

A Novel Polyurethane Sealant Based on Hydroxy-Terminated Polybutadiene

M. Patri, S. K. Rath, U. G. Suryavansi

Naval Materials Research Laboratory, Addl. Ambernath, Ambernath 421506, Maharashtra, India

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ABSTRACT: A novel two component polyurethane sealant has been prepared. Component A, known as prepolymer, is synthesized by capping hydroxy-terminated polybutadiene (HTPB) with toluene diisocyanate. Component B, known as hardener, comprises of a polyol (polyoxypropylene triol) as crosslinker and 4,4'-diamino-3,3'-dichlorodiphenylmethane (DADCDPM) and 4,4'-diamino-3,3'-dichlorotriphenylmethane (DADCTPM) as chain extenders and

fillers. Evaluation of mechanical properties and aging studies indicate that the sealant has excellent mechanical properties and stability in different environment. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 884–890, 2006

Key words: polyurethane sealant; mechanical properties; aging properties; hydrolytic stability

INTRODUCTION

Urethane polymers are good candidates for sealant and adhesive applications because of a number of outstanding properties,^{1–3} such as excellent elasticity and consequently a high recovery, low temperature flexibility,⁴ formulation flexibility, excellent adhesion with a variety of substrates, hydrolytic stability etc. Hence, they find application in diverse fields, such as heavy-duty service in buildings, highways, runways, aircraft parking places, and marine applications.

There are two main classes of urethane sealants: one- and two-component types. One component sealants comprise urethane prepolymers terminated with isocyanate groups, which crosslink in situ with surrounding moisture (mainly from the air). In two component urethane sealants, an isocyanate-terminated prepolymer is first formed and subsequently converted to a high molecular weight elastomer by further reaction with the second component that contains an active hydrogen. The active hydrogen compound can be either alcohol or amine. The properties of the two-component cured sealants cover a wide range of hardness and elasticity.^{4–7} Urethane elastomers are of either polyester or polyether type. The main difference is in the oligomeric compound used as the building block of the urethane polymer.

Hydroxyl-terminated polybutadiene, a low molecular weight reactive liquid, is mainly used as binder in propellant industries. Polybutadiene-based polyurethane elastomers have been found to have excellent

hydrolytic stability, low moisture permeability, good low-temperature characteristics, high elasticity, and superior chemical resistance.^{8–12} Use of polyurethanes based on hydroxyl-terminated polybutadiene as an efficient adhesive,^{13,14} and sealing material^{15,16} has been reported. Terminal hydroxyl groups present in hydroxy-terminated polybutadiene offers broad formulating options to the sealant manufacturer. Several key attributes are responsible for the formulating advantages of hydroxy-terminated polybutadiene resins. The resin end groups are predominantly primary allylic hydroxyl groups. These groups have high reactivity with a variety of isocyanates to yield polyurethane adhesives and sealants. The hydroxyl functionality of these resins are typically 2.4–2.6 per polymer chain. Hydroxy-terminated polybutadiene resins have a hydrophobic, nonpolar backbone, which impart hydrolytic stability to products prepared from it. The stability properties surpass those of polyurethanes prepared from other polyols that have ester or ether linkages, which are more hydrophilic and easier to hydrolyze. Another attribute of polyurethane systems based on hydroxy-terminated polybutadiene resins is their outstanding low temperature properties. This characteristic is attributable to the rubbery polybutadiene backbone. Urethane sealants are customarily modified by the addition of plasticizers, fillers, and adhesion promoters.^{17–19} Obviously, proper choice of chemical building blocks for the urethane elastomer is of primary importance.

In the present study, a two-component polyurethane sealant based on hydroxy-terminated polybutadiene has been developed. Component A, known as prepolymer, is an adduct of toluene diisocyanate with hydroxy-terminated polybutadiene, while component

Correspondence to: M. Patri (mrpatri@rediffmail.com).

B (known as hardener) comprises of amines as chain extenders, polyol as crosslinker and reinforcing filler. Synthesis of prepolymer having good stability has been established. The formulation of sealant components has been optimized and patented.²⁰ The sealant prepared from the mixture of component A and component B has been tested for their tensile, adhesion, and aging properties. Test results indicate that the developed sealant has excellent mechanical properties and is resistant to various environments.

EXPERIMENTAL

Materials

Acetic anhydride, benzoyl chloride, diethyl amine, and pyridine (all A.R. grade) were obtained from S.D. Fine Chemicals. Toluene diisocyanate (TDI) from Emmerck was used as received. Hydroxy-terminated polybutadiene (OH value 50) was procured from ORION Chem Ltd., India. 4,4' diamino 3,3' dichloro diphenyl methane (DADCDPM) was obtained from Jay Elastomer, India. Synthesis of 4,4' diamino 3,3' dichloro triphenyl methane (DADCTPM) was established in the laboratory and the process is patented.²¹ Polyoxypropylene triol (OH value 33), an adduct of trimethylol propane, was procured from Viswat chemicals, India.

Prior to synthesis, all the components, polyoxypropylene triol, hydroxy-terminated polybutadiene, DADCDPM, DADCTPM, and the filler were vacuum dehydrated to moisture content less than 0.05%. The equivalent weight of polyoxypropylene triol and hydroxy-terminated polybutadiene was calculated on the basis of OH value determination by the acetylation method.²²

Synthesis of prepolymer

The prepolymer from TDI and hydroxy-terminated polybutadiene was synthesized at 80°C in a three-necked flask equipped with mechanical stirrer. The molar ratio of NCO to OH groups was 2.1:1. The reaction was carried out for three hours under a dry nitrogen blanket. The resulting prepolymer was stabilized with 0.05% of benzoyl chloride, both to prevent runaway reaction and to improve its stability. Isocyanate content in the prepolymer was determined by titration with diethyl amine.²² The NCO value was 3.38% compared with the theoretical value of 3.54%. The prepolymer synthesized has a viscosity of 30–35 Pa s at 25°C.

Viscosity measurement

The viscosity of the prepolymer was determined by cone-plate method with Haake Rheometer (model no Haake roto visco RT-20) at 25°C.

Preparation of hardener

Three different formulations of hardener were prepared using DADCDPM, DADCTPM, and 50:50 ratio of DADCDPM and DADCTPM. The ratio of amine to polyol and the amount of filler were maintained as established earlier.²⁰ In a typical example, 40 g of DADCDPM (equivalent weight 133.5) was dissolved in 53 g of polyol (equivalent weight 1700) at 140°C. 7 g of carbon black was added to the mixture to form a paste. The paste was ground in a digital muller to a Hegman gauge particle size of less than 5 μm . Similar procedure was adopted for other compositions. The amine values of the hardeners were determined by pH metric titration as per ASTM D2073.

Preparation of sealant

The sealant was prepared by mixing stoichiometric amount of hardener with the prepolymer. After thorough mixing, the mixture was cast on a Teflon mold to form a slab of the sealant.

Curing of the sealant

The sealant was cured in three stages. The prepared slab was left for 24 h at room temperature. Then post curing was done at 80°C for 8 h. It was finally kept at room temperature for 48 h for further post curing. The sealant obtained is thus ready for testing.

Determination of pot life of sealant

About 30–50 g of prepolymer was weighed into a beaker and hardener is added stoichiometrically. The mixture is stirred in a beaker for 3–5 min with a mechanical mixer, at the same time making a record of the beginning of stirring. The well-stirred mixture is spread uniformly with a knife every 10–15 min on a metal or glass plate previously degreased with petroleum ether. The testing is carried out at an ambient temperature and a relative humidity of 70%. The result of the testing is assumed to be the time until when the sealant becomes incapable to be spread uniformly over the surface.

Sample preparation for rubber to sealant adhesion test

The procedure adopted for evaluating rubber to sealant adhesion is as follows: Surface preparation of the rubber samples (160 × 25 × 4 mm³) was carried out by abrading it with emery paper followed by cleaning and degreasing the surface with petroleum ether. The sealant was applied onto the freshly prepared surface. The sealant was reinforced with a strip of stainless wire mesh. A

TABLE I
Effect of Amine Structure on Pot Life

Amine ^a	Pot life (min)
DADCDPM	25 – 30
DADCTPM	120 – 125
DADCDPM + DADCTPM (50:50 mole ratio)	50 – 60

^a 35% amine in each case.

second coat of the sealant was applied. The curing of the adhesive sample was carried out in the same manner as the curing of the slab mentioned above.

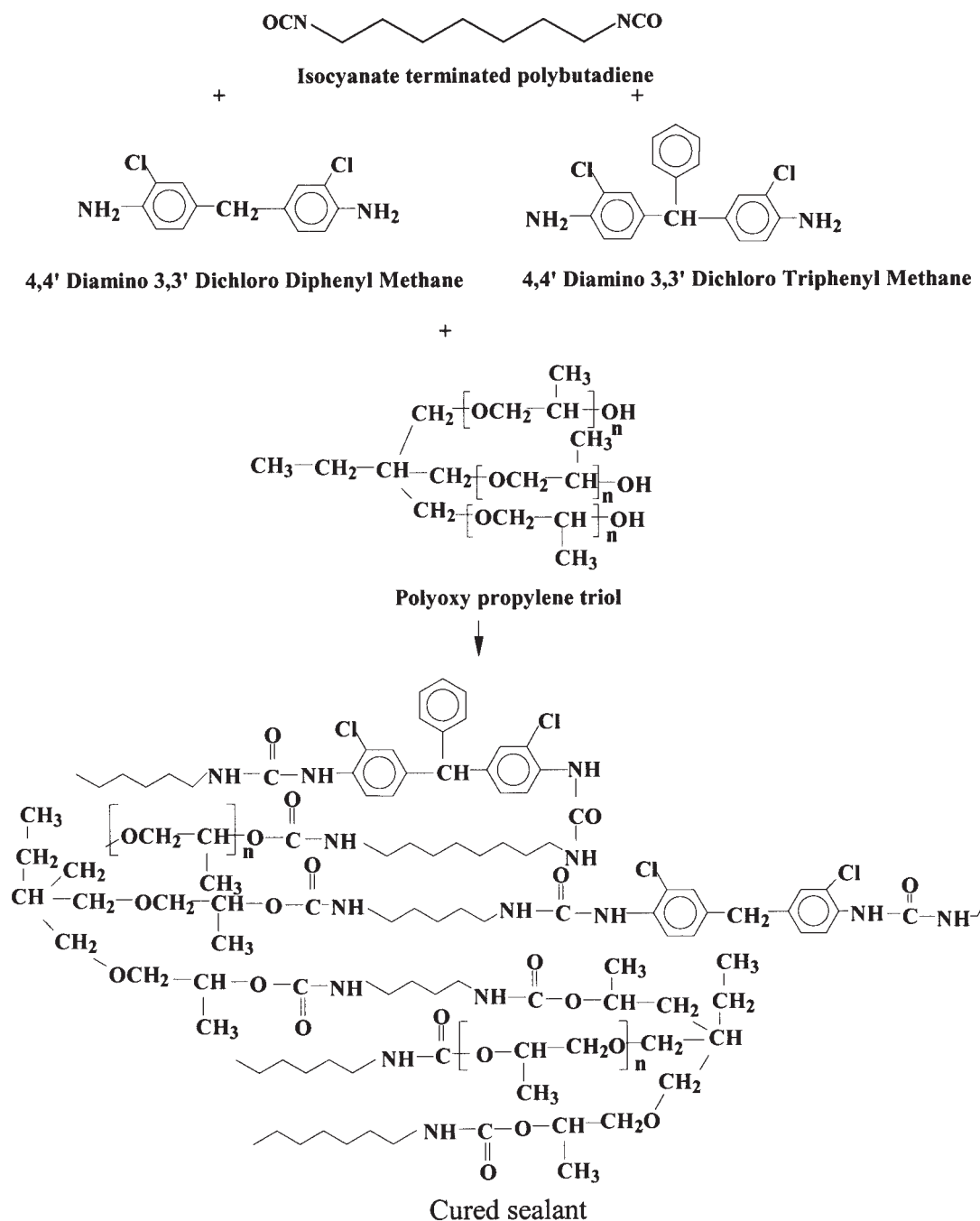
Aging test

The adhesive samples were subjected to the following aging conditions:

1. At 80°C for 40 days.
2. In sea water for 40 days.
3. Open air for 40 days.

Tensile testing

Dumbbell-shaped tensile specimens were prepared from the cured sealant slab. The test was carried out as



Scheme 1 The chemistry of curing of sealant.

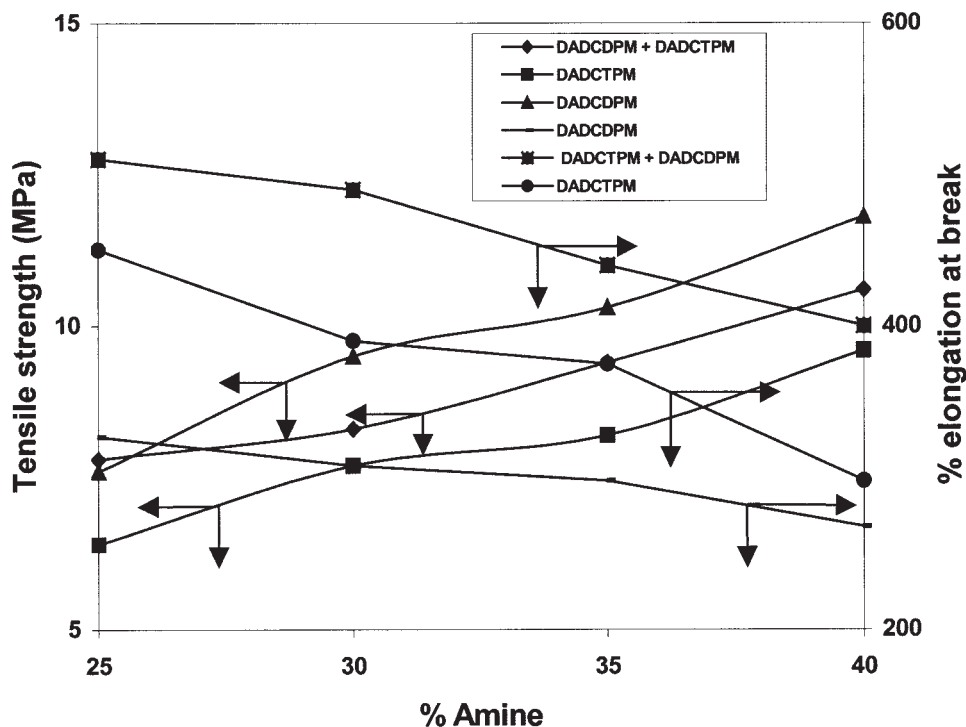


Figure 1 Tensile properties of the sealant versus amine percentage.

per ASTM D638 in a Hounsfield UTM (model no 50K-S). The crosshead speed was kept at 500 mm/min.

Adhesion test

Peel specimens are formed from a rubber substrate and the sealant reinforced with a strip of stainless steel wire mesh. Once cured, the wire is folded back 180 degrees and peeled at the rate of separation of 100 mm/min in the Hounsfield UTM as per ASTM D903 peel test.

RESULTS AND DISCUSSION

Stability of prepolymers, particularly of those having low isocyanate content (3–4%), is generally poor. Because, little amount of moisture ingress would react with the isocyanate group resulting in increase in viscosity of the prepolymer. To improve the storage stability of the prepolymer, there are several types of stabilizers reported in literature. The most frequently used are the Lewis acid type,²³ benzoyl chloride, acetic anhydride, and monoisocyanates.²⁴ In the present case, benzoyl chloride has been used as the stabilizer. Having the reaction mix on the acid side slows the reaction, while a basic mixture causes the acceleration of the rate of reaction of isocyanate with urea and hydroxyl groups. Neutralization of basicity does promote package stability. Hence, use of benzoyl chloride, a volatile Lewis acid, prevents runaway reactions

during processing and improves package stability of the prepolymer. Because the later is important, and so that the reaction will proceed expeditiously, most of the benzoyl chloride is added at the end of the reaction. In the package, benzoyl chloride remains a strong Lewis acid. On exposure to moisture, it forms benzoic acid and HCl.

Two types of amines have been used as chain extender. Selection of diamines is purely based on their structure. Thus, it may be noted that in both the diamines, chlorine is present in ortho position to amino group. Chlorine being electron withdrawing in nature will reduce the electron density on the nitrogen atom, thereby reducing the basicity relatively compared with aromatic diamines. This, in turn, will reduce the reaction rate between isocyanate and amine resulting in longer pot life. From the pot life values in Table I, it can be seen that use of DADCDPM has provided pot life of 25–30 min, whereas the pot life of DADCTPM-based polyurethane (PU) has pot life of 120–125 min. This result indicates that presence of additional phenyl group has further reduced the basicity resulting in increase in the pot life. Use of 50:50 of both the amines has provided reasonable pot life (50–60 min).

The chemistry of the curing of the sealant is illustrated in Scheme 1. Three stage curing is adopted to ensure the complete curing of the sealant. In the first stage, the isocyanate reacts with the NH_2 of the aromatic amines to form urea linkage. In the second stage, the hydroxyl groups of the polyol will react with NCO. These groups being secondary in nature

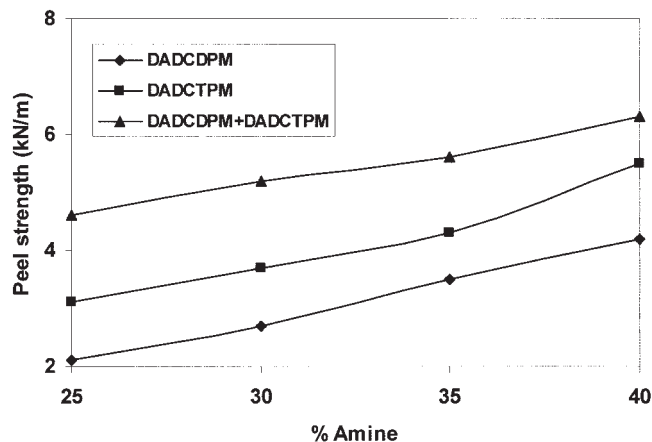


Figure 2 Peel strength versus amine percentage.

are generally slow to react with the isocyanate to form urethane linkage. In the third stage, post curing is done to ensure complete curing. In actual application, this step can be avoided by providing longer period for curing in the second stage. Though a plethora of catalysts are available to accelerate the reaction rate, deliberately no catalyst is used in our formulations so

as to get a reasonable pot life. Presence of urea linkage in the cured sealant imparts strength and stiffness to the cured sealant, whereas the urethane linkage provides the flexibility. The combination of urea and urethane linkages makes sure that the cured sealant behaves as an elastomer with high mechanical properties.

Figure 1 illustrates the tensile properties of the sealant with varying amine percentage. The three formulations chosen were the ones having only DADCDPM, DADCTPM, and the combination of the two in a 50:50 mole ratio. In each of the compositions, the amine percentage was varied from 25 to 40%. From Figure 1, it is found that the tensile strength of the sealant increases linearly with amine percentage. This could be attributed to the increasing polyurea concentration in the sealant, which contributes to the stiffness of the sealant. This trend is confirmed from the fact that there is a corresponding drop in the elongation at break with increase in amine percentage. Further, it is observed that tensile strength of DADCDPM-based PU samples is highest at any concentration of amine, while elongation at break is lower. From the structures of both the amines, it can be seen that DADCDPM has

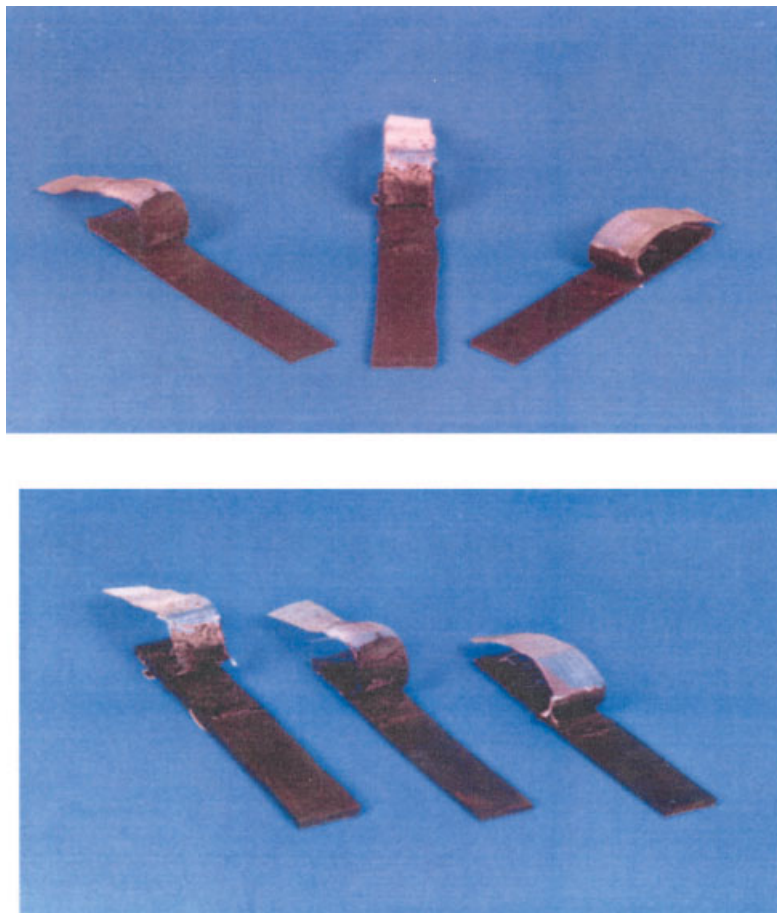


Figure 3 Mode of failure during adhesion test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

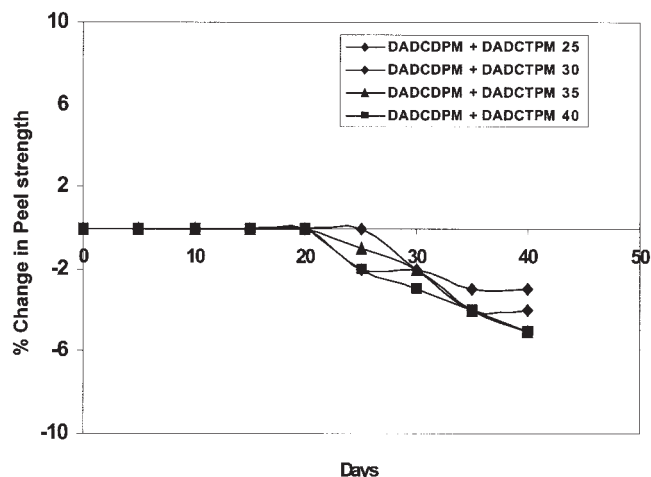


Figure 4 Aging behavior of sealant in seawater.

a planar structure and structure of DADCTPM is bulky. PU based on DADCDPM amine alone will offer more stiff and compact structure, resulting in higher tensile strength and lower elongation at break, whereas DADCTPM-based PU showed opposite trend because of its bulky structure. The mechanical properties with 50:50 combination of the two chain extenders exhibit intermediate properties.

The variation of the adhesion strength of the sealants with amine percentage is plotted in Figure 2. From the results, it is observed that the adhesion strength increases linearly with the amine percentage. However, DADCDPM-based PU showed lowest peel strength contrary to their tensile strength. Since structure of DADCDPM-based PU will stiff, obviously the peel strength will be less. Although DADCTPM-based PU is flexible, the peel strength is not highest because of its inherent poor tensile strength. However, the adhesion of the sealant to rubber substrate was found to be very high in case of the hardener formulation with 50:50 combination of both the amines. Figure 3 illustrates the mode of failure of the adhesive assembly comprising of the reinforcement, rubber substrate, and the sealant as mentioned in the experimental part. From the figure, it can be seen that chunk of rubber substrate has peeled out during the test, which suggests that the failure is cohesive in nature because of the high degree of adhesion of the sealant with the rubber substrate.

To study long term behavior of sealant, aging study has also been carried out. Since PU based on mixture of diamines (50 : 50) has provided optimum results, for aging study, samples have been prepared using mixture of both diamines and exposed to various environment as explained in experimental part. The change in peel strength of the sealant with time due to aging is illustrated in Figures 4–6 in different environment such as open air, seawater, and at 80°C, respectively. From the results, it is apparent that irrespective

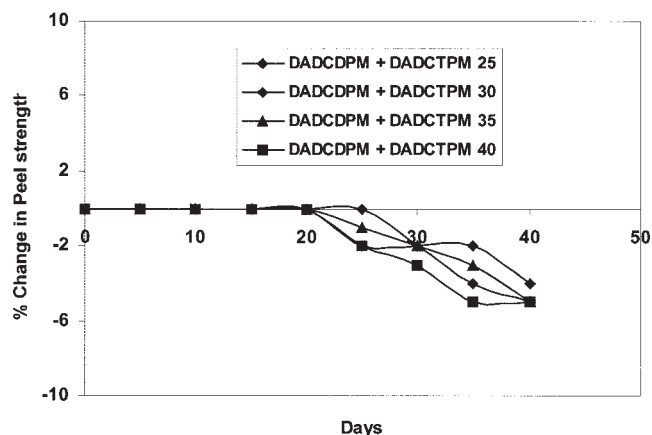


Figure 5 Aging behavior of sealant at 80°C.

of concentration of amine, the properties suffer only a marginal decrease with aging, indicating that the sealant has reasonable stability. Further, maximum temperature during curing as well as aging being 80°C, residual isocyanate groups may undergo reaction forming urea groups. This may contribute to the stiffening of the sealant. Oxidation of the sealant during aging is also a possibility. But it is noteworthy that the sealant retains its properties after exposure to seawater, indicating good hydrolytic stability. This is because of the hydrophobic and nonpolar polybutadiene building blocks of the sealant. This study reveals that the sealant can be used for underwater applications.

CONCLUSIONS

The prepolymer based on hydroxyl-terminated polybutadiene capped with TDI having benzoyl chloride as stabilizer showed good shelf life. Use of chlorine containing aromatic amines (DADCDPM and DADCTPM) has given reasonable pot life. When cured with the aromatic amine-based hardeners formulation to produce a sealant, it imparts excellent

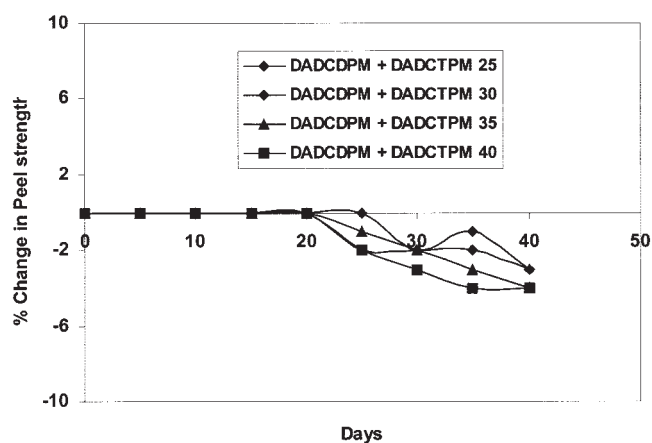


Figure 6 Aging behavior of sealant in open air.

adhesive properties as well as tensile properties. These outstanding properties are maintained after exposure to aging conditions, such as immersion in seawater and heat aging. The sealant is suitable for heavy-duty applications where high cohesive strength and adhesion with rubbers is a prerequisite.

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