to the solid surface. Both the maximum shift of the GPC curves and their increased broadness suggest higher reactivity of Aerosil-300 with epoxy groups.

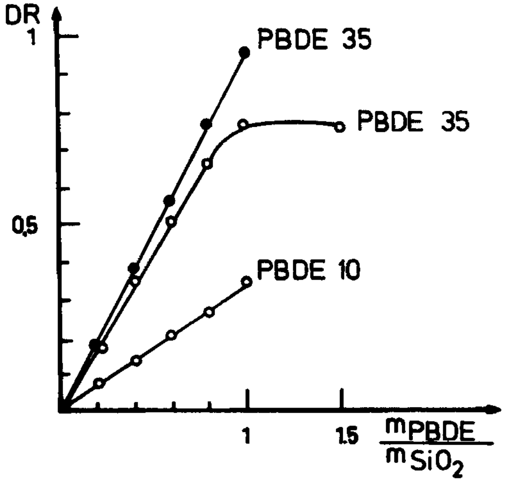


FIG. 3. Dependence of the degree of reaction (DR) of Suprasil/PBDE composites (○), and Aerosil-300/PBDE composites (●) on the ratio of reactants and the epoxy level.

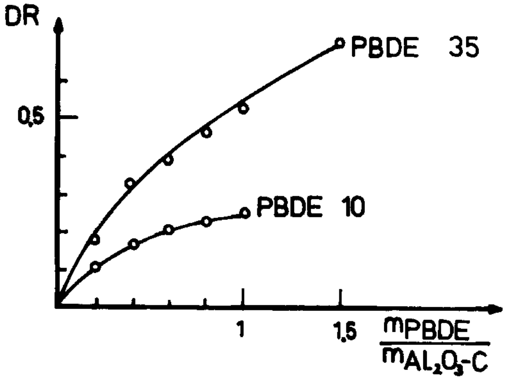


FIG. 4. Dependence of the degree of reaction (DR) of $Al_2O_3$-C/PBDE composites on the ratio of reactants and the epoxy level.

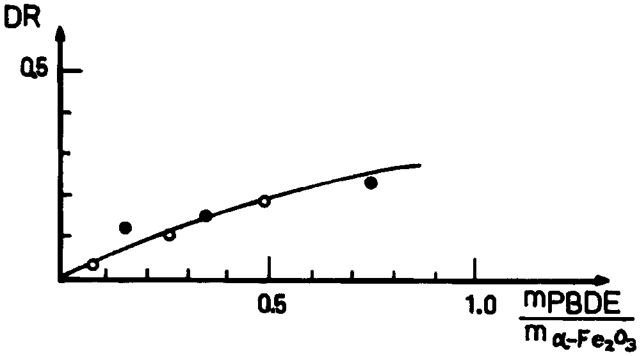


FIG. 5. Dependence of the degree of reaction (DR) of $\alpha$-$Fe_2O_3$/PBDE composites on the ratio of reactants: (○) PBDE 12, (●) PBDE 16.

As another method for determination of DR we used thermogravimetry (Fig. 7). The results of both these methods are in good agreement. Supposing monolayer formation, we have tried to estimate the average area required for one polymer molecule on the oxide surface as the area of a circle with the radius given by [12]:

$$r = (A_{\mathrm{BET}}\bar{M}_n/N_{\mathrm{L}}\mathrm{DR})^{1/2} \tag{2}$$

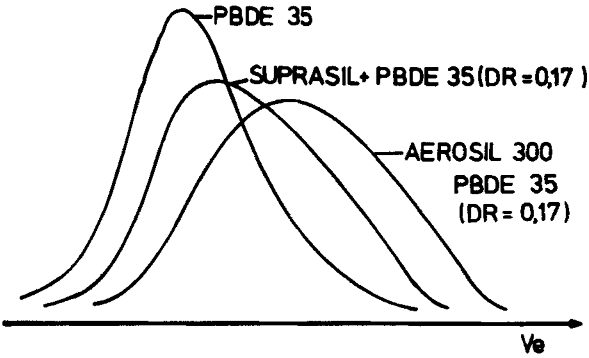


FIG. 6. GPC chromatograms of PBDE 35 and extracted samples from reactions of different silica gels with PBDE 35.

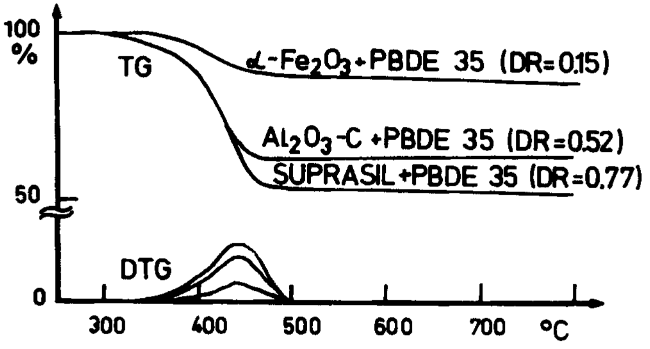


FIG. 7. TG and DTG curves of various oxide/PBDE 35 composites.

For the interaction of PBDE 35 with Aerosil-300 we obtained *r* = 2.5 nm at DR = 0.175 (according to Fig. 3), corresponding to a circle of 20 $nm^2$ area, which would contain approximately 40 silanol groups on the assumption of 2 SiOH groups per nanometer [13]. Since PBDE 35 contains approximately 35 epoxy groups per molecule, one can conclude that the structure forms at the interface rather than in solution (see Fig. 2).

Furthermore, we conclude that reactive bonding of the reactants has taken place by comparing the results of extraction of these composites with those obtained when poly(vinyl alcohol-*co*-acrylic acid) or poly(vinyl alcohol) was allowed to interact with solids under the same conditions as the polyepoxy compounds. In these cases the polymers were completely removed from the solid by hot extraction, indicating that only adsorption had taken place.

Further proofs of covalent bonding at the surface were attempted by means of spectroscopic methods. According to the method described in Section 3, Fig. 8 shows the IR spectrum of a $SiO_2$ disk heated at 973 K, in which the OH stretch vibration of free isolated silanol groups appears as a sharp band at 3733 $cm^{-1}$ [13]. When the disks were kept at 293 K in a solution of PBDE 35 in $CCl_4$ for up to 14 h, the silanol band decreased to one-third, and a broad band appeared between 3100 and 3500 $cm^{-1}$ (maximum at 3350 $cm^{-1}$), which reflects the interaction of silanol groups with PBDE.

Further, the spectrum shows $CH_2{=}CH$ vibrations at 3067 $cm^{-1}$, in line with the amount of unepoxidized 1,2-polybutadiene structure [14], and valence vibrations such as $\nu(CH)$, $\nu_s(CH_2)$, and $\nu(CH_2)$ at 2840, 2910, and 2965 $cm^{-1}$, respectively. After 86 h contact between the disk and the PBDE 35 solution, practically all silanol groups were bonded. Figure 9 shows that there

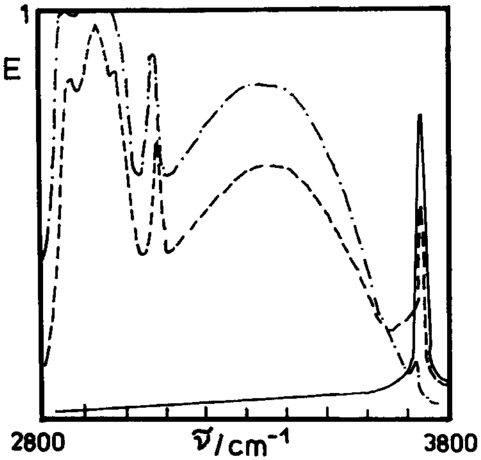


FIG. 8. IR spectra of PBDE 35 on $SiO_2$. (——) $SiO_2$ heated 7 h at 973 K. (– –) $SiO_2$ treated 14 h with PBDE/$CCl_4$ at 293 K. (–·–) $SiO_2$ treated 86 h with PBDE/$CCl_4$ at 293 K.

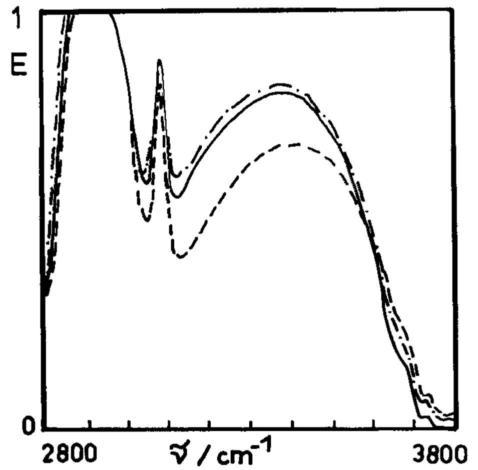
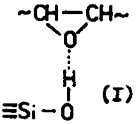
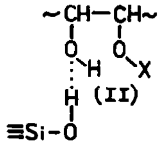


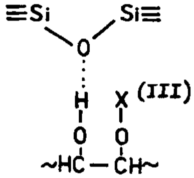
FIG. 9. IR spectra of PBDE 35 on $SiO_2$. (–·–) $SiO_2$ treated 158 h with PBDE/$CCl_4$ at 293 K. (——) $SiO_2$ after removing the PBDE/$CCl_4$ solution and solvent evaporation under high vacuum for 4 h at 293 K. (– –) $SiO_2$ treated as before and heated at 418 K.

is no noticeable change after 158 h of interaction, and that the free silanol group band has largely disappeared. Moreover, one can see that treatment of the disk at 293 K under high vacuum, in contrast to the behavior reported in the literature [13] for low molecular weight compounds under the same conditions, does not cause any change of band intensity. After heating for 7 h at 418 K, there is a small decrease in the absorption at 3350 cm$^{-1}$. However, there is no change in the free silanol group absorptions, which would reflect partial desorption or degradation within the reaction interlayer.

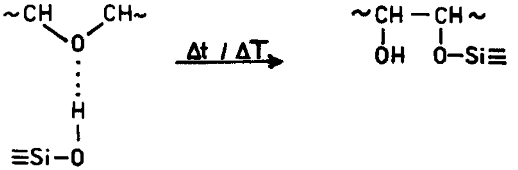
From the spectra, one can conclude that the following interactions occur: (1) Hydrogen bridge bonds to epoxy groups (I) and hydroxy groups (II). Of course, the interactions of hydroxy groups with siloxane bridges are involved in the broad band at 3350 cm$^{-1}$ (III).


(I)


(II)

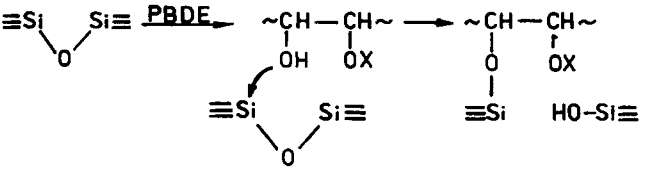

(III)

(2) Dissociative reactions by opening of epoxy groups (I)



(I)

or by nucleophilic opening of siloxane bridges (II)



(II)

The probability of reaction according to (II) is believed to be rather low at normal temperatures, but it might be considerable at elevated temperatures.

It is seen from Figs. 10 and 11 that heating of the disks at 423 or 473 K does not cause noticeable changes, but at 527 K the 3350 cm$^{-1}$ band is sig-

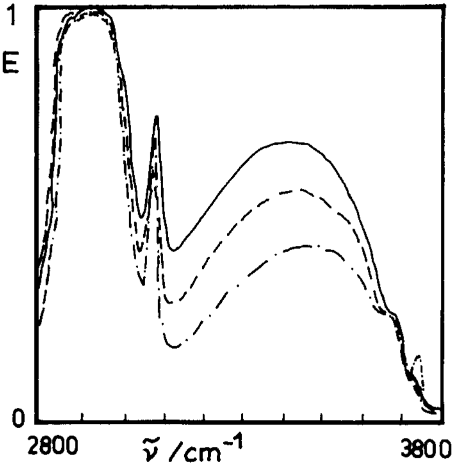


FIG. 10. IR spectra of PBDE 35 on $SiO_2$. (——) $SiO_2$ according to Fig. 9, heated 8 h at 423 K. (— —) $SiO_2$ treated as before and heated 5 h at 473 K. (—·—) $SiO_2$ treated as before and heated 4.5 h at 527 K.

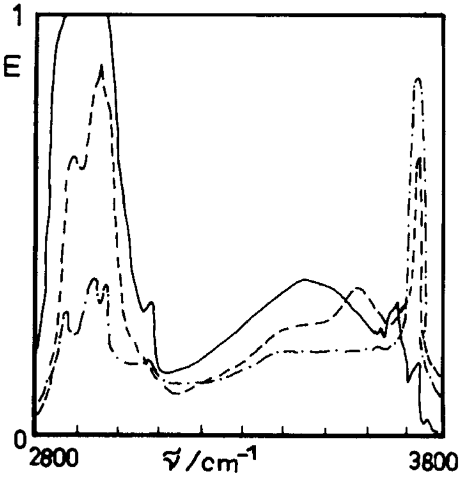


FIG. 11. IR spectra of PBDE 35 on $SiO_2$. (——) $SiO_2$ according to Figs. 9 and 10, heated 2 h at 573 K. (— —) $SiO_2$ treated as before and heated 2 h at 647 K. (—·—) $SiO_2$ treated as before and heated 1.15 h at 873 K.

nificantly reduced and the free silanol band appears increasingly. The intensity of vinyl double bonds at 3067 $cm^{-1}$ and the CH– and $CH_2$ – vibrations may serve as internal standards because they did not change. New bands appearing at 3643, 3667, and 3679 $cm^{-1}$, which can be observed above 573 K (see Fig. 11), suggest the formation of molecularly bonded water, resulting from condensation reactions between hydroxy and silanol groups, as well as further postreactions leading to Si–O–C bonds.

When thermal activation is continued at even higher temperatures (see Fig. 11), degradation of polymers occurs, and besides the band at 3350 $cm^{-1}$, the CH– and $CH_2$– bands decrease markedly, and the free silanol band of the heated surface increases appreciably. In fact, one can conclude from the relative stability of the band at 3350 $cm^{-1}$, particularly at elevated temperatures, that the formation of hydrogen bridge bonds should be reversible even under mild conditions. Unfortunately, direct proof of Si–O–C bonds or the decrease of epoxy bands at 830 $cm^{-1}$ could not be obtained by the technique used, since there is total absorption up to 1300 $cm^{-1}$. However, we have investigated this range for various HPAR's by the normal KBr technique and were able to identify such bands as shown in Fig. 12 for the reaction of $\alpha$-$Fe_2O_3$ with PBDE 12.

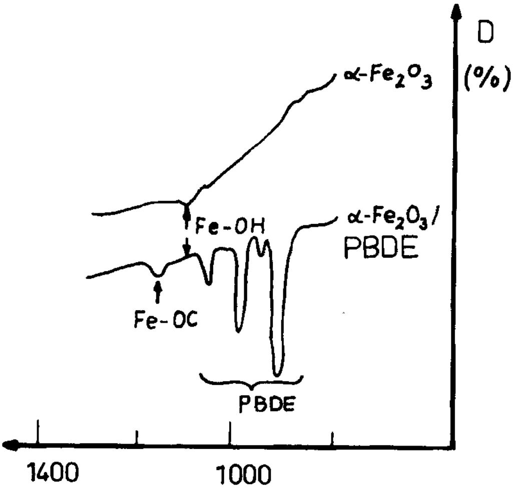


FIG. 12. IR spectra (KBr disk technique) of PBDE 12 on $\alpha$-$Fe_2O_3$ (DR = 0.15). $\alpha$-$Fe_2O_3$ spectrum as reference.

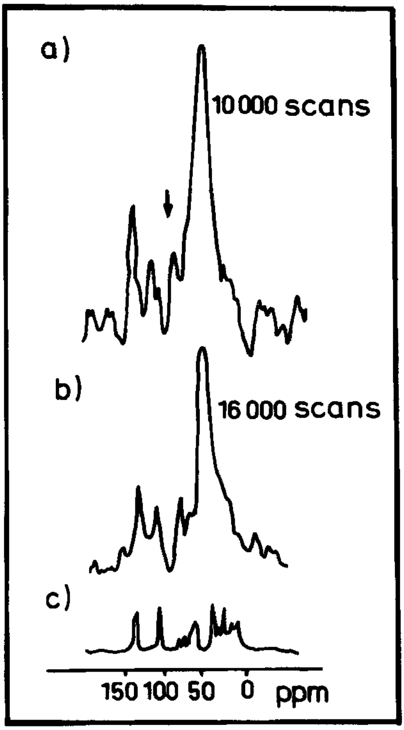


FIG. 13. $^{13}$C-NMR solid spectra of reaction composites. a) Suprasil (57 wt%) and PBDE 35 (43 wt%). b) Aerosil-300 (51 wt%) and PBDE 35 (49 wt%). c) The $^{13}$C-NMR spectrum of PBDE 35 in solution for comparison.

Finally, various methods of NMR spectroscopy were applied successfully to the characterization of bond behavior. Figure 13 shows the $^{13}$C-NMR solid spectra of both the silica gels, Suprasil and Aerosil-300, which were reacted with various amounts of PBDE 35. Figure 13 includes the spectrum of PBDE 35 in solution for comparison. The signals between 110 and 150 ppm belong to the $CH_2-$ and $CH-$ groups of unepoxidized double bonds of the 1,2-polybutadiene structure, the signal at 37-40 ppm to the saturated $CH-$ and $CH_2-$ groups of the polymer chain. A new signal is obtained at 75-80 ppm.

Based on increment calculations and by comparison with $Si(OC_2H_5)_4$ as the model compound (calculated as 78 and 77 ppm, respectively), we con-

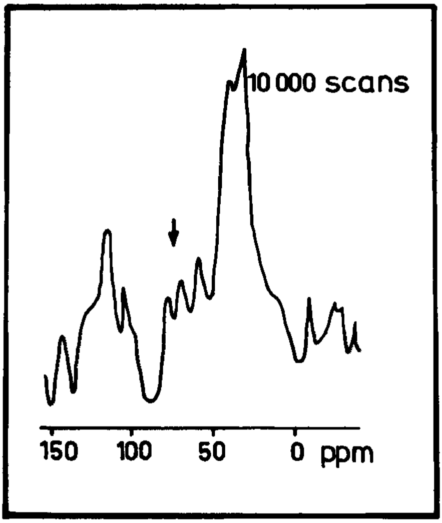
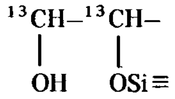


FIG. 14. ${}^{13}$C-NMR solid spectrum of a reaction composite from $Al_2O_3$ (66 wt%) and PBDE 35 (34 wt%).

conclude that the new signal refers to the newly formed bonds of the reaction composite.



$$\begin{array}{ll} {}^{13}\mathrm{CH}- & {}^{13}\mathrm{CH}- \\ | & | \\ \mathrm{OH} & \mathrm{OSi}\equiv \end{array}$$

The spectra of composites obtained from PBDE 35 and $Al_2O_3$ are similar to those obtained with silica gels.

Figure 14 shows the corresponding signal at approximately 75 ppm, where the range from 60 to 90 ppm is considerably broadened by the high nuclear spin of ${}^{27}$Al (5/2).

Clearer and well-resolved ${}^{13}$C-NMR spectra were obtained when we investigated the reaction of bioactive glass ceramic pretreated with $H_3PO_4$ (see Experimental section) and PBDE 60 that was obtained by epoxidation of mainly *cis*-1,4-polybutadiene.

Figure 15 shows the signal of unepoxidized ${}^{13}CH{=}{}^{13}CH$ groups at 133 ppm and of saturated $CH_2$ groups. Here, the new signal appears very clearly

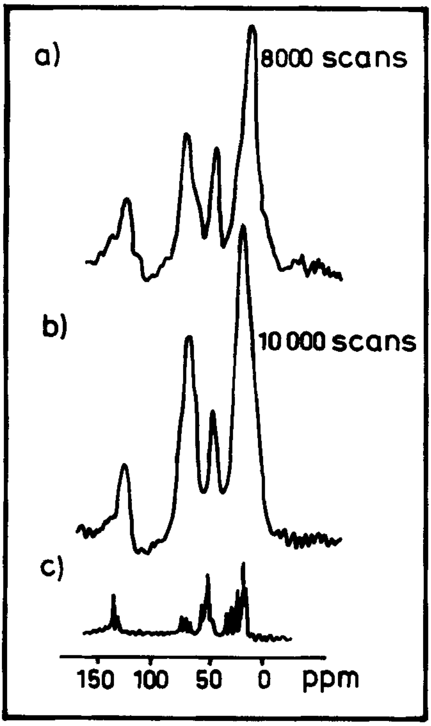


FIG. 15. ${}^{13}$C-NMR solid spectra of PBDE 60 and bioactive glass ceramic, pretreated with $H_3PO_4$. a) Composite formation at room temperature. b) Heated at 373 K. c) The ${}^{13}$C-NMR spectrum of PBDE 60 (obtained by epoxidation of *cis*-1,4-polybutadiene) for comparison.

at 80 ppm, and we propose it as characteristic of covalent bonds between the organic and inorganic components. The relative narrow bands in Fig. 15, caused by the more uniform structure of PBDE 60, allow further band assignments. The signal at 58 ppm suggests the remaining unconverted epoxy groups (solution spectrum at 56.5 ppm).

Furthermore, there can be $-\overset{\|}{\underset{|}{P}}-O-{}^{13}CH$ bonds in that range which are reported in the literature near 60 ppm [15]. The spectra of the composites were reproducible after storage for half a year and also after heating. Only the signal at 60 ppm diminishes in intensity when heated for some days.

Further investigations by means of suitable model compounds may enable us to separate the mentioned signal overlap and to gain more insight into the very complex structure of the interfacial zone.

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