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Effect of anhydride addition to alkyl cyanoacrylate on its adhesive bond durability

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Abstract—The effect of adding various anhydrides, such as succinic, maleic, phthalic, and pyromellitic anhydrides, to alkyl cyanoacrylate on the heat ageing and moisture resistance properties of the adhesive bonds is studied. Such an addition was generally found to improve the adhesion of alkyl cyanoacrylate to metals, in addition to providing other improvements. Maleic anhydride is the only one that appears to act as a crosslinking agent with cyanoacrylate, thus providing improved heat and moisture-resistant bonds.

Keywords: Bond durability; effect of anhydride; propyl cyanoacrylate.

1. INTRODUCTION

Durability is one of the most important aspects of the performance of any structural adhesive joint. The durability of an adhesive joint is the sum total of its responses to environmental effects. Cyanoacrylate-based adhesives have a reputation of poor durability, especially when bonding metal substrates [1]. However, on many plastic and rubber surfaces, the durability of these adhesives equals or surpasses that of the substrate [2].

Cyanoacrylate bonds readily lose strength when aged at temperatures below their glass transition temperatures (T_g's) and this is due to loss of adhesion to the substrates. Cyanoacrylate polymers are thermoplastic and therefore they soften as the temperature reaches their T_g; beyond the T_g, they begin to retro-polymerize. For these reasons the operating temperature of alkyl cyanoacrylates is limited to about 80°C. The operating temperature restrictions have prompted a number of attempts to improve these limitations by adding either crosslinking agents or heat-resistant adhesion promoters to the cyanoacrylate monomers. Crosslinking agents [4–9] improve the elevated temperature performance by raising the T_g of the polymer and thus suppressing the retropolymerization of the polymer. Crosslinking agents such as biscyanoacrylates and cyanopentadienoates are not available in sufficient quantity and are also costly. Heat-resistant adhesion promoters, which are usually anhydrides [10–13], improve heat ageing below the retropolymerization temperature of the adhesive by maintaining good metal adhesion. Unfortunately, these patents did not disclose sufficient data regarding the effect of the anhydrides on the heat and moisture resistance performance of cyanoacrylate bonds.

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Therefore, we report here quantitative data on the heat ageing and moisture resistance properties of the adhesive bonds formed using cyanoacrylates containing different anhydrides, between various metals and other substrates.

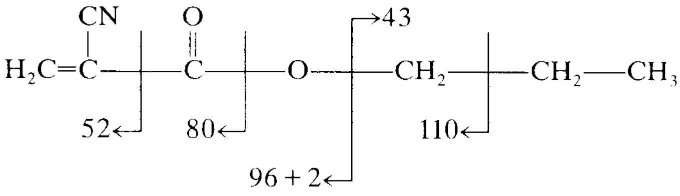
2. EXPERIMENTAL

All the raw materials used in this investigation were at least 98% pure.

2.1. Synthesis of n*-propyl cyanoacrylate (PCA)*

n-Propyl cyanoacetate was synthesized by reacting *n*-propyl alcohol (1.0 mol) with cyanoacetic acid (1.2 mol) in the presence of *p*-toluene sulphonic acid and benzene in an amount equal to the total weight of the reactants. The contents were heated to reflux and the course of the reaction was followed by the amount of water removed azeotropically and collected in a Dean–Stark trap. The reaction took 6–8 h for completion and during this period, 1 mol of water was collected in the Dean–Stark trap. The reaction product was washed to remove catalyst and unreacted cyanoacetic acid, and then dried over anhydrous sodium sulphate. Benzene was stripped off and the product was distilled under reduced pressure (b.p. 106–108°C at 10 mmHg, yield 70–75%). Purity 98% as determined by gas liquid chromatography (GLC); n_D^{30} 1.4040; d_4^{30} 1.0117.

n-Propyl cyanoacrylate was then prepared by condensation of the *n*-propyl cyanoacetate with paraformaldehyde in the presence of piperidine and potassium hydroxide (0.1% each, based on reactants) dual catalysts and using benzene in an amount equal to the reactants for azeotropic removal of water. The mole ratio of cyanoacetate to paraformaldehyde was maintained at 1.30. The reaction product, an oligomer, was then treated with polyphosphoric acid to neutralize the catalyst and decanted to remove the solid phosphates. The oligomer was then subjected to depolymerization at 150–240°C at 0.1–2.0 mmHg pressure. The crude monomer thus obtained was again redistilled for purification at 60–62°C (1–2 mmHg) and stabilized with 80–100 ppm sulphur dioxide and 100–150 ppm hydroquinone (yield 88%; purity 99.5% as determined by GLC; n_D^{30} 1.4314; d_4^{30} 1.0050. It was also characterized by ^{1}H-NMR (80 MHz Varian FT-80A NMR), ^{13}C-NMR (Bruker AM 300 MHz), and mass spectrometry (70 eV Micromass VG 7070, UK) methods. The ^{1}H- and ^{13}C-NMR spectra are illustrated in Figs 1 and 2, respectively. The mass spectral diagnostic fragments are shown below:



$$H_2C{=}\overset{\displaystyle CN}{\overset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$$

2.2. Adhesive mixtures

Adhesive mixtures were prepared by mixing (0.5% by weight) phthalic anhydride (PA), pyromellitic anhydride (PyA), maleic anhydride (MA), and succinic anhydride (SA) separately in PCA and were left for 48 h to obtain clear and homogeneous solutions of the adhesive. They were then used for bonding various substrates and their bond strengths were determined as described below.

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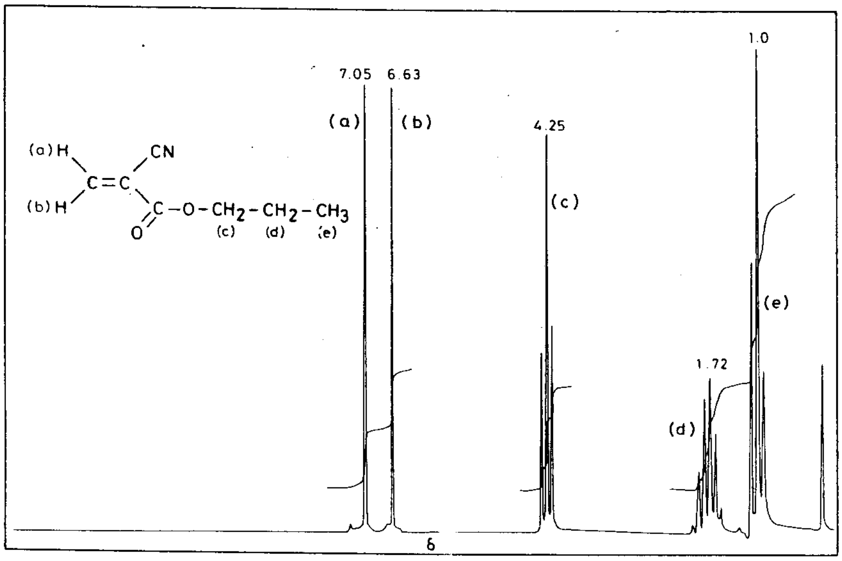

Figure 1. ^{1}H-NMR spectrum of propyl cyanoacrylate.

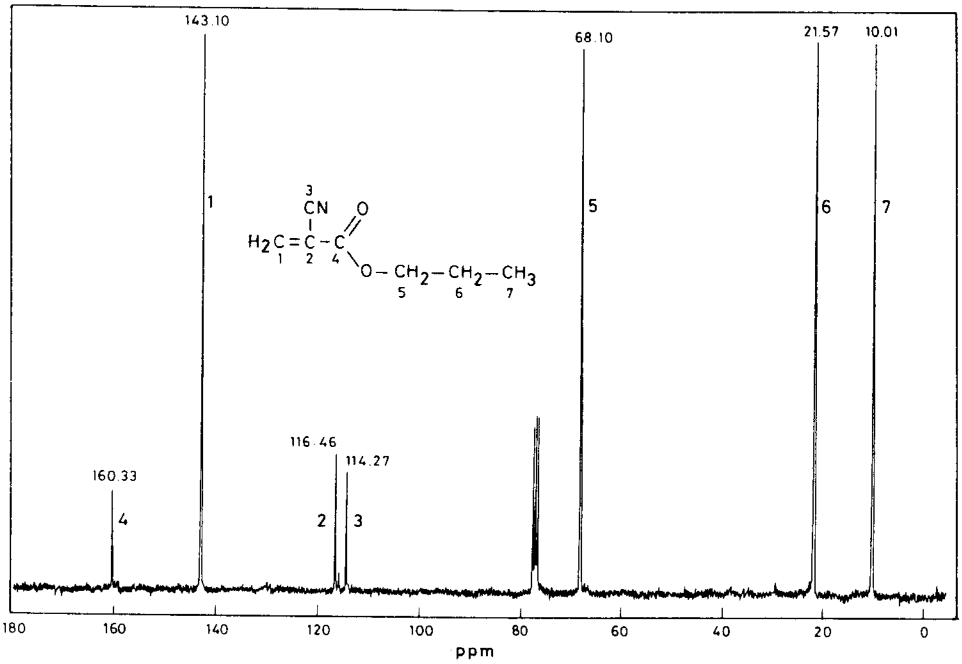

Figure 2. ^{13}C-NMR spectrum of propyl cyanoacrylate.

2.3. Tensile bond strength at different temperatures

Tensile bond strengths at different temperatures were determined according to the ASTM D 897-78 procedure, using pi-tension specimens and a Hounsfield tensiometer (UK). Surface cleaning is the most vital step in the bonding process as the adhesive bonds are extremely sensitive to surface contamination. Therefore, the pi specimens were cleaned with fine emergy paper (No. 120) and then wiped with dry acetone. Cyanoacrylate adhesive compositions (0.03 ml) containing different anhydrides (0.5 wt %) were placed on one of the pi specimens using a micropipette and another pi specimen was placed on top of it to spread the adhesive in a thin film. The glued specimens were left for 24 h at 25°C, then heated for 1 h at various temperatures (100–175°C), and thereafter cooled and tested for resistance to a uniform direct pull at 25°C (see Table 1 and Fig. 3).

2.4. Tensile bond strength at different humidities

The pi specimens were placed in a desiccator maintained at different humidities by placing in it appropriate mixtures of sulphuric acid and water [14] for 24 h.

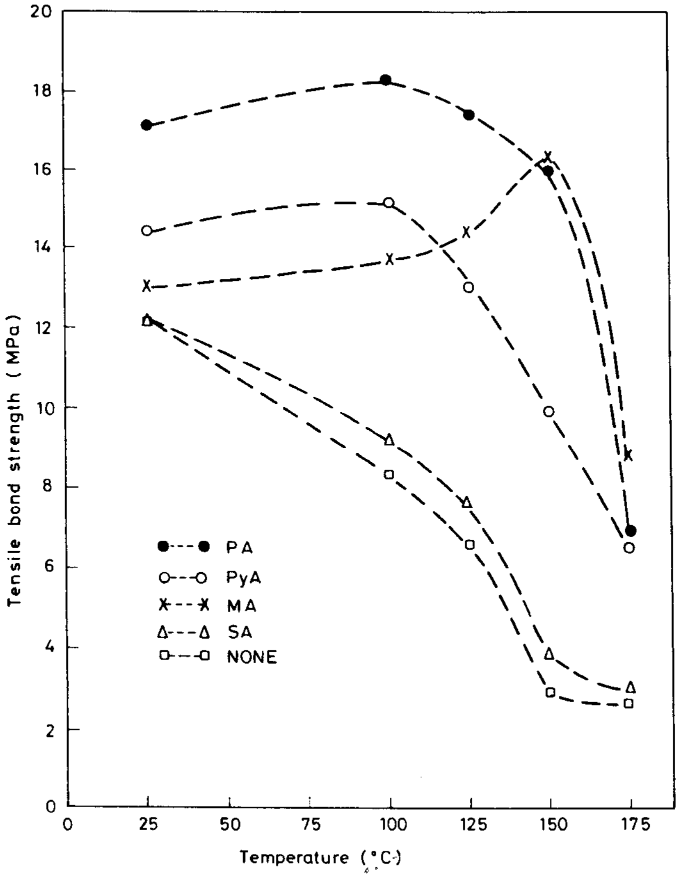

Figure 3. Tensile bond strength of propyl cyanoacrylate containing anhydrides at different temperatures (mild steel substrates).

Table 1.
Tensile bond strength (in MPa) of propyl cyanoacrylate containing different anhydrides at different temperatures

Substrate	Propyl cyanoacrylate with different anhydrides (0.5 wt %)				
	None	SA	PyA	PA	MA
(25°C)					
M–M	12.15	12.15	14.44	17.48	13.00
S–S	13.65	11.39	14.05	18.23	12.50
A–A	8.74	6.84	10.74	11.34	8.37
C–C	10.63	5.77	9.22	10.88	8.00
B–B	13.22	5.80	11.50	13.20	9.30
(100°C)					
M–M	8.29	9.12	15.19	18.23	13.79
S–S	8.00	9.29	15.90	18.60	14.05
A–A	6.21	6.46	11.56	12.90	9.10
C–C	5.10	5.69	10.05	12.00	11.88
B–B	5.60	4.77	11.77	16.90	10.44
(125°C)					
M–M	6.50	7.60	13.01	17.48	14.44
S–S	6.42	7.90	10.63	17.06	14.62
A–A	4.23	4.56	5.04	9.12	9.37
C–C	4.20	4.56	5.32	10.34	9.37
B–B	4.35	3.25	7.98	13.70	11.82
(150°C)					
M–M	2.80	3.80	9.90	15.96	16.33
S–S	3.12	6.12	9.12	15.80	18.27
A–A	2.10	3.34	4.64	6.32	10.62
C–C	2.10	3.80	4.18	4.88	8.70
B–B	2.50	2.32	6.45	7.30	13.08
(175°)					
M–M	2.66	3.00	6.45	6.84	8.74
S–S	2.50	3.38	4.56	7.50	8.32
A–A	1.00	3.04	3.56	5.84	7.08
C–C	1.00	1.52	3.02	3.04	3.80
B–B	1.00	1.42	1.52	2.28	4.56

A = Aluminium; B = brass; C = copper; M = mild steel; S = stainless steel; SA = succinic anhydride; PyA = pyromellitic anhydride; PA = phthalic anhydride; MA = maleic anhydride.

The specimens were then bonded with an adhesive composition as described earlier. The bonded specimens were left for 24 h in a desiccator and the bond strengths were determined according to the ASTM D 897-78 specification. The results are shown in Fig. 4.

2.5. *Impact bond strength at different temperatures*

The impact strength of an adhesive bond is the least force needed to break the bond in a single blow. It was determined by shear loading the specimens according to ASTM D 950-78. The lower and upper blocks were bonded with the adhesive compositions. After 24 h of bonding, the composite unit was placed

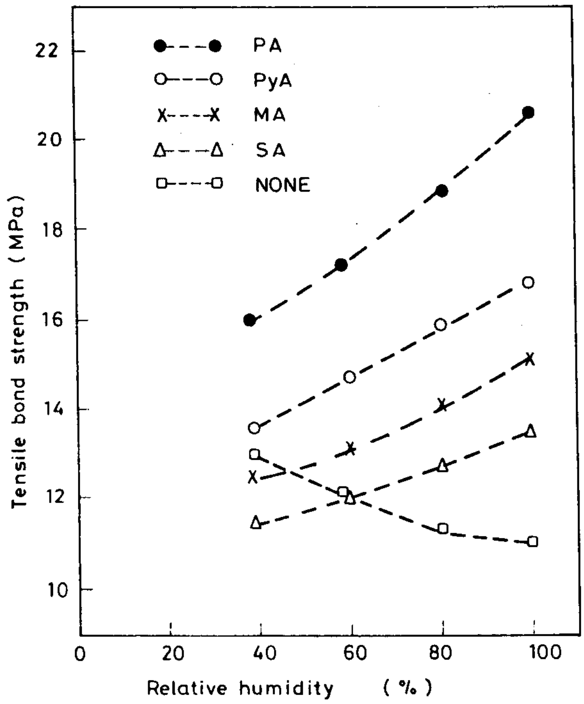

Figure 4. Tensile bond strength of propyl cyanoacrylate containing anhydrides at different humidities (mild steel substrates).

in a hot air oven at 100, 125, 150, and 175°C for 1 h and then cooled to 25°C and tested with an impact caused by a pendulum swinging at a known velocity of 335 cm s^{-1} along an axis parallel to the glue line. The results are shown in Fig. 5.

3. RESULTS AND DISCUSSION

3.1. Tensile bond strength at different temperatures

The tensile bond strength of unmodified PCA reduced gradually (12.15 MPa to 2.66 MPa) with an increase in the temperature from 25°C to 175°C (Fig. 3). This is an inherent limitation of PCA (or any alkyl cyanoacrylate), as has already been well established [1]. Addition of SA to PCA increased the bond strength slightly at all the temperatures over the unmodified PCA. Addition of MA to PCA improved the tensile bond strength up to 150°C; thereafter, the strength reduced. Addition of PA and PyA increased the bond strengths considerably: 17.5 and 14.4 MPa, respectively, against 12.1 MPa obtained from unmodified PCA at room temperature (25°C). At 100°C, the bond strengths increased further to 18.2 and 15.2 MPa for PA and PyA containing PCAs, respectively, as against 8.3 MPa for unmodified PCA. In all cases, the tensile bond strengths decreased after 150°C. Similar observations were also made when other substrate surfaces, e.g. mild steel, stainless steel, brass, copper and aluminium, were used. Increasing the amount of anhydrides from 0.5% to 1.0% in PCA had no significant effect on the bond strength, but the bond formation was slow.

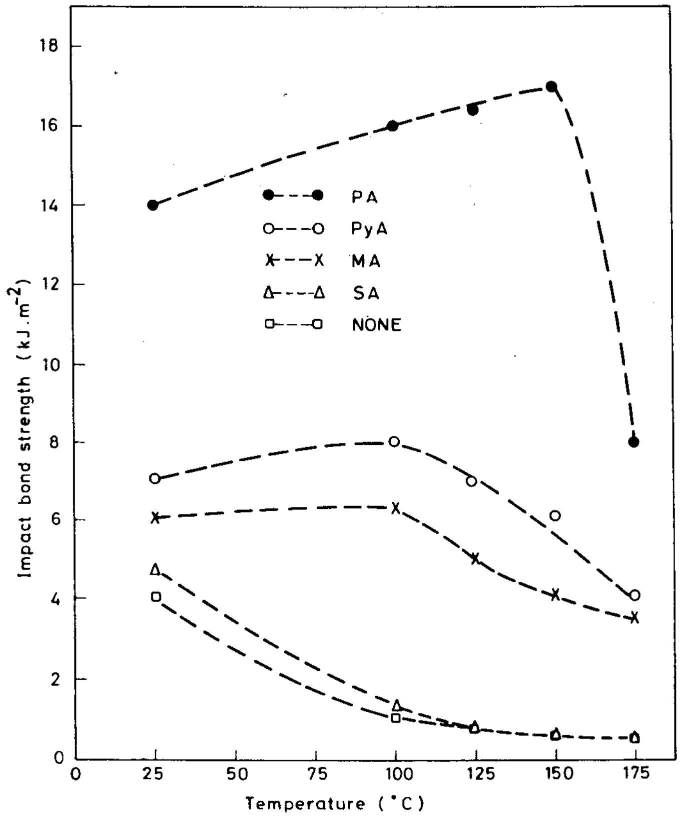

Figure 5. Impact bond strength of propyl cyanoacrylate containing anhydrides at different temperatures (mild steel substrates).

The improvement in adhesive performance can be attributed to improved adhesion due to the anhydride group complexing with the metal surface during bonding and/or co-reacting with cyanoacrylates during polymerization. This enhanced performance also implies that crosslinking is taking place with the unsaturation of MA. This is demonstrated by the increase in T_g of the modified polymer (140°C) as against that of the unmodified polymer (115°C).

We have also noticed from TGA studies that the decomposition temperatures of other anhydride-modified cyanoacrylates are the same as those of unmodified ones. Therefore, it is concluded that no crosslinking takes place in these cases.

3.2. Tensile bond strength at different humidities

With an increase in the humidity, the PCA bonds metal surfaces in a shorter time. It was also observed that the strength decreases with an increase in the humidity (Fig. 4). The cyanoacrylate bonds respond in several ways to high humid environments, as they are very susceptible to alkaline hydrolysis. This hydrolysis is further catalysed by the presence of metallic ions, generated due to mild corrosion, at the adhesive/metal interface.

The addition of anhydrides to PCA increases the humidity resistance by exhibiting higher bond strengths even at higher humidity levels. Of these anhydrides, PA gives the best humidity-resistant bonds. A probable reason for this performance is that the aromatic anhydride does not easily hydrolyse when compared with aliphatic anhydrides. Also, anhydrides will not allow the cyanoacrylate to hydrolyse by neutralizing the basic salts present on the metal surfaces.

3.3. Impact bond strength at different temperatures

At higher temperatures, the impact strength of unmodified PCA adhesive bonds decreased gradually due to the loss of adhesion. However, a substantial increase in the impact bond strength was noticed when MA was added to PCA. This increase is due to the stronger bonds developed due ot the crosslinking of MA with PCA. Other anhydrides, such as PA and PyA, also showed an improvement in the impact bond strength of PCA up to 100°C only; thereafter, the impact bond strength gradually decreased.

4. CONCLUSION

The addition of anhydrides to propyl cyanoacrylate improved the overall performance of their adhesive bonds towards heat and moisture.

Of all the anhydrides studied, maleic anhydride was found to be very effective in providing heat (up to 150°C), impact and satisfactory moisture-resistant bonds. The addition of phthalic and pyromellitic anhydrides to cyanoacrylates gave improved tensile and impact bond strengths up to 100°C. Addition of succinic anhydride produced a slight increase in the overall performance over unmodified cyanoacrylates.

Acknowledgement

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