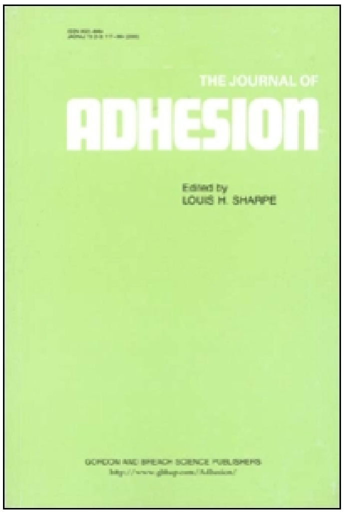

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Influence of the Surface Composition of Metallic Substrates on the Reactivity and Bonding Properties of Structural Adhesives*

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Comprehension of the phenomena and conditions of the crosslinking of structural adhesives is invaluable in making performance structures. This crosslinking obviously depends on the formulation of the adhesive: *i.e.* the nature of the basic resin, of the crosslinking agent, of the various additives and of its composition. The work bears on the study of the crosslinking of epoxy resins in the presence of steels plated with different alloys, with a view to studying the behaviour of the adhesive/support system and investigating the effect on reactivity of the nature of the substrate's surface and the study of the mechanical behaviour of bonded assemblies under shearing. By determining the energy of activation, we have been able to highlight the catalytic effect of the supports on the crosslinking of the epoxy-diamine adhesive under consideration. We have demonstrated the greater efficiency of aluminium on adhesive-substrate interactions. Interaction seems possible between the hydroxyl group of the epoxy and aluminium.

KEY WORDS: Metallic substrates; galvanized steel; aluminum; epoxy resin adhesives; DSC; heating rates; crosslinking; activation energy; chemical interactions; mechanical properties; SEM.

INTRODUCTION

Knowledge of the phenomena and conditions of the crosslinking of structural adhesives is invaluable in making performance structures. Reaction kinetics and the resulting degree of crosslinking govern the mechanical properties of the bonded structures and determines the choice of the bonding parameters. The crosslinking obviously depends on the formulation of the adhesive: *i.e.* the nature of the basic resin, of the crosslinking agent, of the various additives and of its composition. Some authors have demonstrated, however, that adhesives based on epoxy resins could

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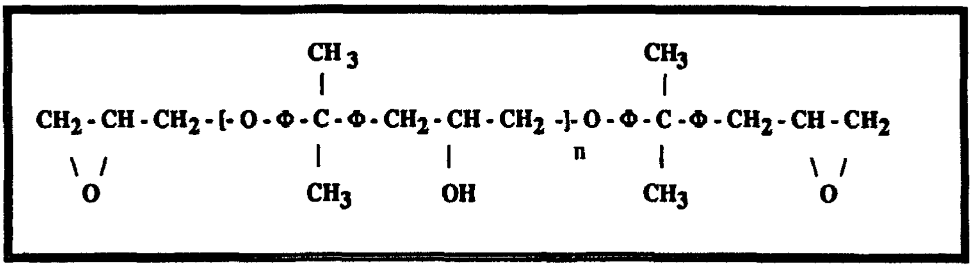
also react with the supports on which they were laid and display a modified reaction process [1,2,3]. Our work bears chiefly on the study of the crosslinking of epoxy resins in the presence of steels plated with different alloys with a view to studying the behaviour of the adhesive/support system and investigating the effect on reactivity of the nature of the surface of the substrate. Subsequently, the study of the mechanical behaviour of bonded assemblies under shearing, and the microscopic analysis of fractured surfaces, will allow us to establish a correlation between the results obtained through differential scanning calorimetry and the nature of the interface.

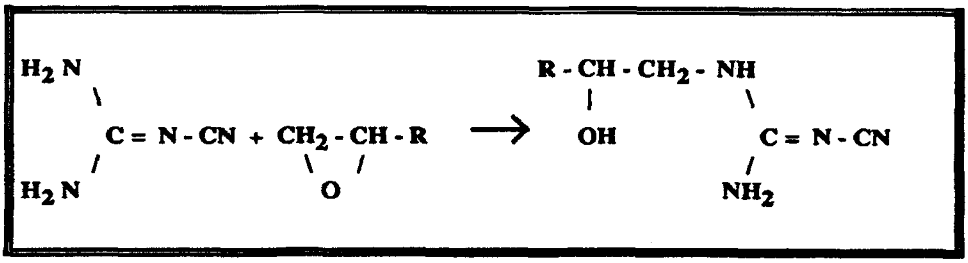
CROSSLINKING OF EPOXY RESINS

From a general epoxy resin structure of the following type:



$$\underset{\backslash\ /\atop O}{CH_2-CH}-CH_2-[-O-\Phi-\overset{CH_3\atop |}{\underset{|\atop CH_3}{C}}-\Phi-CH_2-\underset{|\atop OH}{CH}-CH_2-]_n-O-\Phi-\overset{CH_3\atop |}{\underset{|\atop CH_3}{C}}-\Phi-CH_2-\underset{\backslash\ /\atop O}{CH-CH_2}$$

and a diamine curing agent, such as dicyandiamide (dicy), we can obtain the following initial reaction:



$$\begin{matrix} H_2N & & \\ & \backslash & \\ & & C=N-CN \\ & / & \\ H_2N & & \end{matrix} + \underset{\backslash\ /\atop O}{CH_2-CH}-R \longrightarrow \begin{matrix} R-\underset{|\atop OH}{CH}-CH_2-NH & & \\ & \backslash & \\ & & C=N-CN \\ & / & \\ & NH_2 & \end{matrix}$$

The complexity of the crosslinking process with hardeners was highlighted by several authors [4–7]. The presence of accelerators and the diameter of their particles, for instance, considerably modifies the curing exotherm.

The chemical reaction starts off slowly at first, then speeds up, due to the catalytic action of the hydroxyls formed, by releasing a measure of heat proportional to the degree of crosslinking reached. Differential Scanning Calorimetry (DSC) was thus chosen to study the crosslinking of the adhesive under various conditions to determine reaction temperatures and activation energies.

BASIC MATERIALS AND DESIGNATIONS

Following tests, a single component epoxy adhesive was chosen in view of its ability to adhere to a metallic support. In order to study the effect of different metallic surfaces on adhesive crosslinking, we worked on a range of plated steel supports commonly used in industry (Cockerill et Sambre Company, Belgium) and referenced as shown in Table I.

Three types of measurements were carried out to highlight the catalytic role played by surface elements on the crosslinking of the adhesive:

a) Our study allowed for a thermodynamic follow up of crosslinking to be carried out by DSC, for the diamine hardener/epoxy resin system (ref. NA 84 CECA Company), in contact with the above mentioned metallic substrates.

b) The shearing test method, with a single coating, was chosen to measure the adherence of the adhesive on metallic sheets according to the NFT 76-107 French Standard, equivalent to ASTM test D 1002.
Sizes parameters were chosen as follows:

—thickness of the metallic sheets : 1.6 ± 0.1 mm
—length of the overlap : 12.5 ± 0.25 mm
—width of the overlap : 25 ± 0.25 mm

Before bonding, the sheets were degreased with acetone. An original apparatus,[8] based on movable grips, was used to obtain test specimens with a constant

TABLE I
Coating Compositions

SUPPORT	Coating Composition
Aluminized	90% Al 10% Si
Aluzinc	45% Zn 55% Al
Galfan	95% Zn 5% Al
Galvanized	Zn 0.2% Al
Galvanized with normal spangle	Zn 0.2% Al Pb
Electrogalvanized	100% Zn

thickness of the joint. The adhesive in this joint is polymerized in position under induction heating. The rate of heating is adjustable, for instance, at 10°C/min to 70°C/min.

The resistance of the bonded joint to shearing was determined by tensile loading at a rate of 1.3 mm/min, until rupture of the joint. The linkage is determined by the stress and the type of rupture (cohesive or adhesive).

c) The pattern of rupture after joint failure was studied under a scanning electron microscope in order to observe the distribution of the adhesive on the selected platings.

REACTION MODELS

The rate of the crosslinking reaction, at a programmed DSC heating rate, corresponds to the ratio of peak exotherm area at time, t, to total peak area, assuming, by way of hypothesis, that the molar reaction enthalpy of epoxy functions in the various possible transformation mechanisms are close to one another.

We have chosen to use the simple kinetic model of the Arrhenius type as checked by Ozawa[9,10]:

$$\frac{da}{dt} = A\exp\frac{(-E)}{(RT)}f(a)$$

where

R is the perfect gas constant
T is the temperature (°K)
$f(a)$ is a function of the extent of the reaction
A is the Arrhenius constant
E is the energy of activation

What has also been demonstrated is that for a given extent of reaction, the following relation [11]:

$$\ln\frac{(T2)}{(V)} = \frac{E}{RT} + Cst$$

allows the activation energy to be determined from a series of thermograms carried out at different heating rates, V, where Cst is a constant.

RESULTS

DSC Results

DSC analysis with a Mettler TA 4000 System has enabled the curing exotherm of the exopy adhesive alone, taken as reference, and the epoxy adhesive in contact with the supports, to be determined. The study was done with closed pans, under nitrogen atmosphere at 4 heating rates from 10°C/min to 70°C/min, between 50 and

250°C. The peak integration was obtained automatically by computer and the value is compared with that of an Indium standard chosen as a reference. We endeavoured to work with adhesive samples of similar masses ($m < 10$ mg) evenly spread over the base surface to reduce the possible mass and surface effects ($\varnothing = 5$mm).

Table II shows the results. In a general way, it may be observed that the curing exotherm remains more or less stable depending on the rate for lower heating rates up to 50°C/min, and falls when the rate rises.

The crosslinking peak exotherm temperatures in Table II are spread between 138 and 188°C,rising with heating rate.

The action of the base metallic surface is not very visible; the values are more or less equivalent for all the samples under the same technical conditions. However, peak temperatures for the base-free adhesive alone are lower than for the others.

As regards activation energy, *E* (J/mole), Table III, what was measured in the case of the adhesive alone is much higher than what was measured in other cases.

Low activation energies are noted in the case of aluminized, aluzinc and galfan, substrates containing aluminum, and also in the presence of lead (galvanized with lead).

Microscopy

Test pieces plated with each of the chosen coatings were spread with adhesive and polymerized at a heating rate of 10°C/min. After traction, breaking loads were

TABLE II
DSC results

Heating rate	10°C/min		30°C/min		50°C min		70°C/min	
Enthalpy Coating T° Peak	ΔHJ/g	peak T°C	ΔHJ/g	peak T°C	ΔHJ/g	peak T°C	ΔHJ/g	peak T°C
Adhesive	310	138	310	157	309	167		
Aluminized	312	142	310	165	310	178	230	188
Aluzinc	313	138	315	161	312	173	291	181
Galfan	314	138	320	161	310	172	299	184
Galvanized	318	142	300	164	293	175	270	184
Galvanized with Pb	305	140	309	164	282	177	180	184
Electrogalvanized	302	140	292	163	298	174	279	185

TABLE III
Activation energy (J/mole)

Adhesive	76400
Aluminized	63100
Aluzinc	63500
Galfan	63500
Galvanized	67500
Galvanized with Pb	59900
Electrogalvanized	67020

recorded and the rupture patterns were analysed by scanning electron microscopy.

Comparing breaking loads is only valid if all the basic steels have the same thicknesses and identical elasticity limits; this condition not being met in our basic steels, we shall not quote traction-shearing figures here.

For the rupture patterns analysed, the dark parts represent the adhesive and the light areas the metallic coating. Analysing both patterns in every bonding highlighted the fact that part of the coating, apparent on the micrograph, was not covered by the adhesive before the traction test. Thus, we have a picture of the way in which the adhesive has crosslinked on the coating. The following tendencies were observed:

—for heating rates of 10°C/min :

- * coatings containing little or no aluminium in the zinc bath (electro-galvanized and galvanized) present rupture patterns with a high percentage of coatings not covered by the adhesive (Fig. 1-a)
- * coatings containing 5% aluminium and more are much better covered (Figure 1-b)
- * galvanised coatings containing lead present very few places with attached adhesive (Fig. 1-c).

—for heating rates of 70°C/min:

for all coatings the quantity of polymerised adhesive is smaller by far at 70°C/min than at 10°C/min (Fig. 2).

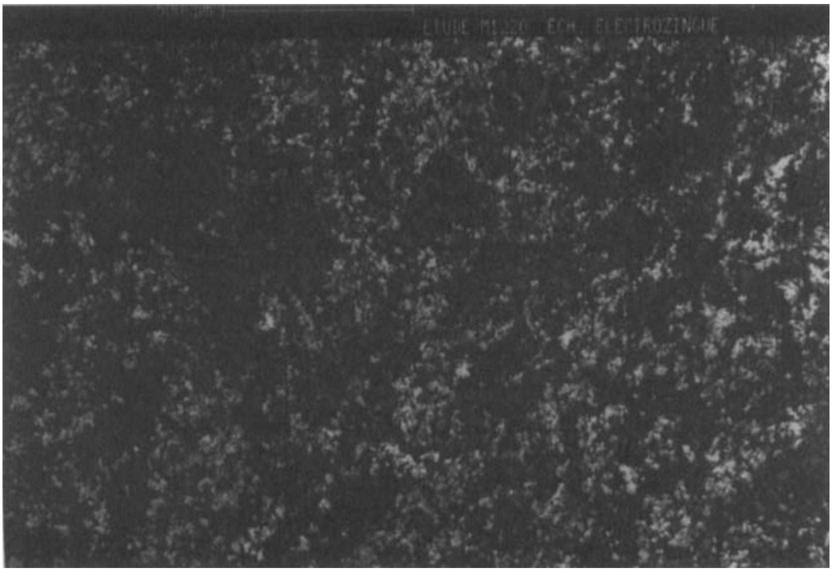


FIGURE 1a Scanning electron micrograph of cohesive rupture on electrogalvanized substrate.

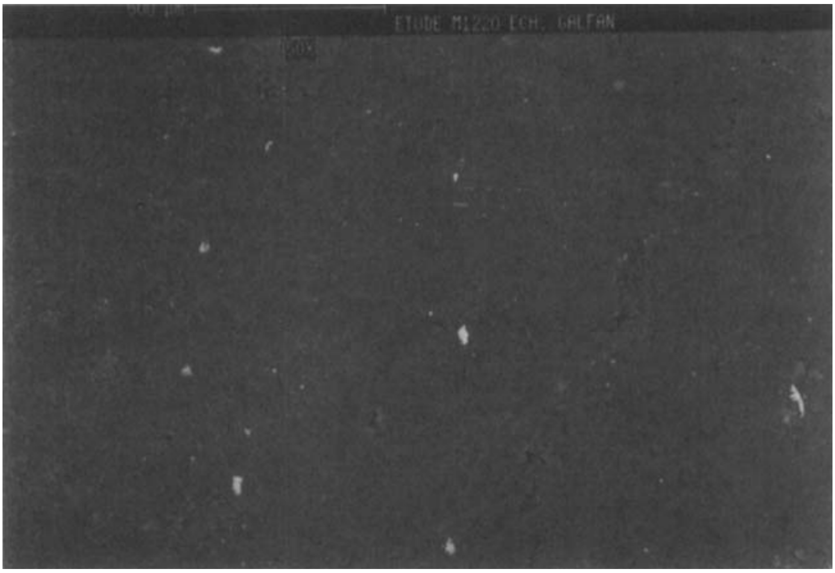


FIGURE 1b Scanning electron micrograph of cohesive rupture on galfan substrate.

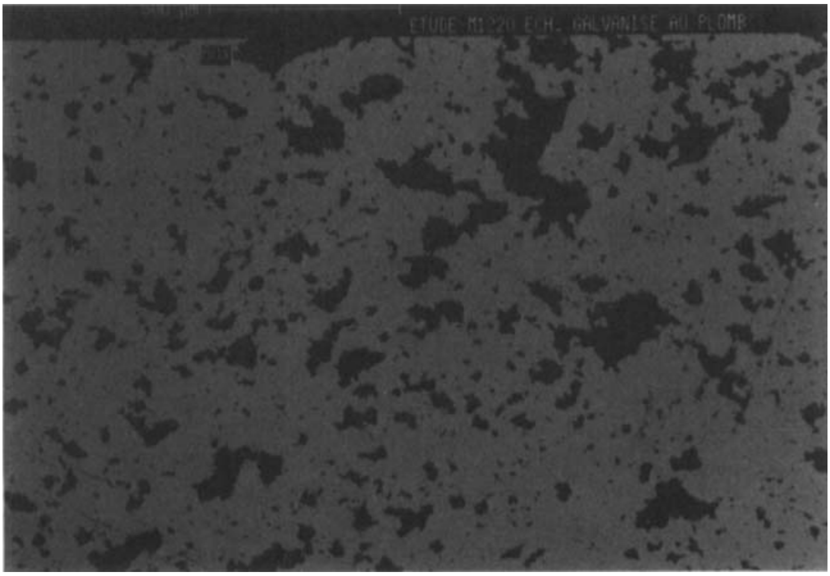


FIGURE 1c Scanning electron micrograph of cohesive rupture on substrate galvanized with lead.

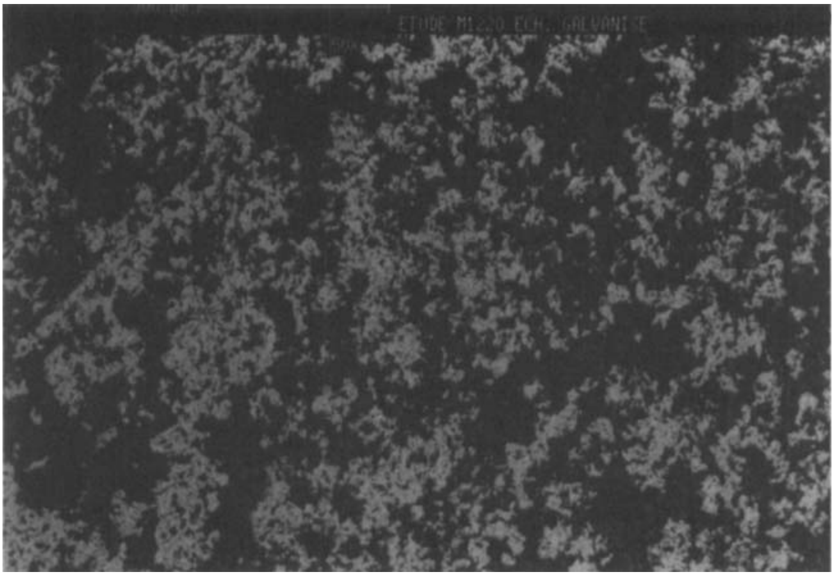


FIGURE 2a Scanning electron micrograph of cohesive rupture on galvanized substrate (Heating rate 10°C/min).

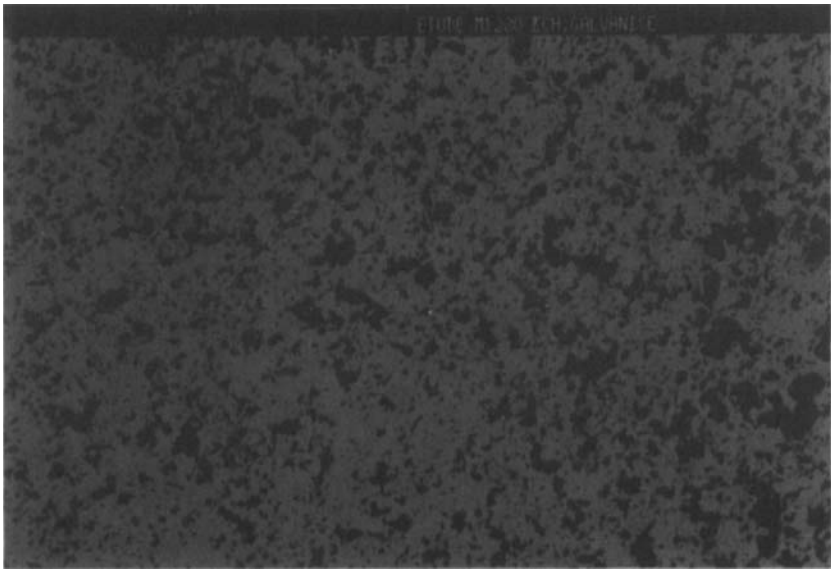


FIGURE 2b Scanning electron micrograph of cohesive rupture on galvanized substrate (Heating rate 70°C/min).

Mechanical Tests

Two substrates with identical elasticity limits and thicknesses were chosen to compare the adherence of the adhesive following two polymerization rates. The results are contained in Table IV.

DISCUSSION

The results of the calorimetric analysis demonstrate that at a relatively low heating rate, the curing exotherm varies little, a fact which can be explained by the progressive nature of curing under these conditions, the molecules organizing themselves in a homogeneous fashion.

For a higher heating rate (70°C/min), the curing exotherm is lower. One may assume that because of the crosslinking starting speed, molecular obstruction occurs and the energy released is on the whole less. This decrease in curing exotherm is observed on all supports. Furthermore, activation energies deduced from calorimetric measurements and assessed on different supports are all inferior to the activation energy of the adhesive alone.

The catalytic effect of these supports on the crosslinking reaction seems to be a natural conclusion. Supplementary tests are necessary, however, to quantify the activity of these supports.

Observations of the rupture patterns carried out by SEM are very revealing in this respect. In the presence of aluminium in the support, the rupture pattern at the level of observation is totally covered with adhesive. Aluminium hence promotes adhesive-substrate interaction, which is not the case of zinc-based supports or zinc and lead-based supports where microsopic observations have revealed pin hole porosity.

The efficiency of aluminium on bonding is confirmed by the results of mechanical tests; indeed, shear rupture stress of the joint is higher for those supports containing aluminium. Aluminium promotes interfacial wetting of the substrate by the adhesive and, hence, also substrate-adhesive interaction.

We have also demonstrated that crosslinking rate had a marked effect on the coating of the support by the adhesive. At high heating rates whatever the nature of the support, the extent of coating is by far lower. Adhesive-substrate interactions under these conditions are hampered by the molecular heterogeneity of the crosslinking reaction due to too-rapid blocking of the epoxy molecules, preventing the mobility necessary for bonding to the substrate.

TABLE IV
Rupture of the samples

	Heating rate	
Sample	10°C/min	70°C/min
Galvanized	12 MPa cohesive rupture	8 MPa cohesive rupture
Aluminized	14 MPa cohesive rupture	11 MPa cohesive rupture

CONCLUSION

By determining the energy of activation, we have been able to highlight the catalytic effect of the supports on the crosslinking of the epoxy-diamine adhesive under consideration. We have demonstrated the greater efficiency of aluminium on adhesive-substrate interactions. Interaction seems possible between the hydroxyl group of the epoxy and aluminium but has not yet been confirmed by the study.

References

1. W. X. Zukas, S. E. Wentworth, M. S. Jennet, *Proceedings, The Adhesion Society* (*USA*), 16th Annual Meeting, pp.187–190 (1993).
2. J. Galy, A. Sabra, J. P. Pascault, *Polym. Eng. Sci.*, **26**, 1514 (1986).
3. C. Berthonneau, G. Villoutreix, *Matériaux et Techniques*, (France), **67**/(6), 210–212 (1979).
4. T. F. Saunders, M. F. Levy, J. F. Serino, *J.Polym. Sci., Polym. Chem. Ed.*, **5**, 1609 (1967).
5. M. Fedtke, K. Bierögel, *Plaste und Kautschuk*, **28**, 253 (1981).
6. S. A. Zahir, *Adv. Org. Coat. Sci. Technol. Ser.*, **4**, 83 (1982).
7. M. D. Gilbert, N. S. Schneider,W. X. Zukas, W. J. Mcknight, *Proc. ACSDiv. Polym. Mat. Sci. Eng.*, **56**, 351 (1987).
8. C. Bretton-Pieters, *Proceedings XIXe AFTPV Congress* (*France*), *Eurocoat 1991*, pp 29–40.
9. T. Ozawa, *Thermal Anal.*, **2**, 301 (1970).
10. T. Ozawa, *Bull. Chem. Soc. Japan*, **38** (1965).
11. L. Reich, *J. Polym. Sci., Part B*, **2**, 621 (1964).