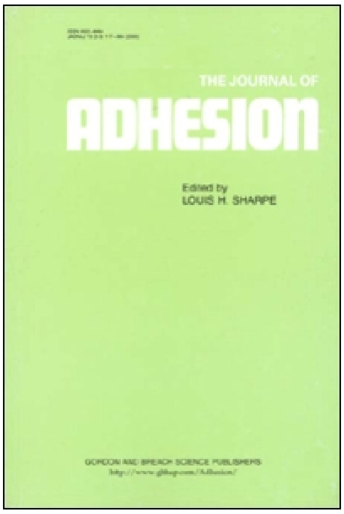

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Oil-covered Substrates: A Model Study of the Evolution in the Interphase During Cure of an Epoxy Adhesive

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To cite this Article Greiveldinger, Marc , Shanahan, Martin E. R. , Jacquet, Denis and Verchère, Didier(2000) 'Oil-covered Substrates: A Model Study of the Evolution in the Interphase During Cure of an Epoxy Adhesive', The Journal of Adhesion, 73: 2, 179 — 195

To link to this Article: DOI: 10.1080/00218460008029305

URL: http://dx.doi.org/10.1080/00218460008029305

J. Adhesion, 2000, Vol. 73, pp. 179–195
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Oil-covered Substrates: A Model Study of the Evolution in the Interphase During Cure of an Epoxy Adhesive*

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(Received 15 October 1999; In final form 27 March 2000)

The car industry uses adhesive bonding for bodywork assembly and, in many cases, application of adhesives is effected without prior degreasing of the steel sheet. As a consequence, oil originally at the steel/adhesive interface may potentially modify both initial and long-term behaviour. Direct study of the evolution *in situ* of such steel/oil/adhesive systems would seem exceedingly difficult, if not impossible, with techniques presently available. Notwithstanding, we have attempted to model the situation, albeit by replacing the steel substrate by a material more conducive to a systematic and intimate study of the zone of contact, with an aim to follow any displacement of the oil in the interphase solid/oil/adhesive during the formation of the assemblage and its influence on behaviour. We have used Infra-Red spectroscopy and, in particular, developed a heated ATR cell. The technique allows evolution of chemical composition to be followed as a function of time during the curing process of the adhesive (appearance or disappearance of chemical species, crosslinking, *etc*...) and over a depth of several microns. As a consequence, a better understanding of behaviour and localisation of oil within a (model) structural joint has been obtained and is discussed. Our results point out the importance of chronology in the phenomena of oil-elimination and curing within the interphase (this chronology has a great influence on mechanical properties of real structural joints). The influence of oil formulation has been considered, as have the cure conditions. Finally, the potential perturbations of oil on the kinetics and mechanisms of interphase formation have been estimated and are discussed.

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*One of a Collection of papers honoring F. James Boerio, the recipient in February 1999 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M. Presented at Adhesion '99, 7th International Conference on Adhesion and Adhesives*, Churchill College, Cambridge University, Cambridge, UK, 15–17 September, 1999.

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Keywords: ATR; Bonding; Epoxy adhesive; Interphase; Oil-accommodating adhesive

INTRODUCTION

A commonly-used method of assembly in the car industry is that of structural bonding, particularly with epoxy resins. Generally, bonding is effected without prior degreasing of steel sheet (the sheet being supplied by the steel producer with a few gm^{-2} of oil on the surface). As a consequence, oil initially at the interface between steel sheet and adhesive may affect the quality of the final structure, both in its initial state and after ageing.

Most work concerning the bonding of oiled steel has aimed at understanding the effects of the lubricant on mechanical performance; only a few consider how the epoxy adhesive may accommodate the oil in order to produce strong interfacial bonds with the substrate [1 – 7]. The problem stems mainly from the difficulties encountered when studying the various phenomena occurring near the interphase metal/oil/polymer.

Debski *et al.* [1, 2] proposed two mechanisms leading to oil elimination, *viz.*, thermodynamic displacement of the oil by the resin and absorption following diffusion. Hong and Shu [7] found that the absorption mechanism was dominant in the case of thin films of mineral oil. Their work suggested that the efficiency of oil displacement by the adhesive depended on the nature of the substrate. According to Ogawa *et al.* [8], diffusion occurs during the first few seconds of the (isothermal) heating cycle. They deduced that diffusion of the oil preceded crosslinking and, thus, metal/resin adhesion was unaffected by the (initial) presence of oil. This is in agreement with ATR work conducted by Hong and Shu [6, 7].

Notwithstanding, the diffusion mechanism is not alone. The switch from diffusion to thermodynamic displacement would seem to depend on the substrate in question [6, 7, 9], the degree of polarity and the thickness of the film [2, 7]. Clearly the composition of the adhesive also plays a role. Hong and Boerio [6, 9, 10] studied the interplay between two constituents of epoxy resins and oiled steel. At ambient temperature, the presence of amidoamine, a crosslinking agent, influenced oil displacement on the metallic surface.

Overall, most authors consider oil absorption as the predominant mechanism of oil elimination at the substrate/resin interface (interphase) during bonding. However, the depth of oil diffusion into the adhesive varies between < 0.3 and 150 µm, depending on the author. Such dispersion demonstrates the insufficiency of present knowledge concerning the effects of oil composition and crosslinking conditions on the evolution of the metal/polymer interphase.

With an aim to follow the influence and whereabouts of the oil in the interphase during the bonding process, at least in a model system, we have developed a heated attenuated total reflection (ATR) cell to be used in conjunction with Fourier transform infra-red spectroscopy (FTIR). This innovation presents the double benefit of being able to model an interphase substrate/oil/adhesive (where, by necessity, the metal is replaced by an ATR crystal) and allowing analytical probing of the interphase over a depth of several microns. Clearly, we cannot be certain that behaviour will be identical to that occurring in the presence of a real, practical, steel substrate, but the results obtained with our model system give considerable insight as to the type of evolution to be expected.

EXPERIMENTAL

Materials

This study was undertaken using the following materials:

- an industrial oil,
- an epoxy resin,
- an attenuated total reflection (ATR) crystal for use in (Fourier Transform) Infra Red spectroscopy (FTIR).

The oil chosen was an industrial oil used for the protection of steel and manufactured by Quaker. This liquid is composed of ca. 75% mineral oil and 12% esters, the remainder being essentially sulfonates and anti-oxidants. It is commonly used on galvanised and other zinc-covered steel sheets destined for the automotive industry, for its corrosion protection and lubricant (during stamping) properties.

The epoxy resin was a model material, nevertheless resembling the basis of many commercial products. It consisted of diglycidyl ether of bisphenol A (DGEBA or BADGE) of molecular weight 380 g mole^{-1} (Epikote 828, Shell) with dicyandiamide (DDA) as the curing agent, imidazole as a catalyst (Epikure P1, Shell) and fumed silica as a thixotropic agent (Aerosil R805, Degussa), in relative proportions by mass of 100/8.46/0.54/5.

The ATR crystal served as the substrate, replacing the steel normally present and, thus, perturbing the system to some extent, but allowing close scrutiny of chemical processes occurring near the interface/interphase during the heating cycle. Given the frequency range to be studied (4000 cm^{-1} – 650 cm^{-1}) and the temperature range of 20 – 180°C, we chose a ZnSe crystal of useful frequency range 5000 cm^{-1} – 600 cm^{-1}, with a variation of refractive index of 0.002 between 0 and 200°C.

Heated ATR Cell

Figure 1 represents the heated ATR cell developed. Analyses were effected with a resolution of 4 cm^{-1} on a Nicolet 740 FTIR spectrometer equiped with a Mercury – Cadmium – Tellurium (MCT) detector. The crosslinking conditions of the adhesive corresponded to those used industrially: temperature increase at 10°C/minute from

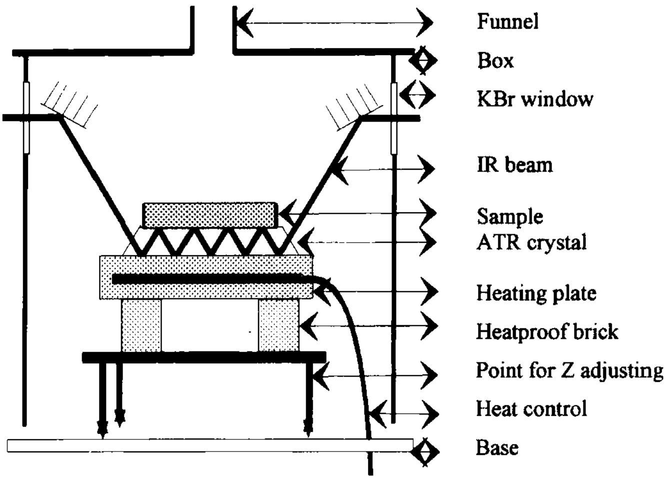

FIGURE 1 Heated ATR cell: essential components.

ambient temperature to 180°C followed by 20 minutes at 180°C. The set-up shown in Figure 1 allows us to analyse chemical components present or appearing at or near the crystal surface over a thickness of several microns.

The following protocol was developed. With the exception of a central window of 2.5 cm^2 area, the ZnSe crystal was metallised with a gold layer. This operation assured good quality infra red spectra (unsaturated bands) and good experimental reproducibility (identical surfaces analysed). The experimental procedure was as follows. First the background IR spectrum was obtained at ambient temperature with the bare crystal. An oil film of ca. 10 gm^{-2} was then deposited on the crystal in *n*-heptane as a solvent (except, of course, in cases where a direct crystal/adhesive contact was required). The oil film was next covered with a layer of adhesive of thickness ca. 1mm. The system being set up, the heating cycle was commenced with a heating rate of 10°C min^{-1} from ambient to 180°C with a plateau of 20 minutes following at the latter temperature. Simultaneously, the acquisition of FTIR spectra was started with a spectrum (16 scans) taken every 9 seconds.

Treatment of Data

The various phenomena occurring in the interphase were followed by tracing various peak heights, or areas, as a function of time during the heating (cure) cycle or, alternatively, temperature directly. Nevertheless, preliminary results showed that the intensity of IR signals could depend on temperature (evaporation is negligible and cannot account for this effect). This temperature dependence of IR bands complicated interpretation considerably! As a consequence, a procedure was developed to correct for this effect. The technique relies on taking spectra from an adhesive layer *already* crosslinked. Figure 2 shows the evolution of the heights of bands at 1510 cm^{-1} and 830 cm^{-1} for this pre-crosslinked layer in the temperature range of 20 to 180°C. The signal/temperature dependence is acceptably linear and practically independent of the frequency (the two slopes are very similar). Thus, we may write an expression for signal evolution:

$$I_\nu(T) = f_\nu(T) \qquad (1)$$

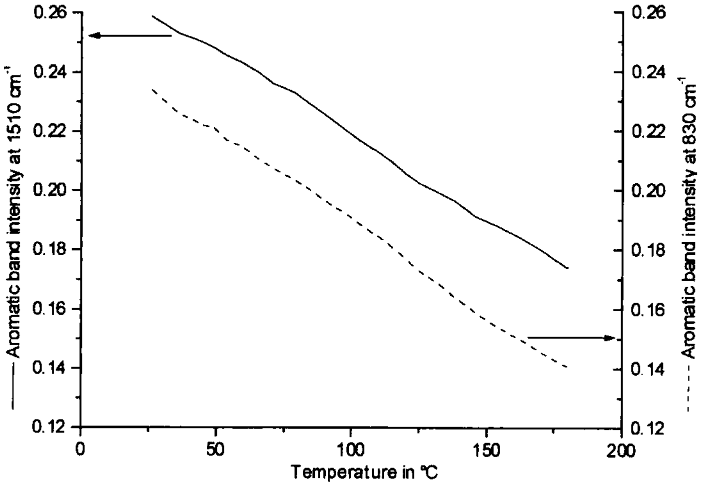

FIGURE 2 Influence of temperature on the evolution of IR band intensity for the system ATR crystal/crosslinked adhesive.

where $I_\nu(T)$ is the intensity of the band of frequency ν at temperature T and $f_\nu(T)$ is the function of dependence of signal on temperature.

For experiments in which crosslinking of the adhesive occurs during the heating cycle, intensity $I_\nu(T, C)$ will also depend on the concentration, C, of the chemical species in question. We shall suppose, that to a first approximation, we may write:

$$I_\nu(T, C) = f_\nu(T) \cdot g_\nu(C) \tag{2}$$

where $g_\nu(C)$ is the function describing concentration dependence of the signal alone (separation of variables). Correction of the signals then consists of dividing experimental values of $I_\nu(T, C)$ by the reference value of the curve of $I_n(T)$ obtained at a frequency of 1510 cm^{-1} with the pre-crosslinked adhesive. Given the weak frequency dependence of the function $f_\nu(T)$ (see Fig. 2), we approximate this ratio to an expression independent of temperature:

$$\frac{I_\nu(T, C)}{I_n(T)} \approx g_\nu(C) \tag{3}$$

Within the limits of the above approximations, it is then possible to follow quantitatively the evolution of IR bands during the heating cycle and to eliminate temperature effects on the signal directly.

Systems Studied

The heated ATR cell was used for comparing and following the evolution of the interphases during the heating cycle of the systems given below:

- system 1: crystal/adhesive,
- system 2: crystal/oil/adhesive,
- system 3: crystal/polar component of the oil (esters)/adhesive.

For both systems 2 and 3, the contaminant (oil) film represented ca. $1-2\,\text{gm}^{-2}$.

RESULTS

The results presented here correspond to the behaviour of the oil and adhesive during the heating cycle. Figure 3 shows a typical example of the evolution of spectra during heating. The spectrum at 22°C is very similar to that of the oil; indeed, the FTIR analysis is of a layer consisting almost entirely of oil at this stage. After the entire heating cycle, the spectrum obtained is identical to that of the crosslinked adhesive as found with system 1. Between these two extremes, the spectral bands evolve. Certain cases of band evolution, representative of the appearance, disappearance or consumption of various compounds during crosslinking, have been chosen as criteria for following interphase evolution during heating. These are given in Table I. It is perhaps worth noting that the hydroxyl signals were not studied in detail due to their being rather wide, and ATR is perhaps not the best technique for their study. In passing, nitrile band(s), near $2200\,\text{cm}^{-1}$, show(s) interesting effects during cure. Although not really understood, this is perhaps related to the presence of different mesomers of DDA.

In order to follow the behaviour of the oil and the adhesive in the interphase, the criteria of presence of oil and adhesive in Table I were applied to the series of spectra obtained during the heating cycle of systems 2 and 3. (It should be noted that the signal from the aromatic cycle in system 1 remains independent of state of crosslinking. The mechanisms of crosslinking of DGEBA/DDA systems have, however, been the object of several studies [11 – 15] and will not be treated in the present context.)

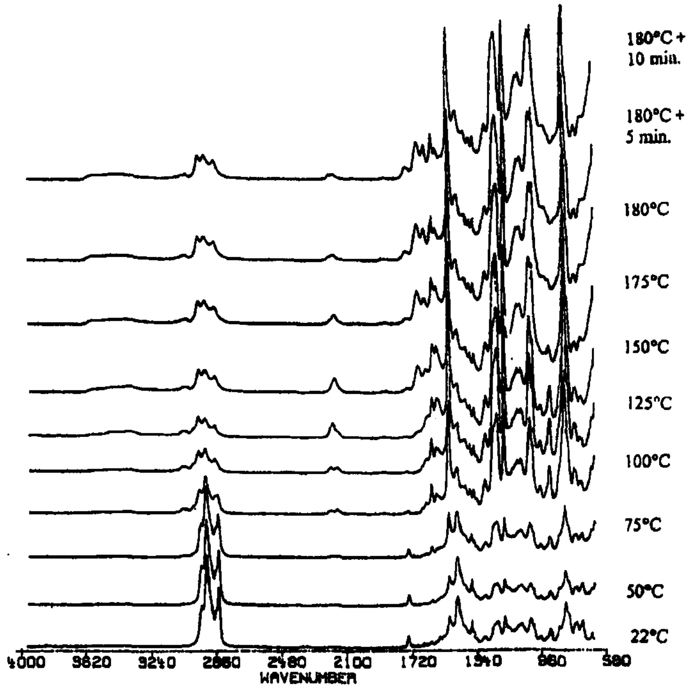

FIGURE 3 Spectra of the ATR crystal/oil/adhesive interphase as a function of temperature during the curing process of the adhesive.

TABLE I Use of the evolution of certain absorbance bands as criteria for following phenomena occurring at the interphase during crosslinking

Functional group	*Band and criterion considered*	*Phenomenon represented*	*Expected evolution*
CH	2852 cm^{-1}–2870 cm^{-1} relative height (base line 2760 cm^{-1})	Diffusion of oil	Disappearance
Aromatic cycle	1504 cm^{-1}–1538 cm^{-1} height	Presence of adhesive	Appearance
Oxirane	926 cm^{-1}–888 cm^{-1} Integration	1st stage of crosslinking	Consumption
Carbonyls (esters)	1781 cm^{-1}–1727 cm^{-1} Integration	Last stage of crosslinking	Appearance

Figure 4 represents the relative percentage present in the interphase, as a function of time of heating, of both the oil (system 2) and the polar component of the oil (system 3).

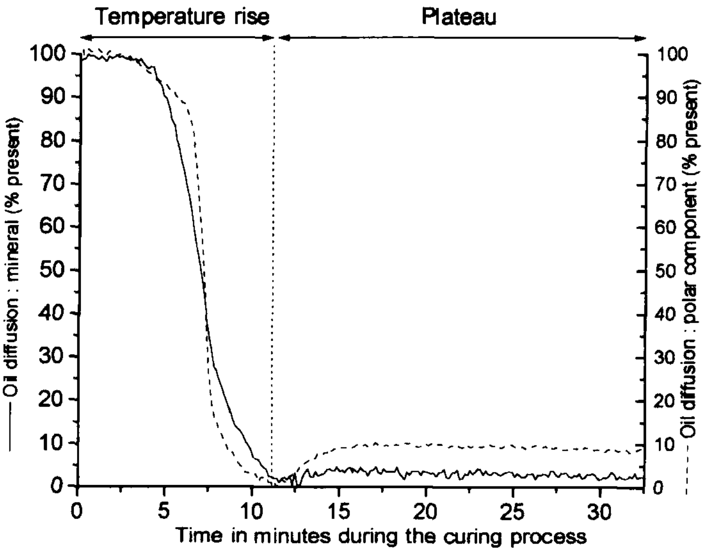

FIGURE 4 Evolution of relative height of CH band during heating cycle. Comparison of the diffusion of oil, essentially mineral (—) and its polar component (- - - -).

The evolution of the interphase of system 2 shows very clearly that the surface oil disappears rapidly during the first 11 minutes of the heating cycle, when the temperature is still increasing. It is particularly marked between the 3rd (60°C) and 9th (130°C) minutes. This disappearance may be attributed to diffusion of the oil towards the bulk adhesive (the crystal is, of course, impervious and potential escape from the edges of the observation window will be exceedingly limited). Comparison of the diffusion of the oil (mainly mineral), system 2, and of the polar component of the oil, system 3, shows that the polar part would seem to start to diffuse significantly rather later than the complete oil but, once initiated, the diffusion rate is higher (different gradients). In addition, the percentages of oil remaining in the interphase after diffusion (15th to 33rd minute in Fig. 4) show that a fraction of the polar component (ca. 10%) stays in the interphase analysed. Experimental reproducibility has been checked and, thus, differences in the curves of Figure 4 are significant.

An interesting feature of Figure 4 is that after a minimum of oil presence in the interphase towards 12 minutes after the commencement of the heating cycle, there is a slight increase. It is suggested that this effect is related to the onset of crosslinking of the adhesive, as described below. Since epoxy resins often shrink slightly on crosslinking, it is quite plausible that this effect is analogous to that of compressing a sponge saturated with water: absorbed oil will tend to be expelled to some extent on volume reduction.

Figure 5 compares the relative evolutions of intensities corresponding to oil and adhesive, complementing Figure 4, and shows with no doubt that in the first few microns of the interphase (near the crystal), the oil disappears rapidly: after ca. 11 minutes, only a small amount of oil remains and the majority of the band intensity corresponds to the presence of adhesive. What we observe is, in fact, mutual interdiffusion of oil within the adhesive and adhesive within the oil. After the twelfth minute, oil has virtually totally disappeared from the interphase. As a consequence, good contact between the substrate and the adhesive is established.

With an aim to determine the influence of oil on crosslinking mechanisms, the formation of the interphase crystal/adhesive was compared in the presence or absence of oil (systems 2 and 1, respectively). Figures 6 and 7 represent the evolution criteria of the initial

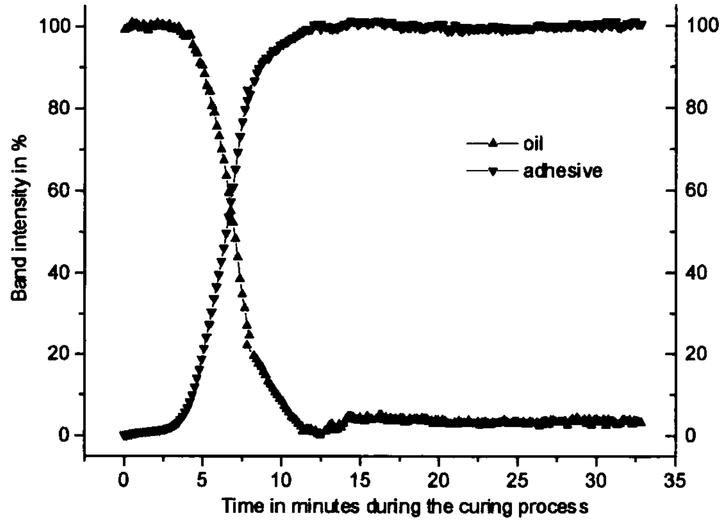

FIGURE 5 Oil and adhesive diffusion as obtained by the heated ATR cell as a function of time during curing cycle.

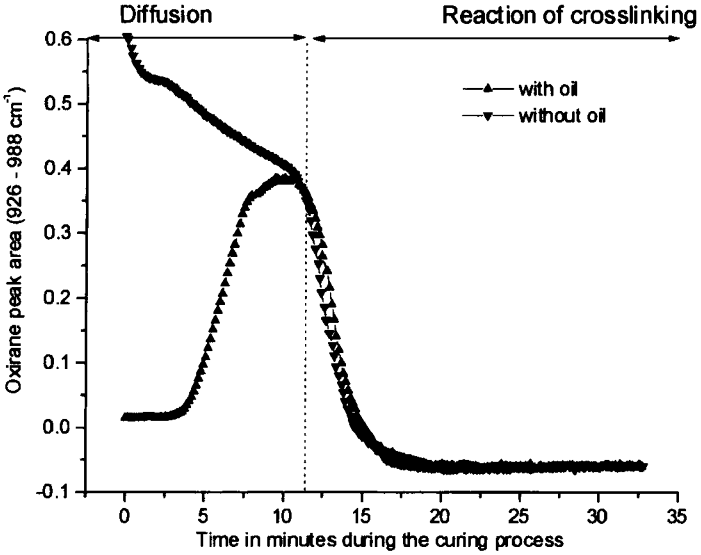

FIGURE 6 Evolution of crosslinking as a function of time during curing cycle. First step: opening of oxirane cycle.

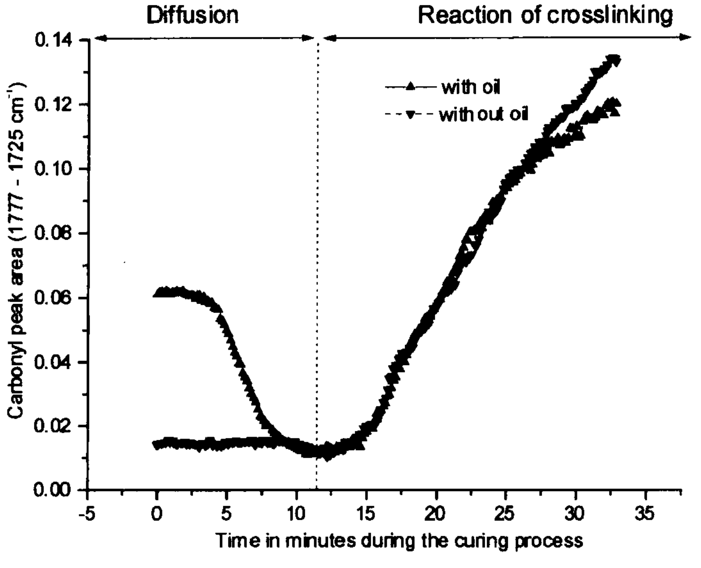

FIGURE 7 As for Figure 6, but: Final step: ester formation.

and final stages of crosslinking (*cf.* Tab. I) for the two systems. The differences between systems 1 and 2 observed in the first twelve minutes are independent of crosslinking. They are uniquely due to the diffusion of oil occurring in system 2 during this stage. In Figure 6, the increase of the oxirane signal can be explained by a significant influx of adhesive to the interphase region, induced by departure of the oil. As for Figure 7, the decrease of the ester band corresponds to the diffusion of esters in the oil towards the bulk resin. Thus, neglecting the first twelve minutes, comparison of the interphases with each crosslinking criterion shows no significant difference between systems 1 and 2: gradients are similar and curves virtually superimposable.

Figure 8 compares oil diffusion and crosslinking phenomena on a temperature scale. For this, we have used the criteria of Table I for oil diffusion and the exothermic peak of reaction obtained by DSC (at 10°C/minute) for crosslinking of the adhesive. Since the latter phenomenon occurs only when diffusion of the oil is complete, we deduce that the phenomena of oil diffusion and crosslinking of the adhesive are consecutive, rather than concomitant, in the system studied.

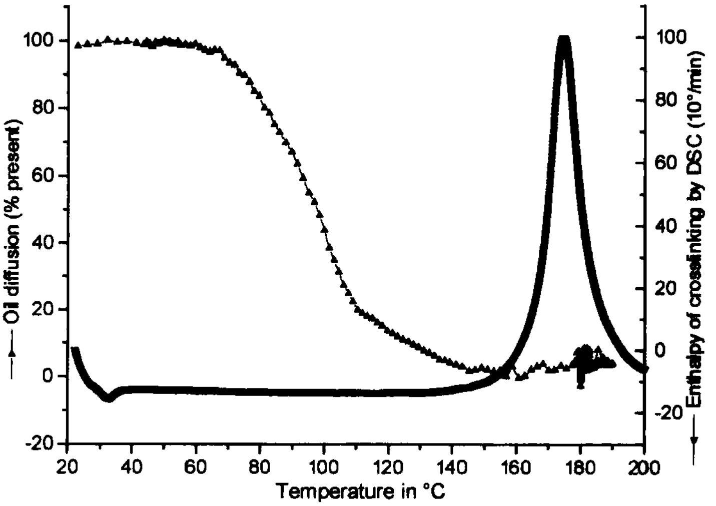

FIGURE 8 Chronology of phenomena occurring in the interphase during the cure cycle. Oil diffusion (obtained by ATR) and crosslinking (estimated by DSC).

DISCUSSION

Our results given in Figure 5 confirm, admittedly for a model system, the postulates of many authors [6–10], *viz.*, that the disappearance of oil at the surface is due to diffusion into the adhesive bulk. By contrast, the second mechanism suggested by Debski *et al.* [1, 2] was not observed in the present study. This work has shown conclusively that the majority of the oil (both mineral and polar components) diffuses into the adhesive (at least in the case of the present materials used). With the present materials and heating cycle, this diffusion occurs within ca. 11 minutes after heating from ambient (principally between ca. 60 and 140°C during the temperature increase). Such rapidity tends to corroborate the results of Ogawa *et al.* [8]. Nevertheless, these authors proposed a very rapid increase in diffusion with temperature, somewhat in contradiction with our experimental results. In Figure 9, we present the evolution of the relative quantity of oil at the interphase (100% representing the onset of the heating cycle) with temperature, together with the viscosity of the adhesive, also as a function of temperature. The *rate* of elimination of oil is very low until ca. 70°C

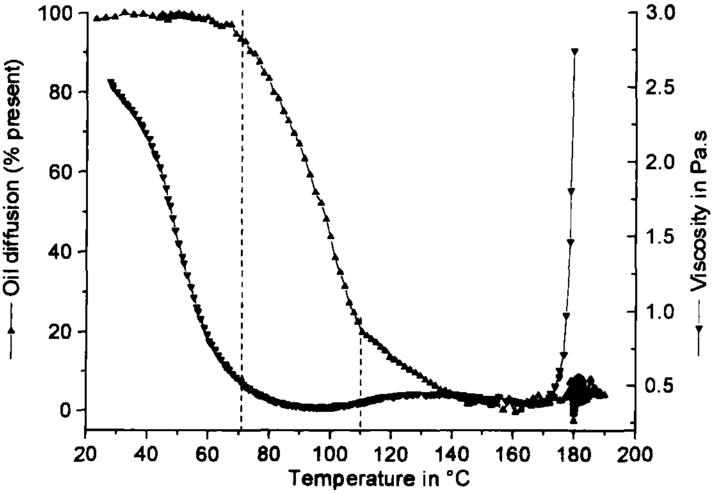

FIGURE 9 Comparison between the relative quantity of oil at the interphase (▲) and the viscosity of the adhesive (▼) as a function of temperature during the curing cycle of the resin.

when it increases quite considerably, remaining high until ca. 110°C (when ca. 80% of the oil has diffused). Comparing this with the curve for viscosity of the adhesive, we note that the onset of a significant oil elimination rate coincides closely with the minimum in adhesive viscosity (as measured using viscoelasticimetry techniques). Thus, the proposal by Ogawa *et al.* [8] that temperature is the "motor" for oil diffusion is here supplanted by the concept that adhesive viscosity is effectively the brake, holding back significant oil diffusion until the resin is sufficiently fluid.

Given the speed of disappearance of the oil and the small quantity of residual oil in the interphase, our results suggest relatively long range diffusion, in agreement with Ogawa *et al.* [8] and with Hong and Boerio [10].

The evolution of crosslinking criteria after the eleventh minute (*cf.* Figs. 6 and 7) when oil has, in the main, already diffused, is very similar for the two systems, with and without initial surface oil, at least within the limits of resolution of our ATR technique. We, thus, conclude that the presence of oil modifies neither the kinetics nor the mechanisms of crosslinking within the interphase. Otherwise, the criteria for crosslinking with and without oil would have different gradients and/or other bands would appear. Alternatively, the curves would show a shift.

Using similar reasoning, it was checked that the polar component of the oil (system 3) does not influence the kinetics or mechanisms of reaction.

In addition, the fact that each criterion of Figures 6 and 7 presents a value independent of the presence or absence of oil (towards the eleventh minute), tends to confirm virtually total diffusion of oil before the onset of crosslinking. A negligible quantity of oil remains compared with the initial surface deposit. Foister *et al.* [16] and Ogawa and Hongo [17] observed negligible differences in adhesion between epoxy resins and clean or oiled steel (using both peel and lap shear tests). There seems, therefore, to be a good correlation between our results on kinetics and mechanisms occurring at the surface during crosslinking and mechanical adhesion as reported in the literature.

The competition between oil diffusion and crosslinking phenomena is fundamental for the mechanical resistance of bonded structures. With the assumption of simultaneous diffusion and crosslinking, the risk of trapping significant quantities of oil at the interface, thus reducing bond quality, would be non-negligible. However, if the phenomena are consecutive, as in our case, this problem is largely avoided. Bearing this in mind, the comparison between the phenomena of oil diffusion at the interphase (by heated ATR) and of adhesive crosslinking (by heated ATR and DSC) would seem to be a useful method for studying the propensity of a given adhesive for "digesting" a given surface lubricant during a given heating cycle. This test represents a necessary condition, but not a sufficient condition, for predicting the strength of such bonds made in the presence of oil, since no allowance is here made for the influence of the oil on the mechanical behaviour of the interphase (nor the influence of fillers, if present). It could, thus, be considered as an initial technique for the selection of pairs of the type oil/adhesive, potentially useful for bonding on oil-contaminated metals. Subsequent checks would, nevertheless, be necessary to verify mechanical properties of the final bonds before a given system could be considered acceptable (and homologated). As a reasonably rapid test, capable of direct interpretation, this test could easily be generalised in order to take into account the behaviour of lubricants and adhesives in an interphase in a host of crosslinking conditions, as well as taking into account the potential effects of other products present, such as fillers and toughening agents.

The principal limitation of the approach described here is that an "artificial" substrate is, of necessity, used, instead of the metallic surface for which the pair oil/adhesive is intended. It is possible, even probable, that the nature of the substrate could influence the overall behaviour (topography and surface free energy effects). This problem could possibly be offset however, to some extent at least, by depositing a thin film before application of the oil (oxides of Zn, Fe, Al, *etc.*).[1] The evanescent ATR beam should be capable of probing the interphase, thus reconstituted, by crossing the metal oxide film (a few tens of nanometers thick). The use of a heated ATR cell imposes the use of a substrate corresponding to a crystal satisfying certain experimental constraints (in particular, low variation of refractive

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[1] Since writing this article, it has come to the authors' knowledge that such techniques have been applied previously, using evaporation [18].

index between ambient and maximum cure temperatures in the range of 4000 to 650 cm^{-1}).

CONCLUSIONS

In this work, we have attempted to study the various phenomena occurring in the interphase of a model bonded system: substrate/oil/adhesive. To do this, we have developed a heated ATR cell to follow the evolution of the interphase ATR crystal/industrial oil/model epoxy adhesive during the curing cycle of the adhesive.

With this technique, it has proved possible to show that the oil, initially present between substrate and adhesive, diffuses rapidly towards the bulk resin during the phase of temperature increase (principally, between ca. 60 and 140°C), the brake to diffusion being adhesive viscosity in the earlier stages. The majority of the oil (both mineral and polar components) diffuses over several hundred microns (*i.e.*, over the typical thickness of an adhesive joint), yet a small residue remains.

Continuous monitoring of the interphase during the cure cycle has shown that the phenomenon of crosslinking of the adhesive commences (significantly) when oil diffusion is virtually complete. With the model system studied, at least, the presence of oil did not influence the kinetics or the mechanisms of adhesive cure.

Finally, given the success obtained with this model system (the oil nevertheless being a practical, industrial oil and the adhesive quite similar to various commercial products), the test developed is suggested as a means for considering the propensity of given oil/adhesive pairs to be employed under various cure conditions, although, clearly, mechanical checks on final bonded strengths must not be overlooked.

Acknowledgements

The authors thank Quaker and Shell for the supply of various materials and the Association Nationale de la Recherche Technique (ANRT) for financial support (MG).

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