

SYNTHESIS AND CHARACTERIZATION OF TWO-COMPONENT ACRYLIC BASED ADHESIVE VIA FREE RADICAL POLYMERIZATION

By

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Abstract

Reactive acrylics are two-component 100% reactive systems, based on methacrylate and acrylate monomers that were polymerized free-radically. The cure of acrylic adhesive was initiated by a two part redox reaction system. In this work properties of acrylic adhesive were analyzed by changing the concentration of monomers keeping the concentration of all other ingredients (additives) constant. It was examined that curing time, viscosity, peel strength and shear adhesion failure temperature were changed when concentration of monomers changed. Additives were also added during polymerization to improve the properties of acrylic adhesive.

Keywords: Reactive system, free radical, redox system, initiator, curative, curing time, viscosity, peel strength, additives, MMA (Methyl Metha Acrylate), MA (Methyl Acrylate), PMA (Poly Methyl Acrylate), PMMA (Poly Methyl Metha Acrylate).

1. Introduction

Curing acrylic adhesive can be defined as reactive, cross linked high strength structural adhesives that cure by way of free radical initiation. Reactive acrylic adhesives are based on acrylic and methacrylic monomers, and polymerise free-radically similar to catalysed anaerobic adhesives (1). However, very substantial differences exist. Whereas the monomers in anaerobics are predominantly difunctional or trifunctional ignored to achieve highly cross linked thermoset system, reactive acrylic are based mainly on monofunctional monomers, e.g., methyl methacrylate or methylacrylate.

Acrylic structural adhesives are relatively new products compared to epoxies or urethanes adhesives. Reactive acrylics are differentiated from other two component adhesive systems like epoxies or urethanes by the fact that the cure is catalytic, relatively insensitive to the amount of catalyst used and does not depend on mixing precise stoichiometric amounts of adhesive and catalyst.

These adhesives will be extremely useful in demanding plastic and metal bonding applications where fixture times of a few minutes and strong, impact resistant bonds are required (2). Applications include fiberglass and sheet steel bonding, magnets, loudspeakers, sporting goods, miscellaneous metal and plastics assembly, particularly when fast curing with no surface preparation is desired. Reactive acrylics have been very successful in applications such as bonding automotive bumpers (3) and assembling boats (4).

These adhesives have never that achieved the market penetration many people anticipated. Because of following defects, unpleasant odours, Low hot temperature strength, Toxic, Flammable, Limited open time. In this experimental work different types of additives were added to improve these defects.

2-Experimental

2.1. Chemicals

Monomers methylacrylate (99.5%), Methyl methaacrylate (99.5%) and benzyl peroxide as an initiator (99.5) were purchased from Fisher Scientific UK limited. polybutadiene as a hardener was obtained from Jameco (Karachi bazaar). N, N-dimethyl-p-toluidine (99%) acts as an accelerator was bribed from Alfa-Aesar. To improve the biochemical properties of adhesive, particulate filler, Titanium oxide was purchased from Fluka chemicals.

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2.2 Preparation of acrylic adhesive

Reactive acrylic adhesive was prepared by free radical polymerization mechanism. Methyl methacrylate, methyl acrylate, N, N-dimethyl-p-toluidine, and polybutadiene were mixed together in a beaker. Monomer ratio was changed from 1 to 10. The syntheses were carried out with reflux condenser, stirrer and thermometer. The initial charge in 250 ml, glass reactor was mixer and initiator and titanium oxide was heated to 75 C for 45 minutes. Chains with double bond converted to single bond, heat was generated as an exotherm, and the adhesive cure. The cure of acrylic adhesive was initiated by a two part redox reaction system. One component of the redox system was present in the base component of adhesive called initiator, and second component was present in the curing component called accelerator. Adhesive was prepared by the reaction of mixer with initiator and stirring at 200 rpm for 45 minutes.

3-Measurements

3.1. 180° Peel strength

The peel strength was measured using LLOYDS UK machine (Model LR5K plus) at room temperature. The Specimen for the peel strength test was cut to a 25 mm width and length 20mm attached to the stainless steel substrate. A 2-kg rubber roller was passed twice in order to press the specimen onto the stainless steel surface. The measurements were carried out at an angle of 180° with a cross head speed of 200 mm/min at 25 C according to the ASTM D3330.

3.2. Viscosity

The viscosities of the acrylic were assessed with Brookfield Model DV-II+Pro viscometer with spindle No. 2 at 25 °C. Containers of same cylinder-shape and 500-ml-capacity were used to reduce effect of resistance by the surface.

3.3. Shear Adhesion Failure Temperature

For the shear adhesion failure temperature (SAFT), the acrylic adhesive samples were pressed onto stainless steel. (Bonding area 25mm × 25mm) by two passes of a 2-kg rubber-roller. The specimens were placed in an oven, and a 1-kg weight was then hung from the end of the sample. The temperature-dependent pull away of the adhesive sample from the plate was measured in heating oven at temperatures ranging from 10 to 250 °C at a heating rate of 0.5 °C/min.

3.4. Environmental Resistance

All values were generated on steel lap shears as described in ASTM D 1002. Adhesive was cured at room temperature for 24 hours prior to environmental exposure. Test pieces were assembled with no induced gap and subjected to continuous exposure for 500 hours at the testing temperature and then the shear strength was tested at room temperature.

4. Results and Discussion

Peel strength versus concentration of methyl methacrylate (MMA) of the adhesive is shown in Figure-1 for polybutadiene containing samples. It was seen that increasing concentration of MMA from 10 to 70 weight percentage has significant effect on peel force. While further increasing the concentration of MMA from 80% to 90% peel strength decreases. As free radical

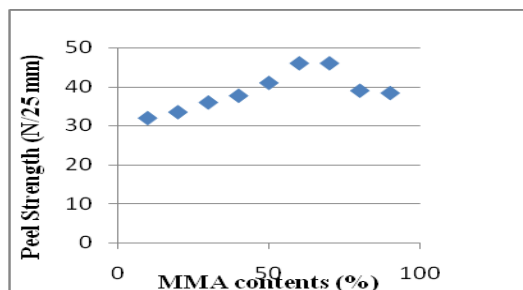


Fig: 4.1 Graph between peel strength and Methyl methacrylate contents

polymerization takes place, chains of (Poly methyl methacrylate) PMMA are grafted through methylacrylate and act a bridge between the chains. Polymerization and grafting of chains occur immediately. In this polymerization reaction methylacrylate (MA) is a limiting reactant while methyl methacrylate (MMA) is an excess reactant. Above the 70% contents of MMA, only MMA polymerizes to form long chains and no grafting takes places between the chains owing to absence of MA. That is why peel strength decreases above 70% contents of MMA.

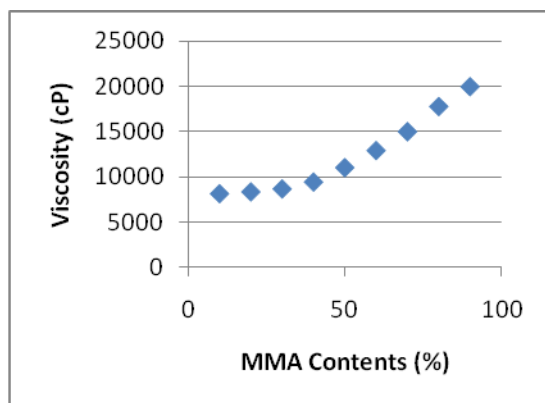


Fig: 4.2 Graph between Viscosity and Methyl methacrylate contents

The polymerization of methyl methacrylate in solution is followed by a marked deviation from first order kinetics in the direction of an increase in reaction rate and molecular weight termed gel effect [5]. The effect is particularly enounced with metyl methacrlate. It is independent of initiator and is due to decrease in the rate at which the polymer molecules diffuse through the viscous medium, thus lowering the ability of two long chains radical to come together and terminate. The decrease in termination rate leads to an increase in overall polymerization rate and in molecular weight. As molecular weight increases viscosity will also increase. As methyl methacrylate (MMA) contents increase viscosity will also increase as shown in fig-4.2.

As viscosity increases adhesion will also increase. Shear adhesion failure temperature is a function of adhesion. More is the adhesion more will be the temperature resistance as show in fig 4.3

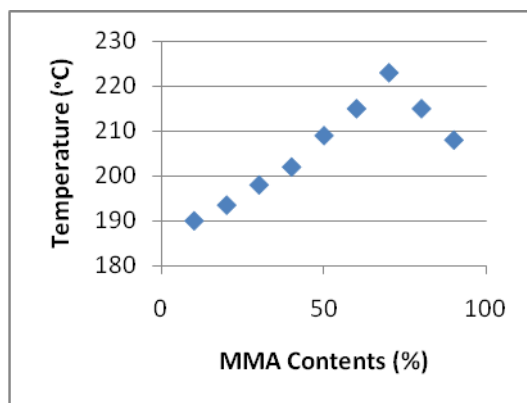


Fig: 4.3 Graph between Shear Adhesion Failure Temperature and Methmethacrylate contents

The peel strength is higher the room temperature control because heating the adhesive solvent evaporates causes it to become more rigid, resulting in a higher strength. But further increase in temperature viscous forces between the layers become weak and causes decrease in strength as shown in fig 4.4

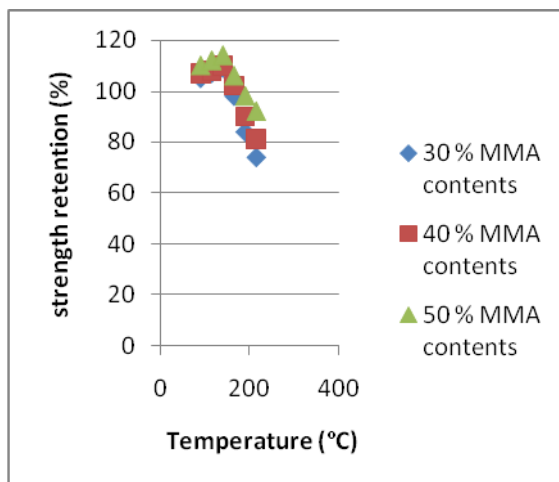


Fig: 4.4 Graph between strength retention and temperature

5. Conclusion

It was observed that properties of acrylic adhesive were affected by varying the ratio of MMA and MA. MMA had a significant effect on peel strength. This was explained on the basis of grafting of MA between the chains of PMMA. Viscosity of acrylic was exponentially increased with increase of MMA contents. This was explained on the basis of autoacceleration or gel effect. Gel effect reduces the termination rate of polymerization. Termination is in fact diffusion controlled for most liquid phase polymerization, even at low conversion, the dependence of diffusion rate on the viscosity of medium leads to the gel effect at higher polymer concentrations, with high-molecular-weight polymer, or in the presence inert solutes increasing the viscosity of medium. It was also observed that viscosity had significant effect on the adhesion.

6. Acknowledgement

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