

The Adhesive Properties of Hydantoin Vinyl Ether Polymers

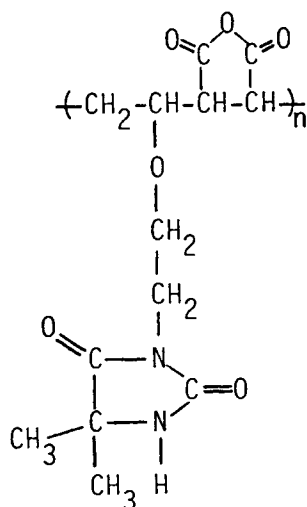
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Synopsis

The hydantoin vinyl ether polymers are alternating copolymers of 3-vinyl-5-oxo-5,5-dimethylhydantoin (HVE) and maleic anhydride (MA). The adhesive properties of HVE/MA and structurally related polyvinyl pyrrolidone (PVP) and methylvinylether/maleic anhydride (MVE/MA) polymers were compared on an approximately 1:1 specific viscosity basis. Lap shear strength measurements showed approximately 10:1 and 4:1 ratios in favor of the HVE/MA polymers as compared to PVP and MVE/MA, respectively. These differences are possibly due to the higher cohesive strength of the HVE/MA repeating unit and to the fact that this polymer would appear to contain more structural elements liable to make physical and chemical contributions to the interfacial attachment strength. Based on these preliminary results, HVE/MA and MVE/MA polymers with identical specific viscosities were applied to carbon pitch fiber via electrodeposition. Using the standard MY 720/DDS epoxy laminating system for advanced composite applications 36% and 13% improvements in interlaminar shear strength were observed for an add-on of 2%.

INTRODUCTION

The title hydantoin vinyl ether polymers are 1:1 copolymers of 3-vinyl-5-oxo-5,5-dimethylhydantoin (HVE) and maleic anhydride (MA):



HVE/MA copolymer

Monomer synthesis, polymerization procedure, polymer characterization, and the results of an investigation of the copolymerization parameters have been reported in a previous paper.¹

The original concept which led to the synthesis of these polymers was to develop water-soluble polymers in which the assumed complexing capability of the hydantoin ring could be utilized. A complexing capability for the hydantoin ring was assumed because of its structural similarity to the pyrrolidone ring.¹ The lactam group of the latter is reported to be the structural element responsible for the almost universal complexing capability of polyvinyl pyrrolidone (PVP).^{1,2} In the HVE/MA polymers the hydantoin moiety has been combined with maleic anhydride. The HVE/MA polymers are therefore also structurally related to the already known methylvinylether/maleic anhydride polymers (MVE/MA).

In a first series of experiments of HVE/MA polymers were therefore, compared to both PVP and MVE/MA on an approximately 1:1 specific viscosity basis. The HVE/MA gave better results (complexing capability and solution viscosity) and this was interpreted as an indication that the structural elements contained in the HVE/MA polymers viz. (2) lactam groups plus the anhydride group were more effective than either 1 lactam group (PVP) or 1 anhydride group (MVE/MA) alone.¹

This work has been continued and the present paper deals with a further comparison of HVE/MA, PVP, and MVE/MA polymers. The property in question is adhesion. Lap shear strengths were determined first and the results are discussed in terms of the surface attachment theory of adhesive joint strengths. Further work was carried out in the area of carbon fiber size. Here both HVE/MA and MVE/MA polymers were deposited on to carbon fiber via electrodeposition. The pretreated carbon fiber was then used for the preparation of unidirectional C-fiber prepreps and finally, in combination with a standard epoxy matrix system, for the preparation of unidirectional C-fiber/epoxy laminates. The effect of the electrodeposited polymer layers on the interlaminar shear strength of the finished laminates was investigated.

EXPERIMENTAL

Polymer Synthesis

HVE/MA polymers with specific viscosities of 0.25, 0.80, and 0.90 (1% solutions in DMF at 25°C) were required for this study. These polymers were obtained by copolymerizing 3-vinylxyethyl-5,5-dimethylhydantoin and maleic anhydride in the solvent mixture toluene/cyclohexane using azobutyronitrile (AIBN) as initiator. The desired specific viscosities were obtained by varying the ratio between the two solvents.³ The HVE/MA polymers were used in the form of their polyamide/ammonium (PAAS)¹ and half ammonium (HAM) salts. The latter were prepared by suspending the parent polyanhydride polymers in water and carefully neutralizing with aqueous ammonium hydroxide.

REFERENCE MATERIALS

Poly(vinyl pyrrolidone) (PVP) and poly(methylvinylether)/maleic-anhydride (MVE/MA) were obtained commercially and used as supplied. The

specific viscosities of the samples obtained, measured according to the procedure outlined below, were as follows: PVP "low-molecular weight grade": 0.27; MVE/MA "low-molecular weight grade": 0.90.

SPECIFIC VISCOSITY

All (specific) viscosity measurements were carried out in dimethylformaldehyde (Pa) at 25°C in an Ubbelohde-type viscosimeter. The solution concentration was 1 g/100 mL in all cases.

LAP SHEAR STRENGTH

The polymers were applied from 50% aqueous solutions. The solutions contained 92.5% polymer and 7.5% glycerine. The lap shear specimens (Anticorrosional B) were dried for 1 h at 80°C.

Lap shear strength was measured on a Zwick Universal Testing Machine 1454 according to the DIN 53283 specification. Ten specimens were tested in each case.

CARBON FIBER

The carbon fiber used for the electrodeposition experiments was Thornel type P (pitch) with 2000 filaments.

ELECTRODEPOSITION

An apparatus for the continuous electrodeposition of polymer on to carbon fiber was used. A schematic representation is given in Figure 1. In the apparatus, the carbon fiber passes over a copper contact (which is in turn connected to the positive pole of a DC source) and acquires a positive charge. It is then drawn through the electrolytic cell containing the negatively charged polymer anion. Polymer is deposited on to the fiber which then passes through a wash bath and a drying zone before finally being taken up on a roll at the far right-hand side of the apparatus. The polymer add on as determined by total combustion at 480°C is controlled by the following parameters:

Applied voltage

Current

Concentration of the polymer solution

Residence time of the C fiber in the electrolytic cell (i.e., take-up speed)

Intensity of the washing operation

In a preliminary series of experiments polymer add on was determined as a function of take-up speed with the concentration of the polymer solution as parameter and with the remaining three variables at constant levels.

Linear relationships were found in all cases. For a given concentration of the polymer solution under defined washing conditions and with the applied

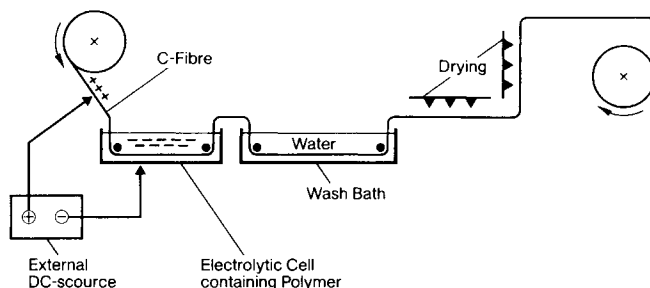


Fig. 1. Schematic representation of electrodeposition apparatus.

voltage and the current at constant levels of 10 volts and 2.5 amperes, respectively, polymer add on could be adjusted simply by varying the take-up speed of the carbon fiber.

The desired add ons could be obtained in this manner to $\pm 0.1\%$.

MATRIX SYSTEM

The matrix system used in this study was MY 720/DDS (diaminodiphenylsulphone). MY 720 is the standard CIBA-GEIGY epoxy laminating resin for advanced composite applications. It is a polyglycidylether made from diaminodiphenylmethane. The MY 720 had an epoxy content of 8.35 val/kg. The MY 720/DDS ratio was 100:52. The DDS used was standard CIBA-GEIGY HT 976.

PREPREG MANUFACTURE

The MY 720/DDS matrix system was applied to the pretreated carbon fiber from a 1:1 mixture of methyl ethyl ketone and acetone. Matrix system add on was adjusted via the concentration of the impregnation solution and the pull through speed of the carbon fiber. The preimpregnated fiber was (continuously) taken up on a revolving drum and the prepreg predried for 15' with an infrared lamp. After cutting to appropriate lengths the prepreps were finally dried in a vacuum exicator at $100^{\circ}\text{C}/0.1$ mbar for 1 h.

LAMINATE PREPARATION

The prepreg units were unidirectionally and uniformly stacked on to one another. Both sides were covered with copper foil and a Tedlar "separation" foil wrapped around the whole. The laminates were prepared in an aluminum form under pressure. The press cycle was:

- Place prepreps in press at 120°C
- Heat to 177°C in 20' without pressure
- Keep at 177°C for 90'; after approximately 4', shortly before gelation, apply pressure carefully

Heat to 205°C and hold for 4 h
Cool to room temperature under pressure

Three laminates with different fiber volume fractions were made in all cases.

INTERLAMINAR SHEAR STRENGTH (ILS)

The tests were carried out according to ASTM D2344-76 on a Roell & Dorthaus flexural tester at a testing speed of 1.00 mm/min. The fiber orientation was paralleled to the length of the specimen. Samples from three different laminates with three different volume fractions were tested in each case. Nine specimens were tested per sample. ILS results were corrected to a fiber volume fraction φ of 0.60.

RESULTS AND DISCUSSION

Lap Shear Strength

Figure 2 shows a first comparison between a PVP reference product and a MVE/MA polymer with almost the same specific viscosity. The 95% confidence limits for the mean values are given directly under the appropriate structural formulae with the mean values themselves written alongside. The difference in lap shear strength is (statistically) significant with the HVE/MA polymer giving a mean value which is approximately 10 times higher than that of the reference product.

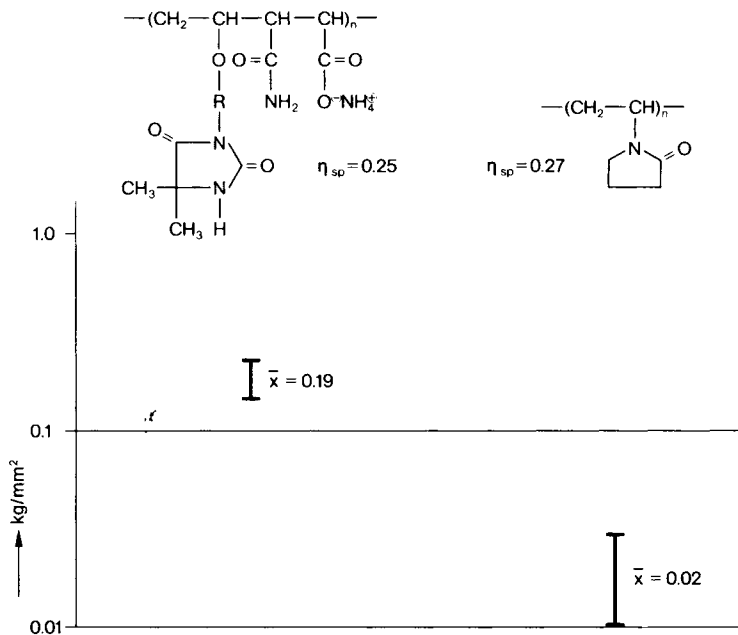


Fig. 2. Lap shear strength comparison: HVE/MA and PVP polymers.

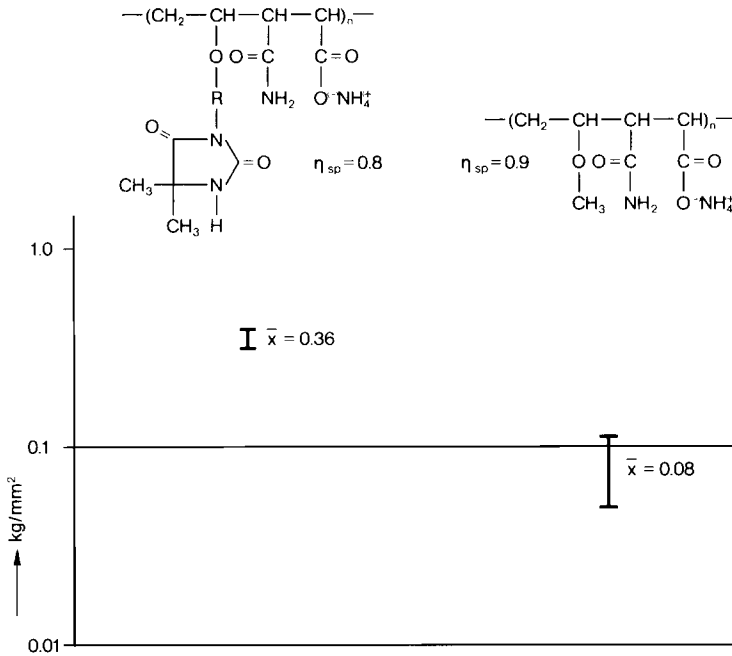


Fig. 3. Lap shear strength comparison: HVE/MA and MVE/MA polymers.

The comparison for HVE/MA and MVE/MA is given in Figure 3. Here again the improvement in lap shear strength is (statistically) significant but the difference between the mean values, approximately factor 4, is less pronounced.

With reference to the surface attachment theory of adhesive joint strengths,⁴ it would appear that the following main headings should be included in a discussion of the lap shear strength (LSS) results:

The cohesive strength of the adhesive

Wetting

Other physical contributions to the interfacial attachment strength

Chemical contributions to the interfacial attachment strength

COHESIVE STRENGTH

The cohesive energies E_{coh} of the HVE/MA polymer unit and of the reference PVP and MVE/MA polymers were estimated via the additivity principle from group contributions. Of the several compilations of group contributions available in the literature only one was of sufficiently large scope as to include almost all the groups and structural elements present in the repeating units of the three polymers.⁵

The fact that this compilation is reported to give a less accurate prediction of E_{coh} ⁶ was not judged to be prohibitive, as only relative values were re-

quired. Furthermore, group contributions to the molar volume are available from the same author. Some difficulties were encountered in the case of the lactam ring for which no contributions are listed. One possibility would have been to use the contributions for "ring closure 5 or more atoms" equal to 1050 J/mol for E_{coh} and 16 cm³/mol for the molar volume V . However, a group contribution of 1050 J/mol for the lactam group, when compared to contributions of the order of 30,000 and 40,000 J/mol for other polar moieties such as carboxyl and amide, does not seem realistic. In fact, it has been shown that lactams have higher dipole moments than their corresponding amides and, accordingly, also higher boiling points.⁷ A contribution larger than or at least equal to that of the —CONH₂ group would, therefore, seem more reasonable and the value listed for this group (= 41860 J/mol) was finally used for the calculations. This means in effect that for the E_{coh} calculations both the pyrrolidone and hydantoin rings were treated as non-cyclic moieties made up of 1 amide and 3 methylene groups and 2 amide, 1 >C< and 2 methyl groups, respectively. For the molar volume calculations, however, the "ring closure 5 or more atoms" value of 16 cm³/mol was used in both cases. The estimates for E_{coh} , the molar volume V , and the cohesion energy density $e_{coh} = E_{coh}/V$ are given below:

Estimated E_{coh} , V , and e_{coh} Values for HVE/MA and Reference Polymers

Polymer	E_{coh} J/mol	V cm ³ /mol	e_{coh} J/cm ³
PVP	65050	31.1	2091.6
MVE/MA ^a	83150	85.9	968.0
HVE/MA ^a	182930	100.6	1818.4

^a Based on the amide/ammonium derivative as structural unit (Fig. 3).

The estimated E_{coh} values differ by a factor of approximately 3 in the case of PVP/HVE-MA and by a factor of approximately 2 in the case of MVE-MA/HVE-MA. There is, therefore, qualitative agreement with the LSS results.

With regard to the cohesion energy density estimates, the ratios for the PVP, MVE/MA, and HVE/MA units are 2.2:1:1.9; i.e., there is qualitative agreement in the case of the polyanhydride polymers.

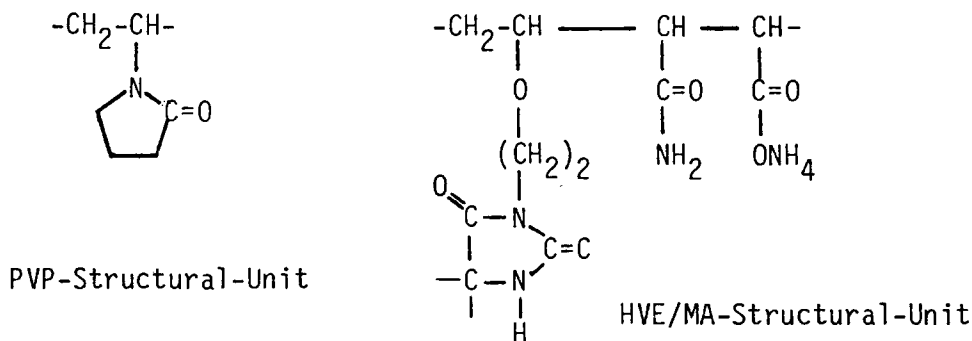
The ratio between the LSS mean values for PVP and HVE/MA was, however, approximately 10:1, so that a significantly higher value for e_{coh} might have been expected in the latter case.

WETTING

Wetting is not felt to be responsible for the observed differences in LSS performance. A brief discussion is given in Appendix A.

OTHER PHYSICAL CONTRIBUTIONS TO THE INTERFACIAL ATTACHMENT STRENGTH

First, a comparison of the PVP and HVE/MA structural units as regards structural features which might make a physical contribution towards interfacial attachment strength:



C—N Bonds

Covalent C—N bonds are fairly polar and provide strong adhesion to polar substrates.⁸ The PVP structural unit exhibits 1 C—N bond, the HVE/MA unit 2.

Lactam Groups

The lactam group is known to introduce polarity and powerful hydrogen bonding into a polymer molecule. In fact, the lactam group has been quoted as being primarily responsible for PVP's almost universal complexing capability.⁹ Both polarity and hydrogen bonding should make strong contributions toward interfacial attachment to a polar surface. The HVE/MA structural unit contains 2 lactam groups, PVP one.

Oxygen

After covalent bonding the oxygen lone pairs of electrons can participate in fairly strong hydrogen bonding with adjacent molecules or suitable groups. It is possibly for this reason that oxygen-containing adhesives have been classified as "high polarity adhesives."¹⁰ The HVE/MA unit exhibits one ether bond.

Amide

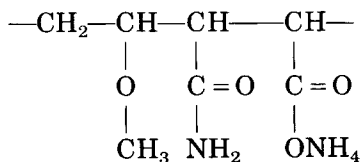
In addition to the two lactam groups mentioned above, the HVE/MA unit contains an amide group. This group should provide additional polarity and hydrogen bonding (amide-containing adhesives have also been classified as "high polarity adhesives."¹⁰

Carboxy Anion

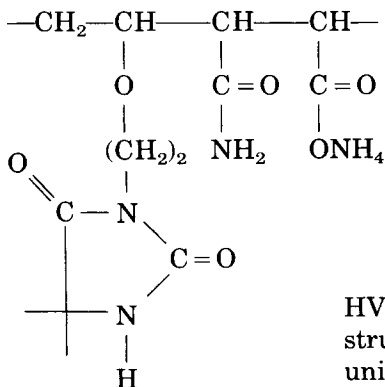
The presence of carboxylic acid groups in the side chains of polymer molecules is known to promote adhesion, particularly to polar substrates. In the ionized form, the contribution toward interfacial attachment (to a polar surface) should be even more pronounced.

On balance, the HVE/MA polymer unit would appear to contain substantially more structural elements liable to make physical contributions toward interfacial attachment strength than the PVP unit.

Moving on to the second comparison viz. MVE/MA—HVE/MA, the structural units are:



MVE/MA structural unit



HVE/MA structural unit

In addition to the oxygen, amide, and carboxy-anion elements already discussed and which are present in both polymers, the HVE/MA unit offers two C—N bonds and two lactam groups. A larger contribution toward interfacial attachment strength is thus hypothetically possible.

CHEMICAL CONTRIBUTIONS TO THE INTERFACIAL ATTACHMENT STRENGTH

With regard to chemical contributions to the interfacial attachment strength, the term encountered in the literature is *chemisorption*. This term is quoted as being equivalent to the formation of coordination bonds between the substrate and the polymer adhesive.¹¹ Chemisorbed sites are reported to be most effective as they are much less mobile, laterally and normally to the surface, than other adhesion forces.¹² In the case at hand, the substrate, a metallic surface, is the same for all 3 polymeric adhesives.

For simplicity's sake a classical case of coordination bonding will be assumed, that is, an acceptor/donor bond in which the metal (surface) acts as the electron acceptor and the electron donor(s) are suitable ligands present in the polymer structures.

The polymers contain lactam groups, amide groups, carboxy groups, and ether oxygen. In the case of the lactam groups both the nitrogen atom (in the form of the >N: -free electron pair) and the carbonyl group (in the form

of an oxygen-free electron pair) could act as monodentate ligands. However, in view of the fact that the N—C—O electrons contributing to the lactam bond are most probably delocalized^{13,14} it seems more reasonable to consider the lactam group as a whole and treat it as one single (potential) ligand. The amide and carboxy groups could be treated in the same manner.

The net result is as follows:

Polymer unit	Group/atom	No. of potential ligands	Total
PVP	Lactam (1)	1	1
MVE/MA	Amide	1	3
	Carboxy	1	
	Ether/oxygen	1	
HVE/MA	Lactam (2)	2	5
	Amide	1	
	Carboxy	1	
	Ether/oxygen	1	

The HVE/MA polymer unit would seem to offer a larger number of possible ligands for coordination bonding than either the MVE/MA or PVP units.

CONCLUSION

The lap shear results given in Figures 1 and 2 have now been discussed from the point of view of cohesive strength of the polymer adhesive, wetting, "other physical contributions to interfacial attachment strength," and chemical contributions to interfacial attachment strength. The HVE/MA polymer unit was found to have a higher (estimated) cohesive energy than the PVP and MVE/MA units; it also seems to contain more structural elements liable to make physical and chemical contributions toward the interfacial attachment strength. These differences may be responsible for the markedly superior LSS performance of the new polymer.

CARBON FIBER SIZE

The application of polyanhydride polymers on to graphite fiber via electrodeposition and the effect of the thus deposited polymer interphase on the mechanical properties of unidirectional carbon fiber/epoxy laminates has been reported in the literature.¹⁵ Improvements in interlaminar shear strength were observed and the results were interpreted as being a measure of increased adhesion between the carbon fiber and the epoxy resin matrix.

The HVE/MA polymers are also polyanhydride polymers and are, therefore, amenable to the electrodeposition process. Furthermore, they have demonstrated superior adhesion when compared to MVE/MA polymers on a 1:1 specific viscosity basis. A comparative study of the effect of electrodeposited MVE/MA and HVE/MA polymer interphases on the interlaminar shear strength of unidirectional carbon fiber/epoxy resin laminates was, therefore, undertaken. Results are given in Table I.

With reference to the electrodeposition process, different speeds were re-

TABLE I
MVE/MA and HVE/MA Polymers as Carbon Fiber Sizes. Matrix System = MY 720/DDS
(See Experimental Section)

	I Control = without polyanhydride polymer size	II Polymer = MVE/ MA-HAM ^a $\eta_{sp} = 0.90^b$	III Polymer = HVE/ MA-HAM ^a $\eta_{sp} = 0.90^b$
Polymer solution	none	←————— 2.5% —————→	
Voltage/current	—	←————— 10 volts/1.6 amp —————→	
Speed of C fiber	—	148 cm/min	175 cm/min
Polymer add on	—	←————— 2% —————→	
Fiber volume fraction	←————— $\varphi = 0.60$ —————→		
Interlaminar shear strength (N/mm ²)			
Mean values	43.5	49.1	59.0
95% Confidence limits	42.0–45.0	45.8–52.4	56.7–61.3

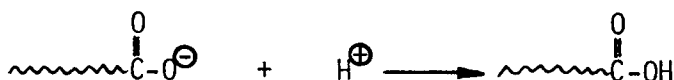
^a HAM = half ammonium salts.

^b 1% solutions in DMF at 25°C.

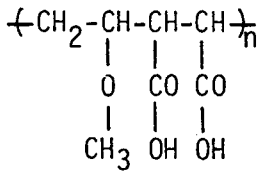
quired for the two polymers in order to deposit the same amount of polymer on to the carbon fiber under otherwise identical experimental conditions. The HVE/MA polymer could be processed at a faster speed. This could be due to faster electrodeposition and/or better adherence of the polymer to the carbon fiber during the washing operation.

With regard to interlaminar shear strength, both polymers have led to statistically significant improvements. Comparing mean values, the improvements are approximately +13% in the case of the MVE/MA and +36% in the case of the HVE/MA polymer. If improvements in the interlaminar shear strength of unidirectional C-fiber/epoxy laminates are indeed due to improved adhesion between the carbon fiber and the epoxy resin matrix as has been suggested in the literature¹⁵ then this result might be interpreted as being a direct consequence of the (relatively) superior adhesive properties of the HVE/MA polymers, as demonstrated in Figure 3 and discussed in detail in the preceding section. Wetting and interfacial adsorption were not thought to be factors responsible for differences in LSS performance.

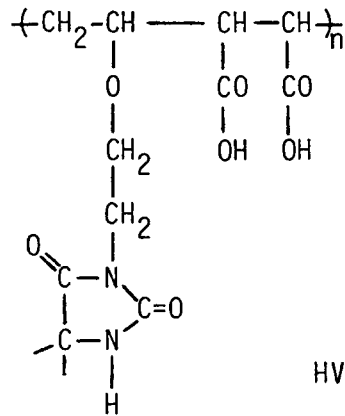
In the present case the HVE/MA and MVE/MA polymers were electrodeposited on to the carbon fiber in the form of their half ammonium (HAM) salts. Further reaction at the (carbon fiber) anode to form the insoluble acid has been suggested in the literature^{15–17}:



In this case the following polymer derivatives would be present on the carbon fiber after electrodeposition and drying:



MVE/MA



HVE/MA

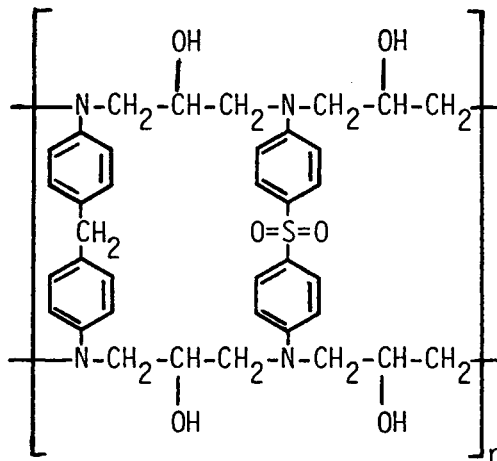
Applying the proviso of Appendix A viz:

$$\gamma_c (\text{adhesive}) < \gamma_c (\text{adherend})$$

in order for wetting and interfacial adsorption to be fully accomplished one obtains:

$$\gamma_c(\text{MY 720/DDS}) < \gamma_c(\text{MVE/MA, HVE/MA}) \quad (1)$$

The idealized structural repeating unit of the MY 720/DDS system is:



Using the same group contribution as used previously⁵ the solubility parameters δ were calculated from the appropriate e_{coh} values ($\delta = e_{coh}^{1/2}$). The former were then used to generate estimates of γ_c according to the relationship

$$\gamma_c \approx \delta \times 4.048$$

This relationship is derived from a correlation between these two parameters

which was found to be statistically significant at the 95% level.¹⁸ An estimated γ_c value of 63.1 dyne/cm was obtained for the MY 720/DDS system. The γ_c estimates for the MVE/MA and HVE/MA polymers, in the form of their dicarboxylic acid derivatives, are 53.5 and 75.6 dynes/cm, respectively. The MVE/MA γ_c value is lower than 63.1 dyne/cm; the HVE/MA-value is higher. According to Eq. (1) this would mean that wetting and interfacial adsorption could only be accomplished with the latter polymer as the adherend surface. In view of the fact that the MVE/MA polymer interphase also leads to a statistically significant (albeit markedly less pronounced) improvement in interlaminar shear strength, it hardly seems likely that wetting and interfacial adsorption are not accomplished in the case of the MVE/MA-MY 720/DDS interface. However, the result of this comparison of estimated γ_c values may be interpreted as an indication that wetting and interfacial adsorption might be *more fully* accomplished in the case of the HVE/MA polymer.

Apart from this particular aspect, the basic differences between the two polymers remain the same independent of the polymer derivative. These differences, and their possible relation to adhesive performance, were discussed in detail in the preceding section so that a repetition would be superfluous.

CONCLUSION

In this paper HVE/MA, PVP and MVE/MA polymers have been compared, on an approximately 1:1 specific viscosity basis, with regard to adhesion—a key property for this type of water-soluble polymer.

Lap shear strength measurements have shown approximately 10:1 and 4:1 ratios in favor of the HVE/MA polymers as compared to PVP and MVE/MA, respectively. These differences are possibly due to the higher cohesive strength of the HVE/MA repeating unit and to the fact that this polymer would appear to contain more structural elements liable to make physical and chemical contributions to the interfacial attachment strength.

Based on these preliminary results MVE/MA and HVE/MA polymers were then applied to carbon fiber via electrodeposition and the effect of the respective polymer interphases on the interlaminar shear strength of unidirectional carbon fiber/epoxy laminates investigated. Both polymers led to a statistically significant improvement, but this was clearly more pronounced in the case of the HVE/MA polymer (+13 vs. +36%). Apart from the structural differences already mentioned in connection with the lap shear measurements, it is possible that the HVE/MA polymer surface may have been more amenable to wetting by the relatively polar epoxy matrix system used in this study, thereby contributing to better overall adhesive performance.

APPENDIX A

Wetting

The critical surface tension γ_c is defined as the critical value of surface tension below which a liquid drop will wet and spread, thereby forming a

zero contact angle on a substrate characterized by γ_c .¹⁹ It has been proposed that

$$\gamma_c (\text{adhesive}) < \gamma_c (\text{adherend})$$

in order that wetting and interfacial adsorption be fully accomplished.^{20,21} In the present case, the adherend is Anticorrosional B, used for the LSS measurements, and the adhesives are 50% aqueous solutions of the PVP, MVE/MA, and HVE/MA polymers. Adequate wetting should be possible in all 3 cases as one is comparing a "high energy surface," with an estimated γ_c of ≥ 500 dyne/cm, with aqueous polymer solution with γ_1 values of ≤ 100 dyne/cm.^{22,23} A corollary to the proviso given above is that the rheological properties of the adhesive should be such as to *allow* wetting to actually take place once the surface tension proviso is fulfilled. As only polymer pairs with practically identical specific viscosities were compared and the polymers were applied from aqueous solutions with the same concentration, possible differences in rheology should not have a significant effect on lap shear results.

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