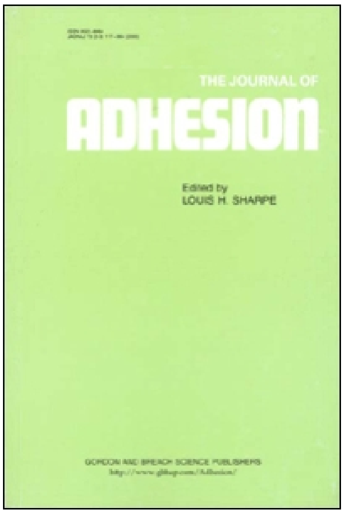

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Effect of Xylene Formaldehyde Resins on Epoxy Resin Adhesive

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ABSTRACT

The effect of some types of xylene formaldehyde on epoxy resin adhesive is studied. Xylene formaldehyde resin or modified xylene formaldehyde resins are mixed into liquid epoxy resin and curing properties of the blends, their adhesive properties and the dispersion state of xylene formaldehyde resin in cured adhesive film are examined. The results obtained are as follows.

1) Generally, by the addition of xylene formaldehyde resins, the degree of curing of blends are decreased, but pot life is prolonged, and tensile shear strength of steel bonds is increased.

2) It is observed that effects of the amount of xylene formaldehyde resins and curing condition on tensile shear strength vary with the kind of xylene formaldehyde resin, because of the difference in chemical structure of xylene formaldehyde resins and their reactivity to epoxy resin.

3) It is found that a limited region of compatibility, between 80 and 100 phr, exists for 100% xylene formaldehyde resin in epoxy resin. It is also found that joint strength is reduced with higher viscosity and molecular weight of 100% xylene formaldehyde resin in the case of 80 phr blends, and that these results have some relation to the dispersion state of xylene formaldehyde resin in epoxy resin, judging from the cured adhesive film observed under a phase contrast microscope.

1. INTRODUCTION

CURED BLENDS of an epoxy resin and an amine hardener are widely used as an epoxy resin adhesive. There are some experiments of improving the adhesive by adding the aromatic hydrocarbon formaldehyde resins such as a xylene formaldehyde resin[1] (hereafter called the xylene resin) and an alkyl-benzene formaldehyde resin[2] to an epoxy resin, but the details are not yet clear. The 100% xylene resin has essentially no reactivity to an epoxy resin in the presence of alkaline materials such as an amine hardener and is used as a diluent or a plasticizer. However, it has advantages such as a good compatability with epoxy resins and the capability of viscosity decrease and of prolongation of the pot life.

In this experiment, not only the 100% xylene resin which has been conventionally used but also the polyol modified xylene resins which are modified so as to have many OH groups at the ends and the amine modified

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xylene resins reacted with aromatic amines are studied in order to elucidate their effects on the adhesive properties of the epoxy resin adhesive, their compatibility and reactivity with the epoxy resin.

2. EXPERIMENT

2.1 Adhesive Mixture

Epoxy resin: Epikote #828
Hardener: Triethylene tetramine (TTA)
Diethylene triamine (DTA)
Xylene resins. Those given in Table 1 and 2 are used (manufactured by Japan Gas Chemical Co., Ltd.). Variable amounts of each component are mixed at normal room temperature (20°C) to make an adhesive.

2.2 Measurements of the Curing Properties

2.2.1 Measurements of Curing Time

Five grams of the blended adhesive was weighed into a 15 mm diameter test tube and heated in an 80°C glycerin bath. The curing time is defined as the period in which the adhesive changes from its low viscosity state to such a hard state that it cannot be stirred. The stirrer consisting of a 1 mm. diameter wire whose end was bent in a 10 mm. diameter circle was moved up and down by hand.

Table 1. Characteristics of the Xylene Resins

Kinds of Xylene Resins	Trade Name	Molecular Wt.	Viscosity (20°C cp.)	End Group (%)
100% xylene resin	Nikanol LL	400	2,500	OH; 0.8
Amine modified xylene	Nikanol B-640	370	10,500	N; 4.8 (total amount)
Polyol modified xylene resin	Nikanol E-1730	600	1,900	OH; 4.2

Table 2. Characteristics of 100% Xylene Resins

Kinds of 100% Xylene Resins	Molecular Wt.	Viscosity (20°C cp.)	OH End Group (%)
Nikanol LL	400	2,500	0.8
Nikanol L	380	5,700	1.0
Nikanol H	470	85,500	0.8
Nikanol HH	570	55,000	1.1
Test Product	800	51°C (melting point)	—

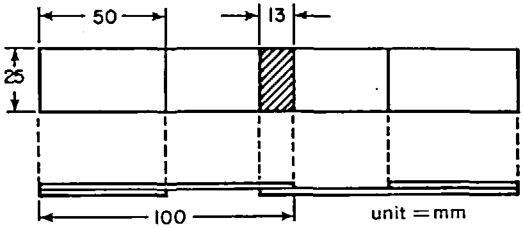


Figure 1. Test specimen for tensile shear strength measurement.

2.2.2 Measurements of the Degree of Insolubility.

Five grams of the blended adhesive was weighed into an iron dish and cured at 80°C for 2 hours. This cured resin was pulverized into 80 mesh granules whose soluble parts were extracted with methylethylketone. The extraction residue was dried in a vacuum desiccator until the weight remained constant. The percentage of dried residue is defined as the degree of insolubility.

2.3 Measurements of the Tensile Shear Adhesive Strength

The test specimens as shown in Fig. 1 were prepared using mild steel plates of fixed size and shape as the adherends.

After the adhering parts of the adherends were polished in advance with an abrasive paper and immersed in trichloroethylene for 30 minutes in order to remove grease, they were dried at 100°C for 10 minutes. The test pieces were prepared by spreading one of the blended adhesives on both surfaces of the adherends which were squeezed tight uniformly (6 kg/cm^2) and heat cured at the prescribed condition.

Five such test pieces were prepared for each adhering condition, and they were kept overnight at constant temperature (20°C, 65% RH). Their tensile shear strengths were measured using the Instron-type universal testing machine at a stretching speed of 3 mm/min. (Toyosokki Co., Ltd., Tensilon Model UTM-1).

2.4 Preparation of Castings and Hardness Measurement

Rockwell hardness (M-scale) was measured at 20°C on the castings prepared following the conditions given in Table 3.

2.5 Compatibility Measurement

A small amount of the adhesive was spread on a glass plate and cured at 80°C for 2 hours with a cover glass on it. The cured film was observed under a phase contrast microscope in order to judge the compatibility.

Table 3. Preparation of the Castings

Composition		Curing Condition
Epikote #828	100 parts	Normal room temperature, 2 hrs.
DTA	8 parts	100°C, 40 minutes
Xylene Resin	Variable amount	

3. RESULTS AND DISCUSSION

3.1 Effects of the Xylene Resins on the Curing Reaction of the Epoxy Resin.

In this experiment, various kinds of the xylene resins shown in Table 1 were mixed with the main components of the bisphenol type epoxy resin adhesive, and the effects of the resulting blended materials on the adhesive properties were studied. Generally, an epoxy resin adhesive is prepared by mixing an epoxy resin with an amine hardener. The percentages of the constituents in the mixture have a great influence on the adhesive strength and the usable period.

When the 100% xylene resin is heated with the epoxy resin in the presence of an acidic catalyst, the oxygen-containing linkages in the xylene resin such as a methylol group, a methylene ether group and a methylene acetal group react with a hydroxyl group or an epoxy group in the epoxy resin resulting in chemical compounds in which the xylene resin and the epoxy resin are bonded through the ether linkage. However, little reaction of the 100% xylene resin with the epoxy resin is expected in the presence of the amine compound which is alkaline such as an epoxy curing agent. The xylene resins used in this experiment as shown in Fig. 2 are the 100% xylene resin (I), the amine modified xylene resin (II) which has an amine structure, and the polyol modified xylene resin (III) which contains many hydroxyl groups. These modified xylene resins may possibly react with the epoxy resin.

The various kinds of functional groups in these three different xylene resins may have different effects on the curing reaction of the epoxy resin - TTA mixture. In order to elucidate these points, the gelation time at 80°C was measured when each kind of the said xylene resins was added to the mixture

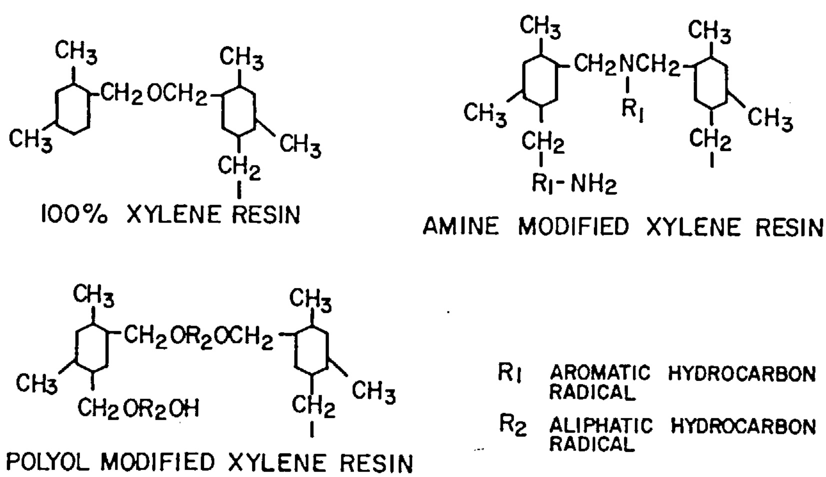


Figure 2. Structure of various xylene resins.

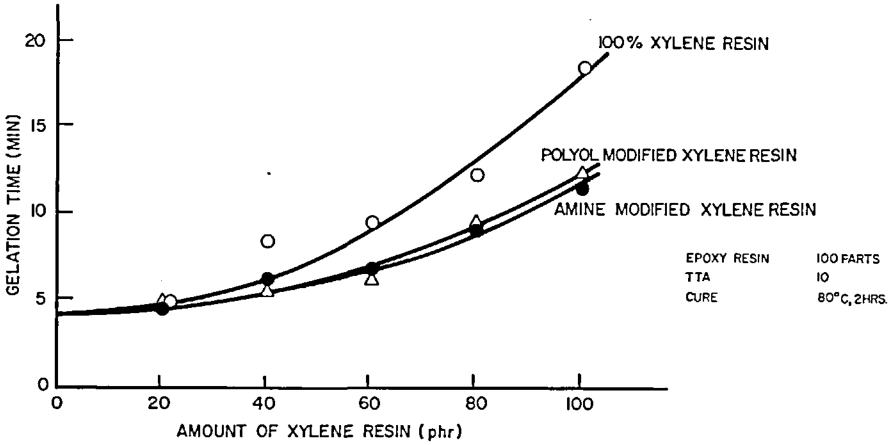


Figure 3. Relationship between concentration of xylene resins and cure rate.

of the epoxy resin and TTA. The results as shown in Fig. 3 indicate that the curing rate decreased as the amount of the xylene resins was increased. Among these three kinds of xylene resins, the 100% xylene resin has the slowest curing rate compared to the other two modified resins. The decrease in the curing rate leads to the prolongation of the pot life of the epoxy adhesive mixtures. This prolongation is in many cases advantageous for a practical purpose. The reason the modified xylene resins have faster curing rates than the 100% xylene resin is considered to be the contribution of the functional groups in the modified xylene resins to the curing reaction. Fig. 4 shows the relationship between the degree of insolubility and the amount of the added xylene resins. The cured resin blended with the 100% xylene resin shows a lower degree of curing and a lower degree of insolubility. On the contrary, the amine modified resin and the polyol modified resin give a slightly higher degree of insolubility, which is considered to be the contribution of their higher reactivity to the epoxy resin.

Gough et al.[3] reported that the third constituent added to the resin took an important role in determining the rate of the curing reaction between a bisphenol-A type epoxy resin and an amine. Furthermore, they studied the relationship between the curing reaction and the kinds of additives, and they concluded that the compounds which have substituent groups such as —OH, —COOH,—SO_3H,—$CONH_2$,—CONHR,—SO_2NH_2 and—SO_2NHR have an accelerating effect and that the compounds which have a substituent group such as—OR ($R \neq H$),—COOR,—SO_3H,—$CONR_3$ ($R \neq H$),—SO_2NR_2, >CO,—CN and—NO_2 have a retarding effect.

The effects of the xylene resins used in this experiment on the mixture of the epoxy resin and the amine hardener are similar to those stated above, i.e. the accelerating and retarding effects of the substituent groups in the xylene resins have the influences on the rate of the curing reactions which are indicated in Fig. 3 and Fig. 4. Namely, although the 100% xylene resin has the ether linkages (—CH_2OCH_2—), the acetal linkages (—$CH_2O(CH_2O)_nCH_2$—)

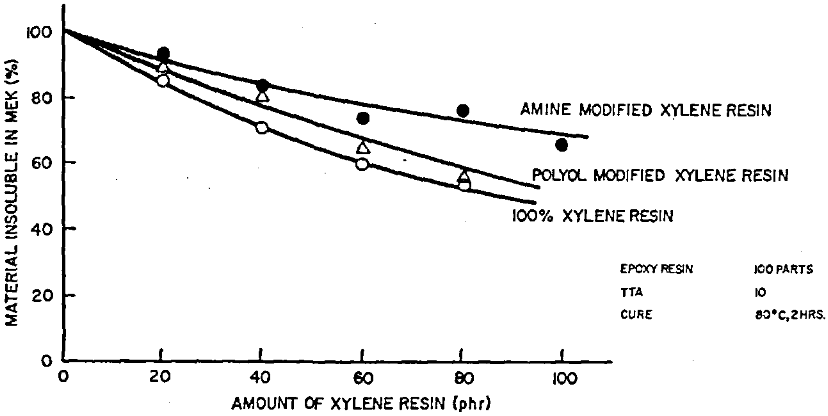


Figure 4. Relationship between concentration of xylene resins and cure degree.

and a small amount of the methylol groups (—CH_2OH), it has the lowest degree of insolubility and the lowest curing rate among the three xylene resins because, as is quite obvious from Table 1, it has few methylol groups which have an accelerating effect and has rather many ether linkages which have a restraining effect. However, as the polyol modified xylene resin has more methylol groups per molecule than the 100% xylene resin, the former has the relatively faster curing rate. It is also known that the methylol group reacts with the epoxy group in the presence of amines. The amine modified xylene resin which contains a primary amine, a secondary amine and a tertiary amine not only has an accelerating effect for curing on the system of the epoxy resin and the amine hardener but also works partially as a hardener. Thus, some xylene resins have the substituent groups which have both an accelerating and a retarding effect on the epoxy resin-amine hardener system. It is believed that these effects complicate the curing reaction.

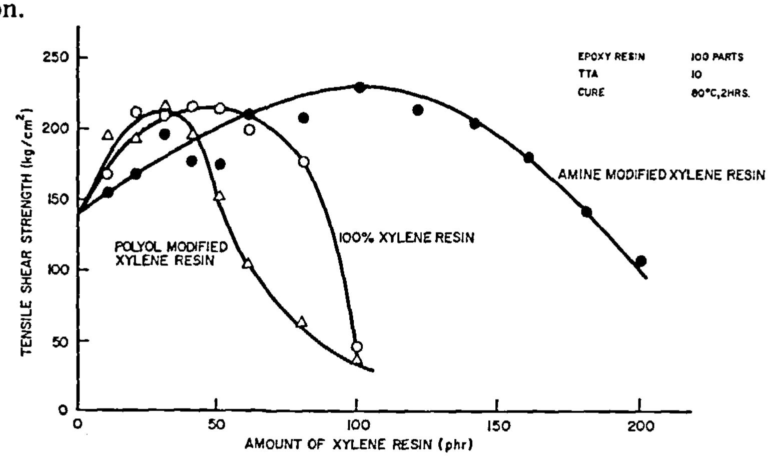


Figure 5. Relationship between concentration of various xylene resins and tensile shear strength.

3.2 Kinds of Xylene Resins and the Adhesive Properties.

The adhesives were prepared by adding various amounts of each kind of the xylene resins given in Table 1 to the epoxy resin-TTA mixture, and their tensile shear adhesive strengths of the steel to steel bond were measured. The results shown in Fig. 5 indicate that the adhesive strengths are increased by adding any kind of xylene resins, but that the optimum amount of addition varies depending upon the kind of xylene resin. Namely, the maximum adhesive strength of the adhesives occurs when the concentration of the polyol modified xylene resin, the 100% xylene resin and the amine modified xylene resin is 20—30 phr, 50—60 phr and about 100 phr, respectively. In particular, a high adhesive strength can be obtained in a wide range of concentrations when the amine modified xylene resin is added. However, when the concentration of the xylene resins is over the optimum amount, the adhesive strength begins to decrease. This strength decline starts in the order of the polyol modified xylene resin, the 100% xylene resin and the amine modified xylene resin.

It is already clear from the literature[4] that a solubility parameter (SP) in general has an additive property. Gardon[5] reported that when the SP of the material is low its critical surface tension (γ_c) tends to be low. It is also made clear that the liquid with lower surface tension wets a high energy solid surface such as steel more. Considering these facts, the increase of the adhesive strength can be attributed to the increase of the wettability of the adhesive on the high energy surface of the steel because, when the low viscosity resins with low SP such as the 100% xylene resin and the polyol modified xylene resin are blended with the epoxy resin, they decrease both the viscosity and the SP of the mixture of the non-cured eopxy resin adhesive.

Above the optimum concentration of the xylene resins, the adhesive strengths decrease as the amount of the added xylene resins is increased. This is due to the fact that the adhesive layer is softened by the xylene resin and is influenced by a sort of plasticizing effect. From the fact that the order of the hardness decline (plasticity increase) of the castings shown in Fig. 6 coincides with the order of the decrease in adhesive strength, it is quite obvious that the degree of plasticization is proportional to the hardness of the cured resins.

Among these three kinds of xylene resins, the amine modified xylene resin has the least tendency to decrease the hardness and the adhesive strength of the cured resin, which indicates that it forms a very hard cured film when reacted with the epoxy resin. Thus, the relationships among the kinds of xylene resins which are blended with the epoxy resin, the hardness of the cured resins and the adhesive strength of the steel to steel bond can be explained by the influences of the structural differences in the xylene resins upon the curing reaction of the epoxy resin-hardener system.

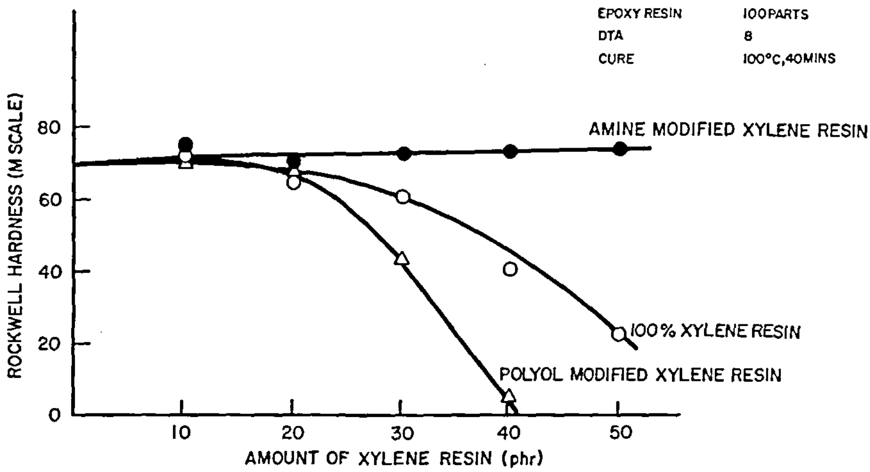


Figure 6. Relationship between concentration of xylene resins and Rockwell hardness of castings.

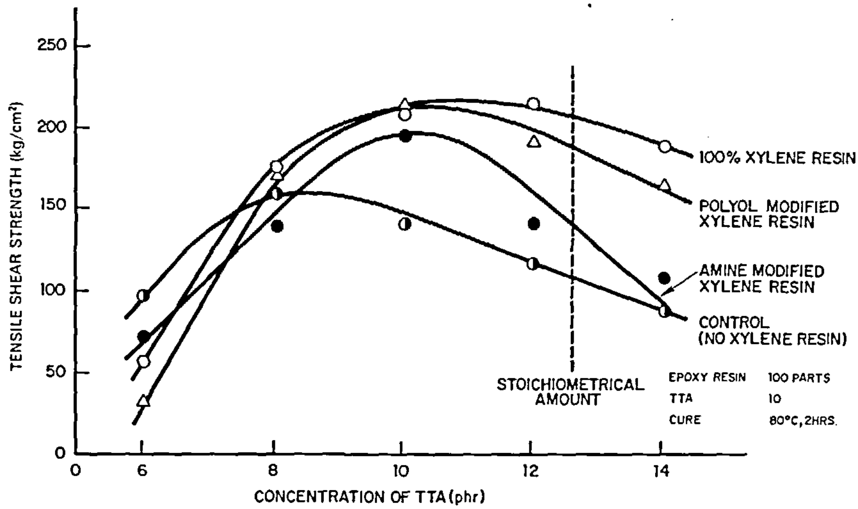


Figure 7. Relationship between concentration of TTA and tensile shear strength.

3.3 Effects of the Concentration of the Hardeners.

The changes of the adhesive properties are shown in Fig. 7 where the amount of the hardener TTA added to the prescribed mixture of the epoxy resin and the xylene resin is varied. Generally, the epoxy resin adhesives have the maximum adhesive strength when the amount of the amine hardener is less than the stoichiometrical amount. This tendency was already reported by Okitsu et al[7]. Even when no xylene resin was added, the data give a similar tendency as shown in Fig. 7. When the xylene resin was added, the maximum adhesive strengths were not only increased but also shifted to a higher concentration of the hardener. This shift of the maximum adhesive strength to the higher concentration can be attributed to the dilution effect of the xylene resin both on the epoxy resin and the hardener. Also, the increase of the adhesive strength due to the addition of the xylene resins can be attributed to the viscosity decrease of the adhesive or to the increase of the wettability as considered in the previous section. Among the xylene resins, the amine modified xylene resin has a slightly different tendency than the 100% xylene resin and the polyol modified resin. When the concentration of the added TTA is over the optimum amount, the amine type xylene resin tends to decrease the adhesive strength more than the other xylene resins. This may be attributed to the excess of the hardener because the amine type xylene resin works partially as a hardener.

3.4 Effects of the Curing Temperature.

The changes of the adhesive properties when the curing temperature was varied are shown in Fig. 8. When no xylene resin was added, the adhesive strengths were increased as the curing temperature was increased. When the 100% xylene resin was added, the adhesive strength in this range of the curing temperature was maintained over 200 kg/cm^2 which was higher than the case when no xylene resin was added.

The polyol modified xylene resin increases the adhesive strength as the curing temperature is increased. The terminal hydroxyl groups in the polyol modified xylene resin may possibly react at high temperatures with the epoxy groups or with the hydroxyl groups in the epoxy resin and may form ether linkages. This will probably cause the different behavior of the adhesive strength compared to the case when the 100% xylene resin was added.

On the other hand, the amine modified xylene resin decreases the adhesive strength as the temperature is increased. This is presumed due to the fact that the amine structures in the resin can work especially at high temperature as the hardener or as the catalyst and consequently cause the decrease of the adhesive strength in a similar manner as the case of the excess hardener. This presumption can also be confirmed from the fact that the adhesive strength increases at higher temperature even when the amount of the

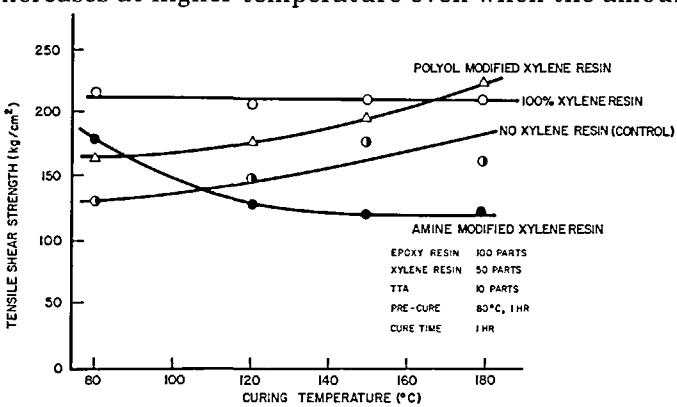


Figure 8. Relationship between curing temperature and tensile shear strength.

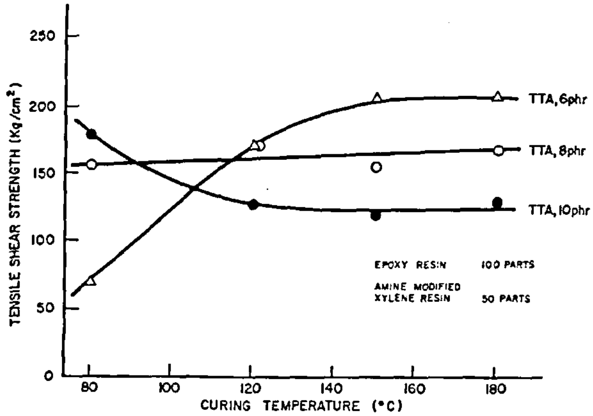


Figure 9. Relationship between curing temperature and tensile shear strength..

hardener TTA is much less than the stoichiometrical amount. Fig. 9 shows the relationship between the curing temperature and the adhesive strength when the amount of TTA is decreased. When the amount of TTA in the epoxy resin is small, the adhesive exhibits low adhesive strength at the relatively low temperature of 80°C because of the incomplete curing, but as the temperature is increased it exhibits high adhesive strength because the amine modified xylene resin works as a hardener at high temperature. On the other hand, when the amount of TTA is large, the adhesive already has high adhesive strength at low temperature curing. As the temperature is increased, the adhesive stength is decreased due to the excess of the hardener since the amine modified xylene resin works as a hardener. The high reactivity of the amine modified xylene resin with the epoxy resin at high temperature is supported by the data shown in Fig. 10. Namely, it is confirmed that the mixture of 1 to 1 by weight has the higher degree of insolubility in methylethylketone as the curing temperature is increased.

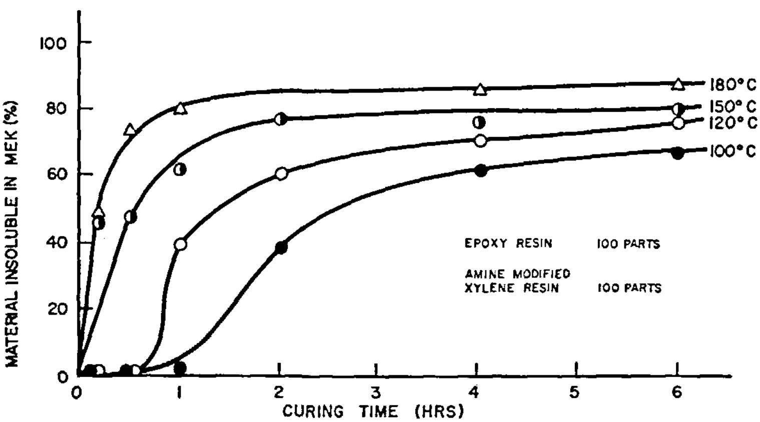


Figure 10. Curing conditions vs. material insoluble in MEK.

3.5 Compatibility of the Xylene Resins and the Adhesive Strength.

The xylene resins generally have a good compatibility with the epoxy resin. Especially the polyol modified xylene resin and the amine modified xylene resin give clear cured materials at any ratio of blending. However, the 100% xylene resin has a certain limit of compatibility. When the compatibility limit is exceeded, phase separation occurs, causing a marked decrease of the adhesive strength. Using the 100% xylene resins with different viscosity and molecular weight as given in Table 2, the relationship between the adhesive strength and the amount of the xylene resin added to the curing mixture of the epoxy resin and the amine hardener was obtained as shown in Fig. 11. There is little difference in the adhesive strength among the 100% xylene resins when the concentration of the resin is below 60 phr. However, when the concentration of the added resin exceeds 80 phr, the adhesive strength decreases considerably and tends to decrease faster when the resin of higher molecular weight and higher viscosity is added. This is due to the facts that the compatibility of the 100% xylene resin with the epoxy resin becomes poor over 80 phr and that there is a difference in compatibility depending on the kind of 100% xylene resins. In order to see whether there is a boundary region in the compatibility, the epoxy resin-TTA mixtures with various amounts of the 100% xylene resin (Nikanol LL), 60, 80, 100 phr, respectively, were heat cured into films whose phase separation was observed by a phase contrast microscope. The results are shown in Fig. 12 a,b,c, respectively. When 60 phr

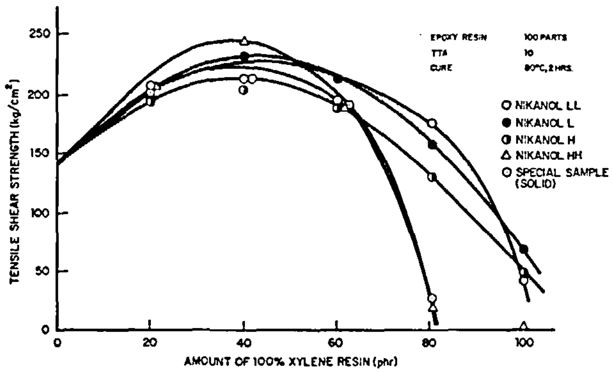
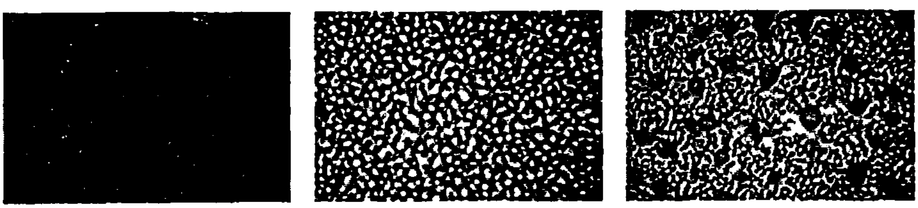


Figure 11. Relationship between concentration of various kinds of resin and tensile shear strength.



60 phr. (a) 80 phr. (b) 100 phr. (c)

Figure 12. Phase separation state vs. amount of Nikanol LL. (700x).

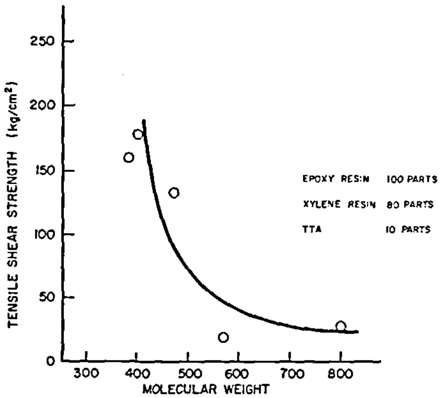


Figure 13. Molecular weight of 100% xylene resins vs. tensile shear strength.

was added there was a sign of a phase separation but no positive phase separation. At 80 phr the phases start to separate rather clearly and a clear phase separation can be seen at 100 phr. For the mixtures with 80 phr of the 100% xylene resin shown in Fig. 11, the relationship between the adhesive strength and the molecular weight of the xylene resin was examined. The data given in Fig. 13 indicate that the xylene resin with relatively low molecular weight yields the higher adhesive strength. Judging from the observations of the fracture surfaces of the adhesive layer, the adhesive strengths seem to be measured by the cohesive fracture. The decrease of the adhesive strength when the relatively large amount of xylene resin, 80 phr, was added can also be attributed to the excess plasticization in the epoxy resin adhesive caused by the xylene resin. Accordingly, from a practical point of view, one can say that the cured resins blended with 80 phr of the xylene resin of higher molecular weight and viscosity have a smaller tendency of being plasticized and consequently of decreasing the adhesive strength. This is true only for the case of good compatibility. However, in the boundary region of the compatibility as dealt with in this report, the degree of the compatibility is a more important factor. Namely, as shown in Fig. 14, the observations of the phase separation by a phase contrast microscope indicate that the cured resin blended with the higher molecular weight xylene resin gives more definite phase separation. Accordingly it can be concluded that the adhesive strength is closely related to the phase separation state.

Generally, the high molecular weight 100% xylene resin contains a number of xylene rings connected by a methylene linkage and consequently has a lower solubility in the epoxy resin. On the other hand, the low molecular weight 100% xylene resin has fewer methylene linkages and contains a higher percentage of polar acetal linkages. Consequently, it has a higher solubility in the epoxy resin. Therefore, the difference in the solubility in the epoxy resin when the molecular weight of the 100% xylene resins was varied may also be attributed to the difference of the internal chemical structure of the 100% xylene resins.

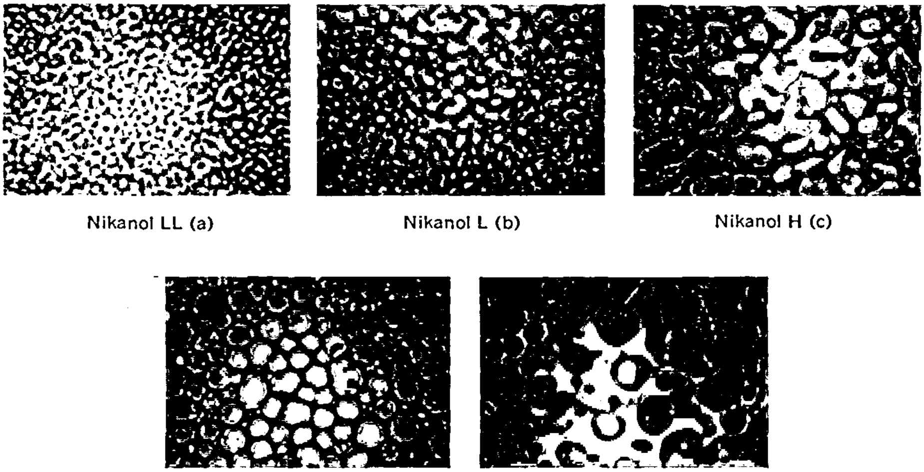


Figure 14. Phase separation state of cured epoxy resin film containing various 100% xylene resins. (700x).

4. CONCLUSIONS

Each of the three kinds of xylene resins with different chemical structure was blended with the adhesive mixture of the epoxy resin and the amine hardener. The results indicate that each chemical structure has a different effect not only on the curing reaction of the epoxy resin and the amine but also on the adhesive strength of the steel to steel bond. The addition of the xylene resins to the epoxy resin-amine adhesives generally tends to increase the adhesive shear strength and to prolong the pot life.

There is a certain boundary limit to the compatibility of the 100% xylene resin with the epoxy resin. It was confirmed from the phase contrast microscope observations that the critical value is 80 phr.

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