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Work of Adhesion of the Adhesive Proteins in Aqueous Solution on the Various Solid Surfaces

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(Accepted for publication: December 17, 1992)

Abstract

The wettability of the adhesive model proteins and Chilean mussel (*Aulacomya ater*) in aqueous solution on high and low energy surfaces were examined by surface chemical approaches. From the results of the contact angle, the surface tension and the work of adhesion, lysine and glycine residues and less bulky residues adjacent to the lysine residues in the adhesive model proteins, were found to contribute to the adhesability of the surfaces. β -Structural conformation and cross-linking caused by tyrosinase enhanced the adhesability on the surfaces. The Chilean mussel adhesive proteins were concluded to have rational primary structure adhering to both the high and low energy surfaces.

(Received: November 9, 1992)

Effect of Adhesive Properties on Thermal Stress of Adhesive Joints

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(Accepted for publication: January 5, 1993)

Abstract

Most adhesives need curing at an elevated temperature and binding shrinkage is generated during the cooling process. The thermal stress due to the binding shrinkage is the cause of cracks and delaminations of adhesive joints. Hence, it is thought that the effect of adhesive properties on thermal stress must be cleared prior to application of adhesives.

In this study, thermal stress analysis of adhesive joints was performed by the boundary element method to examine an effect of elastic modulus and the coefficient of the thermal expansion of adhesives on the thermal stress.

As a result, the analysis showed that the elastic modulus of adhesives has an effect on both deformation and thermal stress of adhesive joints while the coefficient of the thermal expansion has an effect only the thermal stress of the adhesive layer. And it was clear that the main cause of thermal stress is a gap of the thermal strain between the adherends by the calculation of the axial force based on the solid mechanics. It was thought that the adhesive layer may transmit the shear stress between the adherends.

(Received: November 9, 1992)

Study of Acrylic Adhesive Surface Behavior by FTIR-ATR (Part 2)

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(Accepted for publication: April 1, 1993)

Abstract

Recently, a new surface and interface evaluation technology by FTIR ATR and FTIR-PAS applied to an acrylic model polymer with many carboxyl group, resulted in successful detection of carbonyl group depth-profile. Functional group orientation was analyzed. It was found that the surface layer was rich with more ester groups than carboxyl groups and at the air interface, depth-profile of carboxyl groups was changed. These results suggest that the carboxyl group penetrated into the adhesive layer.

(Received: October 1, 1992)

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Adhesive Properties of Polyimides Containing Ether Connecting Groups

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(Accepted for publication: April 2, 1993)

Abstract

Five kinds of polyimides were prepared from the reaction of 3,3', 4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) with five kinds of diamine-compounds containing ether connecting groups between aromatic rings.

Before heat-treatment these polyimides [except the polyimide (ASD/BTDA) derived from 4,4'-diaminodiphenylsulfide and BTDA] showed melting temperatures, and from this result it was found that polyimides containing ether connecting groups between aromatic rings were semicrystalline by DSC. After several kinds of heat treatment, the polyimide (TPE-R/BTDA) obtained from the reaction of 1,3-bis (4-amino phenoxy) benzene (TPE-R) and BTDA exhibited recrystallinity and two melting points; however, other types of polyimides didn't show melting temperatures at all.

Lap shear strength of TPE-R/BTDA, using stainless steel plates, perfectly maintained the initial strength after heat aging (260°C-1000hr) and thermal shock (260°C-30min, 0°C-30min), but fell to half value after pressure cooker test (105°C, 100%RH, 25.5KPa, 168hr).

(Received: February 25, 1993)

The Application of Thermally Stable Polymers to the Hot-melt Adhesives. I.

Mikio Kajiyama*, Hirofumi Sonoda*, Yasunori Hatano**, and Hiroshi Mizumachi*

Abstract

An aromatic polyamide and a polydimethylsiloxanepolyamide block copolymer were prepared by the direct polycondensation of (3-aminophenyl) (4-aminophenyl) ether (3, 4'-ODA), adipic acid (ADA), and carboxyl-terminated polydimethylsiloxane (PDMSA-diacid) in a triphenyl phosphite/pyridine system. Their thermal and mechanical properties were investigated by means of differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and measurements of adhesive shear strength. T-shaped peel strength, and creep response. They had maximum adhesive shear strength about 11 MPa around glass transition temperature and could be used up to 140°C.

**Storage Stability and Heat Resisting Property of Bismaleimide
and Epoxy Resin Modified by Aromatic Amines**

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(Accepted for publication: May 7, 1993)

Abstract

A homogeneous liquid with good storage-stability was obtained by heating the mixture of N, N'-4, 4'-diphenylmethane-bismaleimide (BMI), bisphenol F type epoxy resin (Ep830), and a small amount of aromatic amines (AA). For studying the mechanism of this reaction, N-phenylmaleimide (PMI), phenyl glycidyl ether (PGE) and aniline (AN) were used as model compounds for BMI, Ep830, and AA, respectively. Main reaction was the radical polymerization initiated by the charge-transfer complex formed between PMI and AN. The product $[(\text{BMI})_n]$ of this reaction had good compatibility with unreacted Ep830 and thus the mixture existed as a homogeneous liquid. The products of BMI/Ep830/AA after reacting for 1 minute or 1 hour were cured with the mixture of AA(HT-100B). On the beginning of curing, the tensile shear strength (at 160°C) of the cured resins modified 1 hour was higher than that of the cured systems modified for 1 minute.

(Received: March 25, 1993)

A Study on Heat Resistant Anaerobic Adhesives Containing N-Substituted Maleimide Compounds I. The Effect of Maleimide Compounds on Heat Resistivity

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(Accepted for publication: March 6, 1993)

Abstract

Anaerobic adhesives containing N-substituted maleimide compounds were prepared for developing high temperature adhesives, and their curing mechanism, heat resistivity of adhesion and thermal decomposition behavior of cured adhesives were investigated. N-phenylmaleimide, N-(p-hydroxyphenyl) maleimide, N-(p-carboxyphenyl) maleimide, N-laurylmaleimide, N,N'-(m-phenylene) dimaleimide, Mg salt of N-(p-carboxyphenyl) maleimide were used as the N-substituted maleimide compounds. Curing mechanism was as follows: methacryl double bonds polymerized predominantly at room temperature and maleimide and residual methacryl double bonds polymerized by heating at high temperature above 150°C to final cured state. As for the thermal properties of adhesives, it was found that the adhesives containing aromatic maleimide compounds showed excellent heat again resistance and higher adhesive strength at high temperatures than the adhesives not containing maleimide compounds. These properties were manifested from the diagrams of thermo-gravimetric analyses and activation energy of thermal decomposition of the cured adhesives. Among the aromatic maleimide compounds, differences of the effects of their substituent groups (o-, or p-) on thermal properties of adhesives appeared not clearly.

(Received: February 19, 1993)

Acetylene Terminated Polyimide Adhesive (Part 3)

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(Accepted for publication: April 16, 1993)

Abstract

The application of acetylene terminated oligomer polyimides (isoimide and fluorinated type) to high temperature adhesive is investigated.

Both sides coated film adhesive on polyimide film show both excellent high temperature adhesion and good storage stability.

Adhesive show excellent high temperature peel strength (1.3Kg/2.5cm) at 260°C as well as tensile strength. The temperature dependency curve of peel strength of neat resin slopes monotonously to the right, while those of prepregging glass cloth adhesive have the maximum at 200°C.

(Received: March 1, 1993)

High Temperature Strength of Butt Joints Bonded with a Reactive Inorganic High Temperature Adhesive

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(Accepted for publication: April 16, 1993)

Abstract

High temperature strength of butt joints bonded with a reactive inorganic high temperature adhesive was investigated. Joints were made for three different adherend materials, namely mild steel, stainless steel, and alumina ceramics. For each group, tensile tests were carried out at room temperature and at temperatures ranging from 300°C to 500°C. For each combination of the adherend materials and the test temperatures more than 25 measurements were made for statistical analysis.

For each material, the mean value of strengths became maximum at 450°C, but except for stainless steel the distribution of the strength significantly deviated from the normal distribution and appeared to separate into a weak group and a strong group. At room temperature and 500°C, the mean strength was relatively low but the distribution was nearly the normal.

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**A Simplified Design Process of the Adhesive/Rivet
or Bolt Combined Joints Based on Strength**

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(Accepted for publication: January 14, 1993)

Abstract

Certain assumptions are being made in the planning of a simplified design process of the adhesive/rivet or bolt combined joints based on strength.

First, it is assumed that there is no rivet (or bolt) hole near the edges of the overlap of an adhesive-bonded joint. Second, the rivet (or bolt) carries no load, if a failure of the adhesive-bonded joint does not occur. Third, even though the failure of the adhesive-bonded joint may occur, it is assumed that the rivet (or bolt) carries the total load and the joint does not collapse and therefore a fail safe design is able to be done. Fourth, the assumption is made that a simplified design of two independent joints (riveted joint and adhesive-bonded joint) is able to proceed, paying no attention to the other joints.

These assumptions are made justifiable by assigning lower values to the allowable stresses than pure theory would suggest. A simplified design process of the adhesive rivet or bolt combined joints makes a contribution to the development of the durability of the structural adhesive-bonded joint.

(Received: December 18, 1992)

Study on Application of Long Chain Dibasic Acid to Adhesives.

I. Copolyester Adhesives with Terephthalic Acid and Dodecanedioic Acid

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(Accepted for publication: February 1, 1993)

Abstract

Thermoplastic copolyesters with various compositions were synthesized by condensation polymerization of terephthalic acid, (TP), dodecanedioic acid (DDA) and ethylene glycol.

The peel strength of A1/A1 and polyester canvas/glass laminates using the copolyesters as adhesives were measured and the effects of composition, melting point and molecular weight of the copolyesters on the peel strength was investigated.

The results showed that the highest peel strength was obtained when the molar ratio of TP/DDA was about 0.6/0.4, at which composition of the copolyester was thought to be amorphous.

(Received: January 7, 1993)

**Properties of Epoxy Resin Cured by Phenol Novolac Modified with
N-*p*-Hydroxyphenylmaleimide-*n*-Butylacrylate Copolymer**

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(Accepted for publication: April 1, 1993)

Abstract

Phenol novolac/*N-p*-hydroxyphenylmaleimide-*n*-butylacrylate copolymer (HPMI0BuA) blends were used as an epoxy resin hardener. At first, two HPMI-BuA with different monomer ratios were synthesized. Second, the curing behavior of the above systems and the thermal and mechanical properties, especially toughness of the cured epoxy resin, were studied. Curing behavior was investigated by measurement of gelation time (JIS K 6910) and differential scanning calorimetry. As a result, it was not necessary to use a curing accelerator for this system, because HPMI-BuA caused acceleration of the curing reaction. Properties of epoxy resins cured with phenol novolac/HPMI-BuA blends were examined by flexural test, impact test, fracture toughness, and dynamic thermomechanometry. In case phenol novolac HPMI-BuA (monomer ratio, 1 : 1.1) (copolymer-1) blends were used as hardener, heat resistance of epoxy resin was improved by increasing the amount of copolymer-1 in the hardener and Charpy impact strength and fracture toughness of epoxy resin were improved although flexural strength was maintained. When novolac/HPMI-BuA (monomer ratio, 1 : 3.8) (copolymer-2) blends were used as hardener, Charpy impact strength, fracture strength, and flexural strength of epoxy resin were improved more than those of epoxy resin cured with novolac/copolymer-1, although heat resistance was a little inferior to that of epoxy resin cured with novolac.

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Shear Strength of Steel Plate Bonded with Adhesive for Use on Oily Surface

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(Accepted for publication: February 17, 1993)

Abstract

An epoxy type resin adhesive for use on oily surfaces was evaluated for shear properties. Two strengths of adhesive were measured i.e., the tensile shear strength of adhesive coated between two steel plates and the shear strength of the sheet prepared from adhesive only by a punch tool. Tensile shear strength was hardly influenced by oil thickness on adherent, and slightly changed with the curing temperature, having maximum strength at around 180°C. A similar tendency was also observed in the punch tool test, and the test specimen of the tensile shear was fractured within the adhesive, i.e., cohesive failure. Thus, it was proven that the bonding on the oily surface was strong enough and tensile shear strength depended upon the shear strength of the adhesive itself.

(Received: November 24, 1992)