

Adhesive Properties of Polyisophthalamides

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Synopsis

Poly(hexamethylene isophthalamide) was shown to possess good adhesive properties at temperatures up to 100°C. and under wet conditions. Poly(hexamethylene isophthalamide) was blended with both epoxy resins and plasticizers to give adhesive joints with strengths greater than that of the unmodified polymer. The adhesive bond strengths of the aromatic polyamides to aluminum in homologous series of poly(alkylene isophthalamide) increased with increasing diamine chain length.

INTRODUCTION

Polyamides have been used in blends with epoxy resins to furnish adhesives with high peel and shear strength.¹ Even when used alone as hot melt adhesives, various aliphatic polyamides such as nylon 6 and 66 have shown good adhesion to metals.² In scouting other polyamides, it was found that some products based on aromatic acids gave heat-resistant bonds. Of these aromatic polyamides, several based on isophthalic acid gave a good combination of heat and water resistance with high bond strength, and these are reported here.

EXPERIMENTAL PROCEDURES

Polymer Preparation

A series of poly(alkylene isophthalamides) was prepared by interfacial polymerization³ in which the alkylene group was varied from chains of 2-10 carbons.

In a typical run, poly(hexamethylene isophthalamide) was prepared by dissolving 5.81 g. (0.05 mole) of hexamethylenediamine in 250 ml. of water in a Waring Blendor. To the mixture was added 10.6 g. (0.10 mole) of anhydrous sodium carbonate. To the rapidly stirred mixture was added 10.1 g. (0.05 mole) of recrystallized isophthaloyl chloride in CHCl_3 . The mixture was allowed to stir for 10 min. The precipitate was filtered, washed, and stirred with water four times. The powder was dried at 100°C. for 15 hr. to yield 10 g. of polymer, $\eta_{inh} = 1.35$ (*m*-cresol, $c = 0.5$ g./100 ml.).

The other polymers were prepared in a like manner from the diamines: ethylenediamine (Eastman), trimethylenediamine (American Cyanamid), tetramethylene diamine, and decamethylenediamine (unknown sources).

Adhesive Joint Preparation

All adhesive joints had $1/2$ -in. overlap and were prepared by using 7075-T6 Alclad aluminum strips measuring $1 \times 3 \times 0.063$ in. which had been etched in sodium dichromate-sulfuric acid solution. The joints were formed by applying the powder to the aluminum surface, closing the joint, and heating at the appropriate temperature for the time indicated. Usually, six replicates were made. The thickness of the adhesive layer in the final joint was held to about 1 mil by shims. The joints containing the polymer layer were placed between two blank joints of the same thickness which had a 1-mil shim inserted between the metal surfaces.

The joints were pulled in tension on a Dillon universal tester at a 4-in. jaw separation and at a rate of approximately 0.2 in./min.

The peel tests used T-shaped joints made from etched 1100H14 aluminum measuring $1 \times 0.05 \times 6$ in. The adhesive was applied from the end for 2 in. along the surface. The unglued ends were then peeled back by hand to within 1 in. of the adhesive area to form the T joint. The joint was then pulled in an Instron tensile tester at 4 in. joint separation and at a rate of 0.2 in./min.

Adhesive Joint Testing

The resistance of the joints to water was tested in two ways. In one, the joints were placed in a beaker of water and boiled for several hours. In the other, the joints were placed in an autoclave and heated with live steam at 120°C . and 15 psig for varying lengths of time. The latter test was the more drastic of the two and was the one usually used for accelerated testing. After the water treatment, the joints were cooled to room temperature and their strength determined.

For testing the joints at higher temperatures, a U-shaped electric heater was placed around the joint as mounted in the tensile tester and the joint pulled at the temperature indicated.

RESULTS AND DISCUSSION

Melt Adhesives

The results (Table I) of preparing and testing the aromatic polyamides show that as the alkylene chain length was increased, the joint strength as tested at room temperature tended to increase.

Epoxy Blends

It has already been noted that aliphatic polyamides can be blended with epoxy resins to give adhesive joints which are much stronger than those produced using the polymer alone as a melt adhesive.^{1,4} Several of the polyisophthalamides showed similar improvement in blends with epoxy resins.

TABLE I
Melt Adhesives: Lap Shear Strength of Poly(alkylene Isophthalamides) on Aluminum

No. of carbons in alkylene chain	η_{inh}^a	Polymer melt temperature (PMT), °C.	Application conditions ^b		Lap shear strength, psi ^c	
			Temp., °C.	Time, min.	Average	Range
2	0.94	292-310	315	5	900	840-950
3	0.72	240-288	300	5	1500	1450-1640
4	1.05	230-245	300	5	2200	2040-2300
6	0.68	170-230	232	30	1800	1700-1900
10	0.79	166-194	232	30	3300	3160-3480

^a Inherent viscosity in *m*-cresol at 30°C. and $c = 0.5$ g./100 ml.

^b Lap joints on 7075-T6 Alclad etched aluminum $1 \times 0.063 \times 1/2$ in. overlap; joints formed at the temperature and for the time indicated using films of the polymer; thickness of the adhesive layer in the joint was 1-5 mils.

^c Joints pulled at 0.2 in./min., $4^{1/2}$ -in. jaw separation; room temperature; average of six replicates.

TABLE II
Epoxy Blends: Lap Shear Strength of Poly(alkylene Isophthalamide)-Epoxy Blends on Aluminum^a

No. of carbons in Alkylene chain	Application conditions		Lap Shear Strength, psi.	
	Temp., °C.	Time, min.	Average	Range
2	315	5	300	220-350
3	315	5	400	360-470
4	315	5	1000	400-1580
6	232	15	6000	5700-6440
10	232	60	5400	5050-6000

^a Blends were 100-mesh powdered polymer with Epon 828 in a ratio of ten parts of polyamide to one part of Epon 828. No added curing agent was used. The application conditions and method of testing were as described in Table I.

Most of the blends were made by using a powdered form of the polymer to which Shell's liquid epoxy resin Epon 828 was added and the two blended together by stirring and grinding in a mortar. The joint strength (Table II) of the blends could again be arranged roughly in order of the alkylene chain length in the polymer. It was seen, however, that the effectiveness of the epoxy resin in increasing the joint strength depends on the polymer selected: the polymers with ethylene, trimethylene, and tetramethylene chains showed reduced joint strengths; however, the poly(hexamethylene isophthalamide) blend showed a pronounced increase and gave joints with the highest strengths, equal to those of aliphatic polyamides.⁴

Plasticizer Blends

Since poly(hexamethylene isophthalamide) showed the greatest increase in joint strength when blended with epoxy resins, other additives were tried

with it. Several plasticizers, such as Monsanto's Santicizer 8 (*N*-ethyl-toluene sulfonamide) and Neville's Nevillac TS (coumarone-phenolic resin) also proved effective in improving the joint strength, but only the Nevillac blend maintained its strength at elevated temperatures (Fig. 1). The function of the plasticizer would be both to decrease the melt viscosity and thereby promote wetting of the surface, and to promote flexibility in the polymer so that the adhesive film would become more resistant to brittle failure. In the case of the Santicizer 8, it appeared that its effect was principally through the latter, for when the joints were allowed to age at 232°C. and the Santicizer slowly volatilized from the joint, it was seen (Fig. 2) that the joint strength dropped back again to about the value for polymer with no added plasticizer.

Water Resistance and Temperature Performance

Since poly(hexamethylene isophthalamide) gave the best epoxy joint strengths under ordinary test conditions, it was selected for comparison with the alcohol-soluble commercially available Zytel 61 nylon resin.

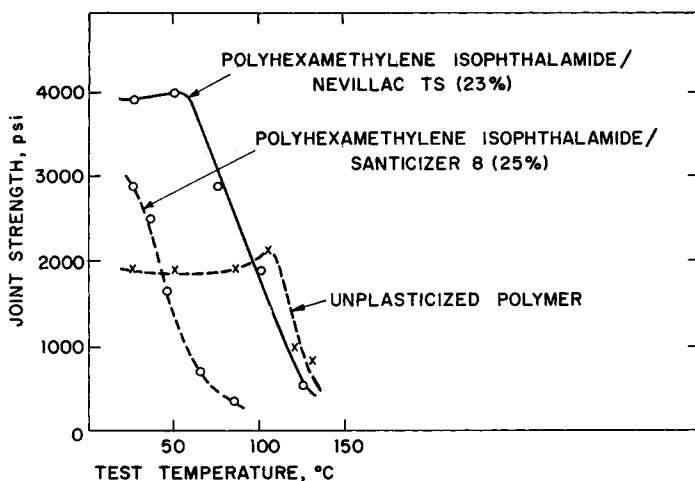


Fig. 1. Joint strength vs. test temperature for poly(hexamethylene isophthalamide) plasticized with Santicizer 8 and Nevillac TS.

For both epoxy-cured polyamides (Fig. 3), the point on the strength versus test temperature curve at which the strength dropped rapidly was near the T_g of each polymer [50°C. for Zytel 61 nylon resin and 110°C. for poly(hexamethylene isophthalamide)]. However, the temperature at which the loss of strength occurred should be rate-dependent, and the creep might become excessive at lower temperatures than that indicated on the curve.

The water resistance (Fig. 4) of the epoxy blends of poly(hexamethylene isophthalamide) was greater than that of the Zytel 61 blends. At least two effects may be operating here; one is the undercutting of the film of polymer

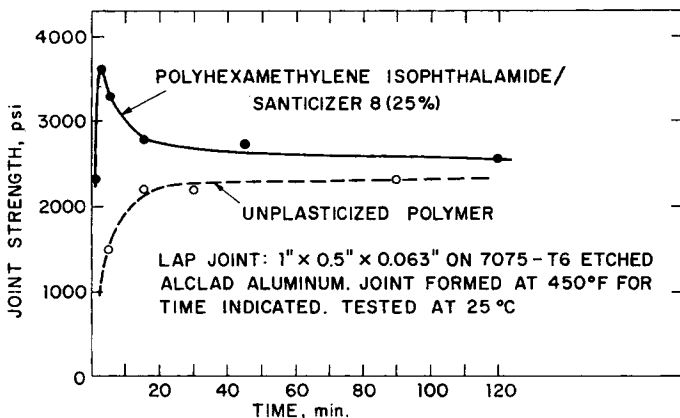


Fig. 2. Effect of dwell time on the joint strength of poly(hexamethylene isophthalamide) plasticized with Santicizer 8.

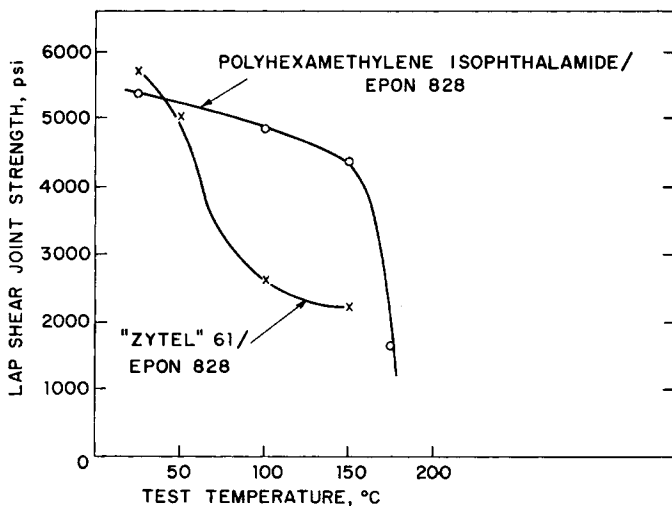


Fig. 3. Comparison of joint strength vs. test temperature for Epon 828 blends with poly(hexamethylene isophthalamide) and Zytel 61.

on the metal by the water, the other is a swelling and hydrolysis of the bulk polymer. It was noted that the blends of poly(hexamethylene isophthalamide) with Nevillac TS which were not crosslinked were inferior to those of the crosslinked polymer. This suggested that the entrance of water into the bulk of the polymer was important to the weakening of the adhesive joint.

The greater rigidity of the isophthalamide as compared to that of Zytel 61 appeared to lower the peel strength of the former. The peel strength of the Zytel 61 blended with 15 parts of Epon 828 and 1.5 parts of dicyandiamide was 115 lb./in., while that of poly(hexamethylene isophthalamide) with 10

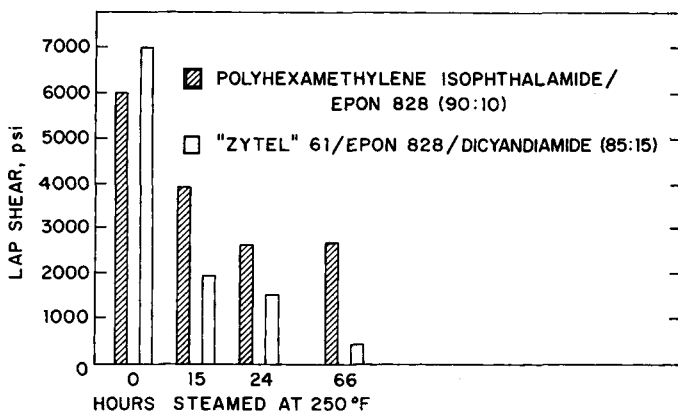


Fig. 4. Comparison of the water resistance of Epon 828 blends with poly(hexamethylene isophthalamide) and Zytel 61.

parts of Epon 828 was 45 lb./in. The latter value was an improvement over the peel strength of the poly(hexamethylene isophthalamide) applied without any additives.

References

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Résumé

Le polyisophthalate d'hexaméthylène-diamine possèdent de bonnes propriétés adhésives à des températures jusque 100°C et à l'humidité. Ce polyamide a été mélangé avec des résines époxy et des plastifiants en vue de former des joints adhérents qui sont plus forts que ceux à base de polyamide non-modifié. Les forces d'adhésion à l'aluminium de polyamides aromatiques isophthaliques croissent avec une augmentation de la longueur de chaîne de diamine.

Zusammenfassung

Polyhexamethylenisophthalamid besitzt bei Temperaturen bis zu 100°C in Gegenwart von Feuchtigkeit gute Adhäsionseigenschaften. Polyhexamethylenisophthalamid wurde mit Epoxyharzen und Weichmachern gemischt und lieferte Klebeverbindungen, deren Festigkeit grösser war als diejenige des nichtmodifizierten Polymeren. Die Klebefestigkeit der aromatischen Polyamide an Aluminium nahm in der homologen Reihe der Polyalkylenisophthalamide mit steigender Kettenlänge des Diamins zu.

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