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Adhesion behaviour of polyamic acid cured epoxy

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The adhesion behaviour or lack thereof, of polyimides is well known. The inherent brittleness of epoxy resins has also led to a search for additives to improve the physical properties of epoxy. In order to improve both of these properties, we utilized a unique strategy to cure a diepoxy (diglycidyl ether of bisphenol A) with a polyamic acid derived from oxydianiline and pyromellitic dianhydride. The polyamic acid synthesis was conducted in a low boiling point solvent consisting of tetrahydrofuran and methanol (80/20) and *not* traditional high boiling point aprotic solvents such as dimethylacetamide. This resulted in a material that had adhesion superior to both the pure epoxy and the pure polyimide. The state of cure was also seen to have an effect of the adhesion strengths. © 1997 Elsevier Science Ltd.

(Keywords: adhesive; epoxy; polyimide)

INTRODUCTION

Epoxy resins are inherently brittle due to extensive crosslinking and are typically quite poor adhesives. Polyimides (PIs) usually display poor adhesive properties and need to have an additional treatment or chemical adhesive applied to them whenever they are used in situations where good adhesive qualities are necessary[1]. The literature has many examples of epoxy adhesion, of which there are two quite thorough reviews. However, there is little in the way of epoxy modified with polymeric entities[2,3]. We have found that when epoxy is cured with a polyamic acid (PAA) solution both the physical properties of the epoxy and the adhesive strengths of the polyimides increases dramatically.

EXPERIMENTAL

PAA as a 10 wt% solution was prepared by reacting stoichiometric amounts of oxydianiline and pyromellitic dianhydride (PMDA) for 3 h. In a three-necked flask under a nitrogen purge, the diamine was first dissolved in 40–60 ml tetrahydrofuran/methanol (THF/MeOH, 8/2) solvent by mechanical stirring[4–6]. Upon complete dissolution of the oxydaniline, addition of the pyromellitic dianhydride as one batch resulted in a curd-like mixture. Continued stirring resulted in homogeneous solutions. To these solutions epoxy was added, and after homogeneity was achieved by mechanical stirring, solutions were cast onto steel plates. After evaporative solvent removal under ambient conditions, a copper backed Kapton® film was placed over the adhesive layer and the whole sandwich was cured in a press under 50 kg cm^{-1} pressure at 125°C for 1 h, and then for 2 h at 250°C to simultaneously cure the epoxy and imidize the PAA in the films. If additional dianhydride was added to the solutions it was added to the epoxy prior to addition to the PAA solution. All diamines and dianhydrides were purified by either sublimation or recrystallization from toluene prior to use. THF and methanol were used as received. A 180°C peel test was employed to test the adhesive strength of the epoxy–PI adhesive layer.

DISCUSSION

The cure cycle had some effect on the strength of the adhesive *Figure 2* shows that a two-stage cure is required for high adhesion strength. For most compositions, but most notably at 90/10, the single stage cure (250°C, 1 h) resulted in extremely low adhesive bond strength. This is attributed to the incomplete cure of the PI and the epoxy due to either the dearth of reactive groups contributed by the polyimide or the lack of mobility of the polymeric entity during cure. The PAA, at low percentages, has highly restricted mobility due to reaction with the epoxy network. At these compositions, an ester crosslinked network of PI and epoxy formed in the early stages of cure. Due to its polymeric nature dictating low molecular mobility and slow reaction kinetics, PAA does not act as an efficient hardening agent. Consequently, when short reaction times are used incompletely cured systems result. This is also due the hindering of molecular motion early in the reaction sequence forming a nascent epoxy network around the PAA molecules. Thus, a two

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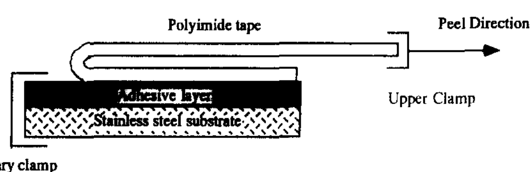

Figure 1 180°C peel test

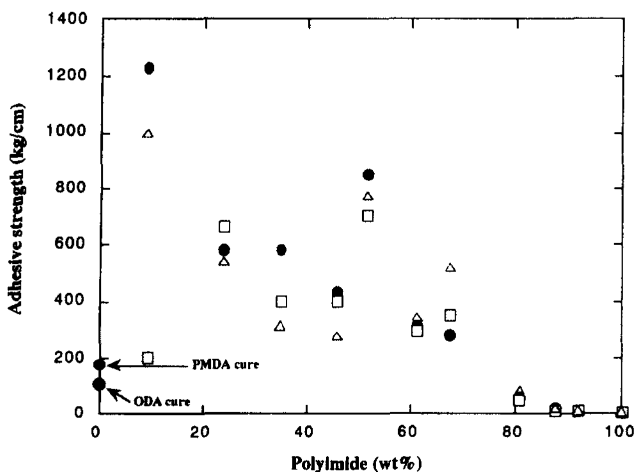

Figure 2 Results of 180°C peel adhesion tests for epoxy cured with PAA sytems (circles = cure for 1 h at 125°C, 2 h at 250°C, squares = cure for 1 h at 250°C, triangles = low molecular weight PAA, cure for 1 h at 125°C, 2 h at 250°C)

stage cure regime consisting of a low and high temperature stage is required for full cure of the epoxy and imidization of the PAA. This resulted in systems which exhibited good adhesive qualities.

The data in *Figure 2* demonstrate that longer curing times and less than 50% PAA are desirable, for these compositions have predominately higher adhesive strengths. Also, the longer the cure cycle, the better the adhesion of the epoxy-PI adhesive to the steel. The 90/10 (Epoxy/PAA) system had the highest adhesive strength of the systems tested (1230 g cm^{-1}). This large increase in the strength of the adhesive results is due to the reinforcement of the epoxy network by the highly disperse PI molecules[7]. The PI molecules could, at full cure, contribute to the increase in the toughness of the epoxy, via a fibrous reinforcement effect which would in turn influence the strength of the adhesive bonds of the material. However, the substantial improvement of all samples was not observed for all concentrations, so no general rule could be drawn.

It is also apparent from *Figure 2* that the PAA regardless of molecular weight or state of cure has little or no adhesive qualities. Only after the incorporation of 25% epoxy do samples show any but nominal adhesive strength (peel strength < 20 g cm^{-1}). This is not surprising, for the lack of any PI polymer–substrate chemical interactions prevents the polyimide from having any but mechanical interactions with a smooth steel surface.

It has been noted that stoichiometric systems generate the highest physical properties in epoxy resin systems[8]. There is a local maximum in *Figure 2*, at approximately 56/44, indicating that the polyimide and epoxy are interacting synergistically, which results in improved adhesion. Since the stoichiometry of the epoxy–polyamic acid systems could not be determined due to the spread in the molecular weight of the polymetric mixture (PAA equivalent hydrogen weight would be variable), this could be an indication of the maximum extent of reaction between the PAA and the epoxy. This could be an indirect measure of the system achieving the stoichiometric ratio. In fact, when this proportion of EP/PAA was tested using only a PI film as the adherent in the 180°C peel test, the strength of the adhesive exceeded the strength of the polyimide film and consistent results could not be obtained due to film tearing and breakage. Consequently, pure PI tapes were replaced by copper-backed PI tapes, because they demonstrated much higher tensile strengths than PI tape not backed with copper.

The higher strength of the systems high in epoxy content could, however, be attributed to the greater diffusion of the interdiffusion of the smaller and more mobile epoxy molecules or polyimide molecules into the Kapton® tape. This runs counter to the previous argument that the PI film was impervious to chemical attack, but there are few other reasons for the vast improvement in the adhesive strength of these systems. The system may also for a well bonded interfacial region between the individual polyimide molecules and the epoxy that could resist the forces of the adhesion test. However, the formation of these types of bonds is diminished with the addition of more PI, due to the intrinsic non adhesive capabilities of the PI itself.

The effects of the addition of additional hardener (PMDA) to the epoxy on adhesion properties can be seen in *Figure 3*. The addition of even small amounts of hardener resulted in the large improvement in adhesion strength. This occurs due to the phase separation noted in these systems. This phase separation was not noted in the epoxy–PAA systems without additional hardener[9]. However, this two phase morphology does not result in the toughening of the systems as observed in the epoxy–polyimide systems[7], so the fundamental reasons for this behaviour could not be elucidated. All systems showed poor adhesion to copper, which is indicative of the weakness of the strength of a metal carboxylate, if one forms at all, between the copper and the adhesive[10].

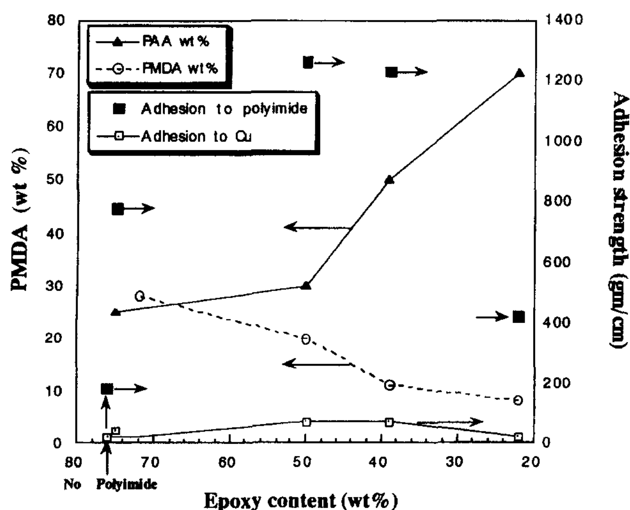

Figure 3 Synergistic effects of PMDA addition on adhesive strength (solid blocks = adhesion strength, polyimide/adhesive/steel, squares = copper/adhesive/steel, broken line = PMDA content wt%, triangles = PAA wt%)

CONCLUSIONS

The adhesive qualities of the epoxy were dramatically improved with the incorporation of a PAA as the curing agent. The increase in the adhesive strength is attributed to the improvement of the strength of the material and not to the presence of C = O groups in the PI/PAA. The material was seen to form a polyester-like graft copolymer at the concentrations which exhibited the largest adhesion strengths. Addition of additional PMDA resulted in the improvement of adhesion. The use of the THF/methanol solvent system and its ease of removal allowed the epoxy/ PI adhesive system to be fabricated.

ACKNOWLEDGEMENT

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RESULTS

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