

Adhesion of Polymers to Shale Rock Surfaces

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Synopsis

In the course of a project on the application of polymers for rock bonding and reinforcement of coal mine structures, the adhesion of epoxy resins to shale mine rock was studied by infrared and Mössbauer spectroscopy. Two types of bonding were identified: primary bonds between silicates and polymer, and hydrogen bonds from organic compounds on the surface of the shale to oxygen in the polymer. These bonds contribute to the adhesive strength when epoxy resins are used to bind shale. The bonding model, when applied to furfuryl alcohol and polyester resins, predicts inferior binding in the shale system.

INTRODUCTION

When an epoxy resin (Epon 828, Shell Chemical Corporation) containing a monofunctional amine (*n*-butylamine) was polymerized in the presence of shale powder and then extracted with methyl ethyl ketone, about 10% of the resin remained with the shale. Under the same experimental conditions, resin samples polymerized in the absence of shale were completely soluble in this solvent.

This was considered as an indication that some grafting may have taken place between resin and shale surfaces. In order to prove polymer grafting and to arrive at a bonding model for polymer-shale interactions, infrared and Mössbauer techniques were applied to the study of these systems.

It is known that the formation of new bonds can be detected by infrared spectroscopy through the appearance of new bands, band broadening or narrowing, and/or their shifting. By the introduction of a multireflection unit (attenuated total reflectance, ATR), interfaces and surfaces can be examined in depth and the resultant bands be strengthened. From the optical spectra obtained, conclusions can be drawn as to the type of new bonds formed.

Mössbauer spectroscopy, which is based on the recoilless emission and resonant absorption of gamma rays, can be applied to determine the type of bonding in compounds, organic or inorganic, provided that they contain certain elements (e.g., iron) as part of the lattice structure. Consequently, if one were to polymerize an epoxy resin on the surface of olivine, a magnesium-iron silicate, a change in the Mössbauer spectrum would be

observed if new bonds were established between the silicon or oxygen atoms in the silicate and carbon or any other atom in the epoxy resin. Since shale is known to contain iron, it was thus considered possible that the Mössbauer effect could be used to detect bond formation between rock and resin, provided that the iron in the shale is part of one of the component silicates and not solely present as an unrelated impurity. Biotite and chlorite, both containing iron in the molecule, were identified in mine shales originating from West Virginia coal mines and used in this study.

STRUCTURAL CONSIDERATIONS

The molecular structure of the shale substrate used in the experiments is not accurately known. On the basis of chemical analysis, thermal analysis, and infrared studies, it is possible to obtain an approximate concept of what this structure might be. The shale was found to contain 71% silica; other major components were the oxides of iron, aluminum, and calcium. Further, there were traces of vanadium, titanium, boron, phosphorus, magnesium, manganese, copper, zinc, nickel, and chromium. Thermal analysis showed that the shale contained less than 1/2% moisture but about 5% organic compounds. Infrared analysis of shale, which had been heated to remove these organic compounds, indicated that the silicate structure was similar to that of other silicate rocks, with iron, aluminum, and calcium ions presumably replacing sodium and magnesium ions. Organic compounds may occupy holes left by defects in the silicate network, so that organic-free shale or Ottawa sand was used in some experiments to clarify the bonding picture. Ottawa sand is high in silica content and relatively free of metals other than sodium.

As to the resins used, the epoxy resin is the diglycidyl ether of bisphenol A (Epon 828), cured with trifunctional diethylenetriamine which reacts to extend and crosslink the polymer chain. This resin system contains numerous potential sites for bonding with the shale substrate. Hydroxyl or amine groups could bond to the silicates in the shale either by hydrogen bonds or by the elimination of water to form primary bonds. In the case of hydrogen bonds, heat curing of the resin-shale system would remove some of these by promoting crosslinking between hydroxyl groups of the resin. Another possibility of hydrogen bonding may take place from the organic compounds on the shale surface to groups in the resin (e.g., hydroxyl or ether). Interaction of the aromatic rings with metal ions in the shale is less likely. Other possibilities include the involvement of electrostatic forces, van der Waals forces, and diffusion of the long resin molecules into defects in the silicate structure.

Furfuryl alcohol may condense, in the presence of an acid catalyst, by forming $-\text{CH}_2-$ bridges. Additional polymerization and crosslinking may occur through the double bonds in the furan ring. In essence, the same bonding possibilities exist for the furfuryl resins as for the epoxy resins, except that the furan ring is less likely to interact with the shale. An

additional bonding possibility exists in the double bonds of the furan ring, although their reactivity is uncertain. A significant point is the absence of large numbers of hydroxyl or amino groups, which could be involved in primary bonds to the shale.

Much the same situation exists in the case of the polyester Hetron 26869 (Hooker Chemical Company), made by the condensation of hexachlorocyclopentadiene with maleic anhydride and then reacted with dibasic acids and dihydric alcohols.¹ However, here it is almost certain that the double bonds are used up by crosslinking with a styrene monomer.

EXPERIMENTAL

Thus, three resins were investigated. The epoxy resin was prepared by mixing Epon 828 with diethylenetriamine in a weight ratio of 9.5 to 1.03. The furfuryl alcohol resin was made by mixing furfuryl alcohol, concentrated hydrochloric acid, and urea (added for reaction rate control) in a weight ratio of 8.6 to 1.1 to 0.3. This latter reaction is still very fast and had to be further controlled by maintaining the reaction mixture near 0°C until the resin had hardened. The polyester resin was a 47% solution of the Hetron 26869 in chlorostyrene. A 20-g portion of this solution was divided into two 10-g portions. The first portion was mixed with 0.2 g 6% cobalt naphthenate and 0.1 g diethylaniline; to the second portion, 0.3 ml of Lupersol Δ (Lucidol Division of Wallace and Tiernan, Inc.) was added. These two portions were mixed in order to activate and polymerize the polyester resin.

Five grams of each of these resin samples were blended, immediately after preparation, with 10 g of the powdered substrate (shale or Ottawa sand) and allowed to polymerize (coreact). After curing was complete, the sample was ground in a Wiley mill through a 60-mesh screen. Another portion of each resin was cured with no substrate added. After curing was complete, these samples also were ground in the Wiley mill, and 5-g portions were blended with 10 g of the powdered substrate.

In most cases, two sets of samples were prepared which were cured by different procedures. One set was cured at ambient temperature, while the second set was heat cured. The heat-curing process consisted of placing the hardened samples in an oven at 50°C for 6 hr, at 85°C for 2 hr, and at 150°C for 4 hr.

Three powdered substrates were used: (1) shale rock from U.S. Steel Mine No. 4, ground and passed through an 80 mesh screen; (2) substrate (1) heated to 900°C for 6 hr; and (3) Ottawa sand ground and passed through an 80-mesh screen.

A total of 28 samples were thus obtained by different combinations of the above materials and conditions. The composition of each sample is shown in Table I.

Infrared spectra were obtained on a Perkin-Elmer Model 621 recording spectrophotometer. ATR spectra² were collected with a Barnes Model

TABLE I
Survey of Sample Preparations*

Sample no.	Sample key	Resin	Substrate	Curing conditions	Type of mixing
1	1a*	E	—	A	—
2	1b*	—	S1	—	—
3	1c*	E	S	A	M
4	1d*	E	S1	A	C
5	1ah	E	—	H	—
6	1ch	E	S1	H	M
7	1dh	E	S1	H	C
8	2b*	—	S2	—	—
9	2c*	E	S2	A	M
10	2d*	E	S2	A	C
11	2ch	E	S2	H	M
12	2dh	E	S2	H	C
13	3b	—	S3	—	—
14	3c	E	S3	A	M
15	3d	E	S3	A	C
16	3ch	E	S3	H	M
17	3dh	E	S3	H	C
18	4a	F	—	A	—
19	4c	F	S1	A	M
20	4d	F	S1	A	C
21	4ah	F	—	H	—
22	4ch	F	S1	H	M
23	4dh	F	S1	H	C
24	5a	P	—	—	—
25	5c	P	S1	A	M
26	5d	P	S1	A	C
27	5dh	P	S1	H	C
28	6d	P	S2	A	C

* S1, U.S. Steel Mine #4 powdered shale (unheated); S2, U.S. Steel Mine #4 powdered shale (heated to 900°C); S3, Ottawa sand; E, Epon 828 epoxy resin; F, furfuryl alcohol, acid catalyzed; P, Hetron 26869 polyester resin, in chlorostyrene; A, cured at ambient temperature; H, heat cured; M, mechanically blended; C, coreacted; * samples used for Mössbauer work.

ATR-4 fixed-angle (45°) apparatus. All ATR measurements were made with a 2-mm KRS-5 ATR crystal. Potassium bromide pellets were prepared by thoroughly mixing 0.1 g of the sample with 2 g infrared-quality potassium bromide. This mixture (0.35 g) was pressed in a 13-mm pellet die to give a clear disc of 1.5-mm thickness.

The Mössbauer instrument and techniques used have been described in the literature.³⁻⁷ The source used was ⁵⁷Co diffused in palladium (New England Nuclear Co.), with an initial radiation rating of 3 millicuries. The samples were pressed between two 1-cm discs to provide a sample 2 mm thick. The sample size was adjusted to provide 200 mg of shale in each sample, which gave an iron concentration of about 10 mg/cm². This low concentration ensured that any observed line broadening was not due to

thickness broadening. The samples used for Mössbauer work are marked with an asterisk in Table I.

Mössbauer spectra of all samples were collected at room temperature over a period of several days. The spectrum for sample 1b was also collected at 78°K (liquid nitrogen coolant). A baseline of at least 7×10^5 counts per channel was collected for each spectrum.

RESULTS AND DISCUSSION

In view of the nature of the samples and the characteristics of the ATR apparatus, the ATR spectrum from 4000 to 900 cm^{-1} was of little value in this investigation. However, the portion of the ATR spectrum from 850 to 250 cm^{-1} proved most useful. Figure 1 shows this portion of the spectrum for powdered shale (sample 1b). At the outset, it would seem almost impossible to observe changes in bonding in spectra of this type. Fortunately, the resin contribution to the spectra in this region was minimal, and the resin peaks were readily identifiable. The procedure used was to compare the spectrum in Figure 1 with those obtained from mixed and coreacted samples (e.g., samples 1c and 1d, or 1ch and 1dh). Slight shifts were observed in several peaks, and attempts were made to assign these peaks on the basis of published spectra of silicates, aluminum oxide, and iron oxide.⁸ Assignments were not possible, however, until the shale was heated to 900°C, in order to remove the organic compounds from the surface of the shale. The inorganic residue (sample 2b) produced the spectrum shown in Figure 2, and the peaks could now be assigned with more confidence. The peaks at

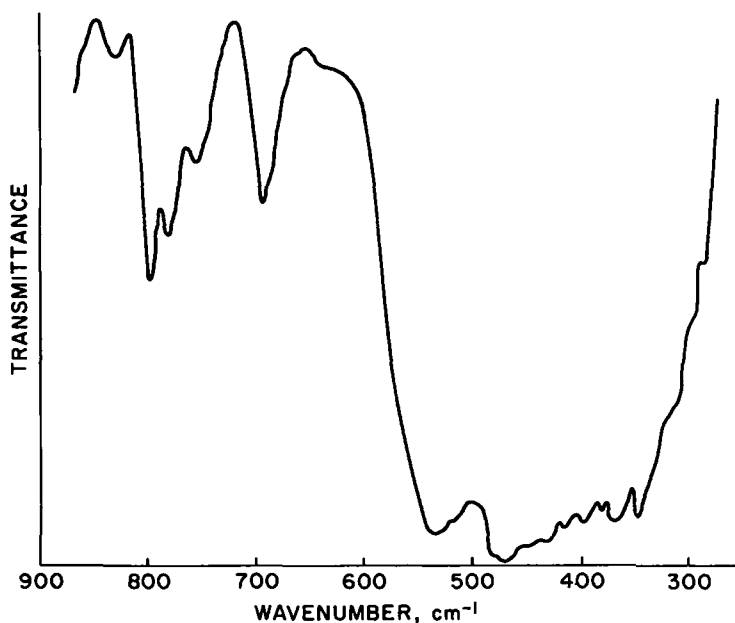


Fig. 1. ATR spectrum of shale (sample 1b).

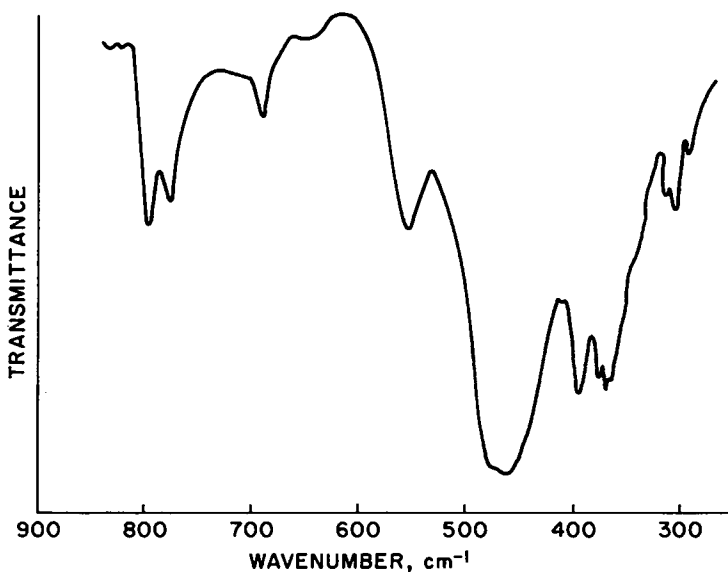


Fig. 2. ATR spectrum of heated shale (sample 2b).

800, 780, 690, 400, and 360 cm^{-1} are due to silicate, those at 325 and 315 cm^{-1} to iron oxide, while the peaks at 570 and 370 cm^{-1} are assigned to both iron and aluminum oxides. The peak at 460 cm^{-1} contains a silica peak at 450 cm^{-1} and a shoulder at 510 cm^{-1} , an iron oxide peak at 470 cm^{-1} , and an aluminum oxide peak at 435 cm^{-1} . Thus, there are ten peaks that can be identified in most ATR spectra, and their positions are listed in Table II. These data show significant differences in the positions of peaks assigned to silica. Where shifts occur, there is frequently a new shoulder observed on the peak. All this makes it likely that the silicates are involved in some type of bonding.

In addition to shifts in frequency, the peak at 530 cm^{-1} in Figure 1 shows a broadening as illustrated by the broken line in Figure 3. The 570 cm^{-1} column in Table II is marked with an asterisk where this phenomenon is observed. This type of behavior is characteristic of hydrogen bonding.⁹ Since this phenomenon was observed only when unheated shale was used as the substrate, it is assumed that the organic compounds on the shale are involved in some type of hydrogen bonding. This conclusion is further substantiated by the observation of this apparent hydrogen bonding in the furfuryl alcohol resin system. The resin itself has no peaks in this area (530 cm^{-1}).

Consideration of the epoxy resin system (samples 1a through 3dh) leads to several significant results. When shale is used as the substrate, the bonding to silicates is increased by heat curing. When the substrate is Ottawa sand, heat curing eliminates the bonding to silicates. These results suggest the formation of primary bonds to silicates in the shale system and of hydrogen bonds to silicates in the Ottawa sand. Possibly, the

TABLE II
Positions of Selected Peaks from ATR Spectra*

Sample	800		775		690		570		460		370		325		315	
	Silica	Silica	Silica	Iron and aluminum oxide	Silica	Silica and iron and aluminum oxide	Iron and aluminum oxide	400	Silica	Iron and aluminum oxide	360	Iron oxide	Iron oxide	Iron oxide	Iron oxide	
1b	797	776	692	530	465	376	394	364	308							
1c	797	778	693	535	470	376	395	366	308							
1d	798	780	696	540*	470	376	397	368	308							
1bh	797	776	692	530	465	376	394	364	308							
1ch	797	777	692	535	470	376	394	365	309							
1dh	799	779	694	540*	470	376	397	370	308							
2b	798	777	691	557	470	376	394	364	306							
2c	798	778	692	557	470	376	394	367	306							
2d	797	776	696	558	470	376	398	366	306							
2eh	798	777	691	557	470	376	394	368	306							
2dh	796	775	694	558	470	376	398	366	306							
3b	797	777	693	513	460	368	394	368	—							
3c	797	778	692	515	462	368	394	368	—							
3d	795	775	694	520	464	370	397	370	—							
3ch	797	778	693	515	460	368	394	368	—							
3dh	797	778	693	515	460	368	394	368	—							
4c	797	776	693	533	465	376	392	364	306							
4d	797	776	693	536*	468	376	392	364	306							
4ch	797	776	693	533	465	376	395	364	306							
4dh	797	776	693	535*	469	376	395	364	306							
5c	800	778	693	535	467	—	394	368	309							
5d	800	778	694	540*	467	—	394	368	—							
5dh	794	776	693	536	468	377	396	369	—							
6d	800	778	693	—	465	377	394	368	—							

* Asterik denotes peaks showing line-broadening effect illustrated in Figure 3.

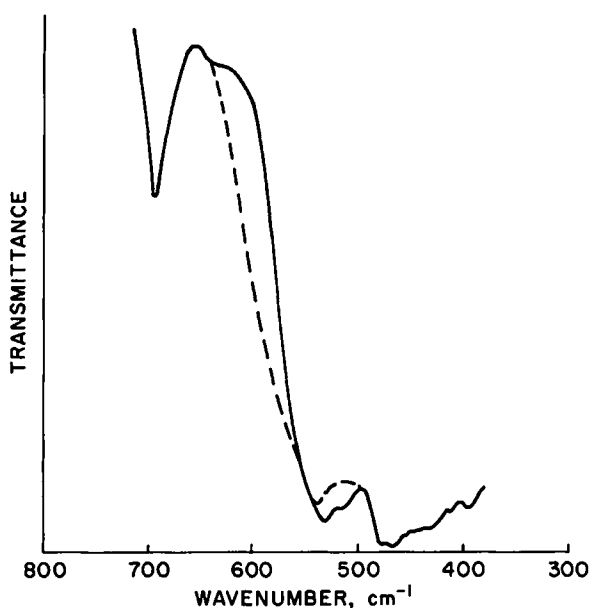


Fig. 3. Schematic representation of line broadening (dashed line) observed in the 530 cm^{-1} peak of the ATR spectrum.

difference in the type and quantity of metal ions in the shale is sufficient to effect bond formation. In addition, there appears to be hydrogen bonding between organic compounds on the substrate and the resin in the shale system (samples 1c through 1dh). This is deduced by the absence of hydrogen bonding in the heated shale and in the Ottawa sand (samples 2c through 3dh).

Potassium bromide pellets were prepared in the effort to identify the resin group involved in bonding to the silicates. Figure 4 shows the useful portion of the KBr pellet spectrum. The peaks in which a shift was observed, indicated by arrows and tabulated in Table III, can be associated with substituents on the benzene rings.¹⁰ Since shifts were observed in the same samples that indicate shifts of silica peaks, it is concluded that bonding to the silicates is through the hydroxyl groups of the resin.

TABLE III
Positions of Selected Peaks from Spectra of KBr Pellets

Sample	2930	1605	1580	1510
1b	—	—	—	—
1ah	2920	1612	1588	1512
1ch	2920	1610	1580	1512
1dh	2930	1605	1583	1508
2b	—	—	—	—
2ch	2920	1610	1577	1512
2dh	2930	1605	1580	1509
3c	2920	1610	1578	1512
3d	2930	1606	1582	1508

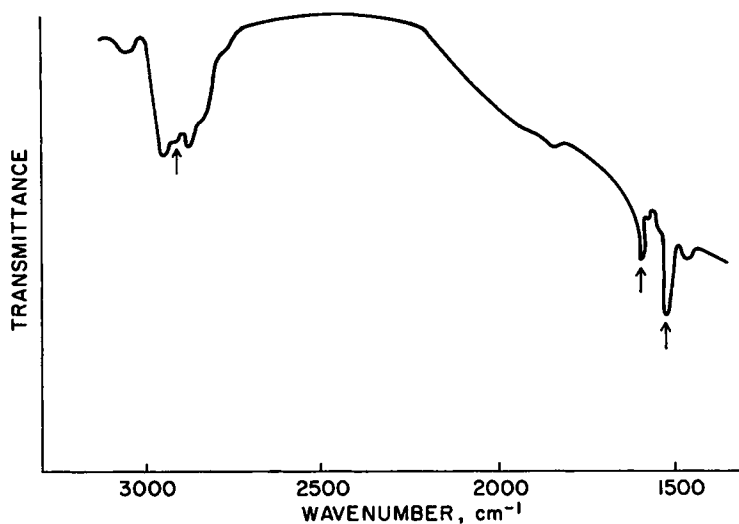


Fig. 4. KBr pellet spectrum of sample 1d. Arrows indicate peaks which show shifts and are tabulated in Table III.

The epoxy resin system was also studied by Mössbauer spectroscopy. The spectrum of the shale (sample 1b) is shown in Figure 5. Well-resolved quadrupole doublets, attributed to nuclear quadrupole splitting of iron(II) in an octahedral environment, are observed at -0.35 mm/sec and 2.2 mm/sec. The small resonant absorption peak at 0.4 mm/sec is attributed to the presence of a small amount of iron(III) in an octahedral environment, while the other portion of this peak is presumably overlapping the iron(II) peak at -0.35 mm/sec. This spectrum differs from that of the shale-resin system (samples 1c and 1d) only in the relative intensities of the resonant absorption peaks. The relative intensities of these peaks are

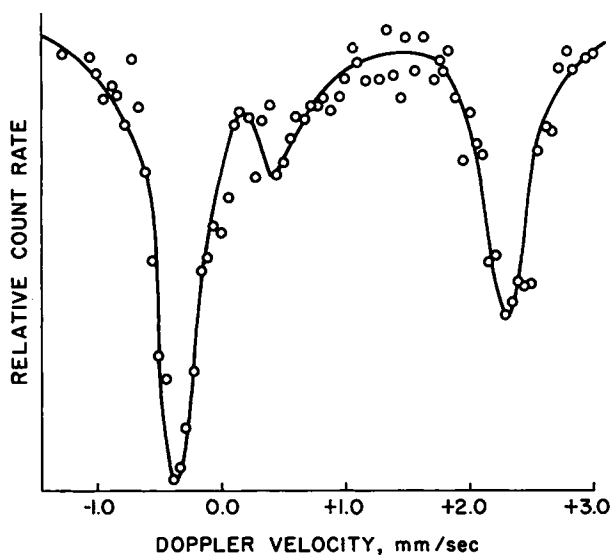


Fig. 5. Mössbauer spectrum of shale (sample 1b).

TABLE IV
Relative Intensity of the Fe(II) Quadrupole

Sample	Temperature	Relative intensity of Fe(II) resonant absorption doublet
Shale (1b)	room	1:0.66
Shale mixed with resin (1c)	room	1:0.80
Shale coreacted with resin (1d)	room	1:0.97
Shale (1b)	liquid nitrogen	1:0.73

listed in Table IV. No isomer shift is observed, and the quadrupole coupling constants do not change for the room-temperature samples.

Normally, doublets produced by quadrupole splitting are of equal width and intensity. Deviations from this rule, as seen in Figure 5, may be caused by spin-lattice relaxation phenomena¹¹ or by anisotropic vibrational displacements (Karyagin-Goldanskii effect).¹² These phenomena can be distinguished by collecting the spectra at a low temperature. In the case of spin-lattice relaxation, a reduced temperature would tend to increase the difference in the relative intensities, while this difference would become smaller if it were due to the Karyagin-Goldanskii effect. Indeed, when the spectrum of sample 1b was run at liquid nitrogen temperature, the results, included in Table IV, showed that the differences in the relative intensities observed in Figure 5 were due to the Karyagin-Goldanskii effect. This indicates that changes observed in the relative intensities are caused by changes in the vibrational displacement of the iron atoms.

The absence of changes in the isomer shift and in the quadrupole coupling constant indicates that there is no change in direct bonding to iron or its neighboring atoms. However, the changes in relative intensities of peaks listed in Table IV suggest weak or distant interactions. The change observed in the mixed sample (1c) indicates that some interactions are simply caused by physical contact between shale and resin. The increase in these interactions in the coreacted sample (1d) suggests some stronger interaction.

The above conclusions are further substantiated by the Mössbauer spectra of samples 2b, 2c, and 2d. The spectra of the heated shale (sample 2b) and of the heated shale coreacted with the resin (sample 2d) are compared in Figure 6. The difference in the appearance of the spectra in Figures 5 and 6 is due to the conversion of iron(II) to iron(III). Again, the difference in the spectra of the three samples (2b, 2c, and 2d) is not in the isomer shift or in the quadrupole coupling constant, but in the relative intensities of the peaks at -0.8 , -0.45 , and -0.1 mm/sec. The first two peaks increase through the series, while the latter peak decreases. The change in the relative intensities of these peaks in the mixed sample (2c) is barely perceptible while the change in the coreacted sample (2d) is quite obvious, as shown in Figure 6. Thus, it may be concluded that there is no bonding to iron or its near neighbors, although it may be assumed that electrostatic interactions and/or hydrogen bonding do occur between the resin and the shale.

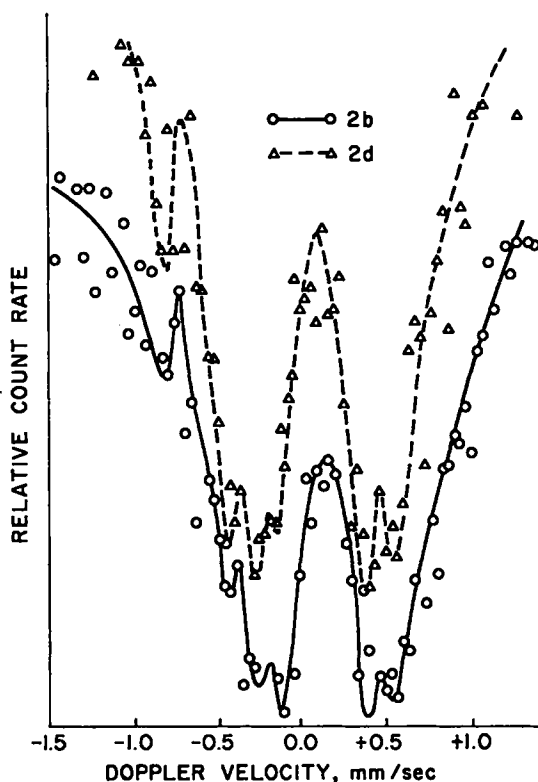


Fig. 6. Mössbauer spectrum of shale heated to 900°C (sample 2b) and of shale coreacted with epoxy resin (sample 2d).

A furfuryl alcohol resin and a polyester resin were investigated by ATR only (samples 4a through 6d). The positions of peaks identified as shale peaks in these spectra were included in Table II. No interaction is observed except in the appearance of the peak at 530 cm^{-1} in the furfuryl alcohol resin. This peak could not be observed in the polyester resin because of interference by resin peaks. Since no change is noted in the silicate peaks, it is concluded that no bonding to the silicates takes place in the furfuryl alcohol or the polyester resins. However, hydrogen bonding from organic compounds on the shale to oxygen in the furfuryl alcohol resin is observed. Similar hydrogen bonding may also occur in the polyester resin, but its presence cannot be detected with certainty due to the nature of the resin spectrum.

SUMMARY

The results of this investigation indicate that organic compounds on the surface of the shale tend to form hydrogen bonds to appropriate sites on the polymer molecules. Hydrogen bonds can be expected to add to the adhesive forces between shale and polymer whenever the polymer contains functional groups which can accept hydrogen bonds. The presence of these hydrogen bonds may be observed by the deformation of the shale peak near 530 cm^{-1} in the ATR spectrum.

A much stronger adhesive force is provided by primary bonds that are formed by the reaction of hydroxyl groups in the polymer with silicate groups in the shale. This reaction is apparently catalyzed by the metals present in the shale. Where large numbers of hydroxyl groups are available in the polymer molecule, the bonding can be observed by noting shifts of certain shale peaks in the ATR spectrum.

Applying this model to the epoxy resin system, one expects good adhesive properties due to formation of both hydrogen and primary bonds. When this bonding model is applied to the furfuryl alcohol resin system, one expects lesser adhesion through hydrogen bonds with an occasional primary bond formed by reaction of a hydroxy group at the end of a polymer chain. The least adhesion is expected for the polyester resin system. Although this resin does have numerous groups which could accept hydrogen bonds, these groups may be well separated or interfered with by the chlorostyrene used for crosslinking.

Thus, two types of bonding have been identified. These are primary bonds between silicates and polymer and hydrogen bonds from organic compounds on the surface of the shale to oxygen in the polymer. These bonds contribute to the adhesive strength when epoxy resins are used to bind shale. This bonding model, when applied to furfuryl alcohol and polyester resins, explains their inferior binding in the shale system.

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