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Effect of fillers on the degradation of automotive epoxy adhesives in aqueous solutions

Part I *Absorption of water by different fillers-incorporated automotive epoxy adhesives*

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Absorption of water in epoxy adhesives containing different types of fillers was studied after immersion in distilled water and in NaCl solutions during several periods of time. The amount of water uptake in the adhesives was found to increase with the concentration of water-soluble fillers incorporated in the adhesive matrix. The water absorption behaviour of the adhesives investigated was found to be non-Fickian. Owing to reverse osmosis, the amount of water absorbed in the adhesives decreases with the concentration of the bulk NaCl solution.

1. Introduction

At present, most structural bonding applications in automotive industries involve the use of epoxy-based adhesives and metallic adherends. Many spot-welded automotive parts, such as doors, hood and deck-lid panels, are currently being replaced by adhesive-bonded components. This is due to the serious difficulties encountered in welding of galvanized and otherwise coated steels. The excellent mechanical properties of epoxy resins have led to their wide use as adhesives which bond well, especially to treated metal surfaces. In a liquid state, epoxy resins are endowed with good wettability. Their highly active functional groups allow epoxy resins to be adsorbed on adherends with close proximity [1]. The low shrinkage upon curing (less than 0.5%) and their abilities to cure without producing volatile by-products, lead epoxy resins to be an attractive foundation for metal-bonding adhesive systems [2]. Specific epoxy adhesives are usually formulated with fillers, which are employed to increase surface hardness, improve thermal conductivity, enhance adhesive properties, reduce cost, lower the coefficient of thermal expansion, and reduce shrinkage of the epoxy adhesive. Fillers are defined as solid particles that are incorporated into adhesives in a relatively large volume fraction [3]. They play an important role in the adhesive industries, and are commonly used as cheap adhesive extenders. After fillers are incorporated into the unfilled adhesive system, the resin content is reduced while many properties of the adhesive system are enhanced. Fillers are either inorganic or organic, metallic or non-metallic. Chemical composition, physical and electrical properties of fillers are important factors for their use in adhesive formulations. Hurlbut [4] has categorized fillers into five different chemical classes. They are oxides, salts, silicates, elements, and organics. Effects of fillers on adhesive properties have been summarized by Skeist [5] and Carey [6].

Upon deleterious environmental exposures, durability of adhesive-bonded automotive structural joints, especially for those comprising metallic adherends, can be seriously influenced. It is well known that water, humidity, ionic contaminants such as chloride anions in chemicals used for deicing roads in winter, and atmospheric impurities, especially sodium chloride in seacoast or marine environment, are the main factors in offering multiple opportunities for structural degradation of adhesive-bonded automotive joints. The mechanical strength and physical properties of epoxy adhesives are adversely influenced by water absorption and exposure to other detrimental environments. Epoxy resins which are continually exposed to ambient atmospheric moisture or water will absorb water very rapidly [7–9]. Because all epoxy adhesives are permeable to water, water diffuses through the matrix, and eventually invades the metal substrate underneath. The detrimental effects that result from water absorption are also strongly influenced by the presence and nature of fillers in adhesive materials [10].

Comyn [11] has proposed that water may cause degradation in adhesive joints by:

(i) inducing plasticization of the adhesive, thus changing the mechanical properties of the adhesive in a reversible manner;

(ii) altering the properties of the adhesive by hydrolysis, and by generating cracks or crazes;

(iii) inducing swelling stresses in the adhesive/adherend interface; and

(iv) attacking the adhesive joint either by displacing the adhesive or by hydrating the metal or metal oxide surface of the adherend.

Degradation in adhesive-bonded joints can result from one or a combination of the above actions. Evidence obtained by Gazit [12] and Shirrell and Halpin [13] has clearly shown the dimensional change and swelling of adhesive materials during exposure to water or moisture. As the severity of the changes in mechanical properties of adhesive materials depends on the amount of water absorbed, it is therefore essential to study and evaluate the water absorption characteristics of adhesives in order to predict their long-term durability. Starting from the mid 1950s, extensive studies have been conducted to understand the fundamental mechanism of moisture absorption and desorption in adhesive materials. Three types of water diffusion behaviour in adhesive materials have been differentiated in the work of Alfrey *et al.* [14]. Three basic water-diffusion categories are: (i) Case I, or Fickian diffusion; (ii) non-Fickian, or anomalous diffusion; and (iii) Case II, and super Case II diffusion. Using the equation [14]

$$M_t/M_\infty = kt^n \tag{1}$$

where M_t is the relative weight gain at time, t; M_∞ is the equilibrium relative weight gain; k and n are constants, the above three water diffusion categories can be distinguished from the slopes of various water absorption curves ($\log(M_t/M_\infty)$ versus the logarithm of time). From the study conducted by Alfrey *et al.* [14], Fickian diffusion behaviour is obtained when $n = 1/2$, Case II diffusion is obtained when $n = 1$, and super Case II diffusion is obtained when $n > 1$. For the anomalous or non-Fickian diffusion system, n is found to be greater than 1/2, yet less than 1. Absorption with n less than 1/2 is termed as "pseudo-Fickian" diffusion.

In the majority of studies, water absorption in adhesive materials occurs according to Fickian diffusion [15–18]. In many other cases, however, the complex water-absorption phenomenon in adhesives can lead to various kinds of absorption anomalies [19–27]. Crank [24] has reported three major absorption anomalies: (i) pseudo-Fickian behaviour; (ii) Sigmoid behaviour; and (iii) two stage sorption behaviour. Sigmoidal absorption curves of mass uptake versus square root of time have been reported by Andrews *et al.* [25] using PMMA tested in a series of alcohols; however, excellent linear sorption kinetics have been obtained by Hopfenberg *et al.* [28] when the same weight gain data have been replotted against time. Shirrell [26] and Ishai [27] have found that non-Fickian absorption processes occur during cyclic exposure to water or moisture followed by drying. Adhesive cracking and degradation have been reported. Wong and Broutman *et al.* [29] have reported that absorption anomalies are caused by (i) molecular relaxation that result from successive absorption cycles, (ii) further cross-linking upon absorption of water as a result of insufficient curing, and (iii) oxidation of resins which produces a higher absorptive affinity towards water.

The choice of which adhesive or adhesive/adherend system to use in an automotive application requires assessment of its behaviour in the real service environment. This assessment involves exposure of the adhesive or adhesive-bonded system to the simulated environment for a certain period, and evaluation of the exposed specimen for changes in physical and mechanical properties. Water- and fluid-immersion tests have been widely utilized to evaluate changes in the properties of adhesives and adhesive-bonded systems. Water-immersion tests are performed by immersing test specimens in distilled or deionized water, whereas fluid-immersion tests are performed by immersing test specimens in any fluid to which the adhesive system may be exposed to in real-life situations [30]. A sodium chloride solution is one of the most commonly utilized test solutions for testing adhesive-bonded automotive joints. Both water- and fluid-immersion tests are rapid and very severe tests for adhesives and adhesive-bonded structures. Results obtained from these accelerated tests are used for predicting long-term behaviour of the adhesive or the adhesive-bonded system. Both the water- and fluid-immersion tests are effective techniques in evaluating the absorption rates of solutions in adhesives, the stability of adhesives, swelling of adhesives, colour changes in adhesives, and delamination of adhesives from metal adherends [30].

In this work, emphasis was placed upon determining the absorption behaviour of four automotive epoxy adhesives under complete immersion in distilled water and in NaCl solutions. The water absorption rate of the adhesives was measured as a function of the filler content, concentration of the sodium chloride solution and exposure time.

2. Materials and experimental procedure

Four different fillers-incorporated automotive epoxy adhesives (A, B, C and D) were investigated in this study. They were formulated and produced by different companies. Table I lists the composition of the adhesives. Five test solutions used in this investigation were: (1) distilled or deionized water; (2) 100 p.p.m.

TABLE I Compositon of adhesives investigated (percentage by weight)

Adhesive	Composition
A (one part epoxy)	Epoxy > 80% Fillers: < 16%–17% silica (SiO_2) and calcium carbonate ($CaCO_3$), < 3%–4% acrylic epoxy as reinforcing filler
B (one part epoxy)	Epoxy: 40% Fillers: 57.6%–59.4% magnesium aluminum silicate ($MgAlSiO_4$), and 0.6%–2.4% cabasal silica (porous type)
C (two parts epoxy)	Epoxy: 50%–55% Fillers: 15%–20% calcium carbonate ($CaCO_3$), 5%–10% calcium oxide (CaO), 5%–10% silicon dioxide (SiO_2), and talc clay
D (one part epoxy)	Epoxy: 60% Fillers: 35% silicon dioxide (SiO_2), and 5% calcium carbonate ($CaCO_3$), calcium silicate ($CaSiO_4$)

sodium chloride solution; (3) 1000 p.p.m. sodium chloride solution; (4) 0.5 M sodium chloride solution; (5) 1.0 M sodium chloride solution.

Water absorption was determined by measuring the weight gain of the adhesives after exposure to the solutions as a function of time. Small pieces of adhesive specimens (0.1 cm × 0.5 cm × 1.0 cm) were prepared. Ten pieces of each particular adhesive were immersed in a solution for 7 weeks at room temperature. All test specimens were suspended in the test solutions without making contact with each other. At various time intervals, test specimens were removed from the solution, dried and weighed by an analytical balance that gave a relative precision of 10^{-4} g.

3. Results

Figs 1–4 show the water absorption curves for the four different tested epoxy adhesives. In all cases, a linear relationship between the percentage of water uptake, $M_t(\%)$, and time, t, was clearly observed within the first 3–7 days. After the initial linear stage, the percentage of water uptake in each adhesive decreased. Regardless of the test solutions in which the adhesives were immersed, an equilibrium water content, $M_\infty(t)$, for adhesives A, B, and D was observed after 35 days. For adhesive C, a gradual continuous increase in the percentage of water uptake was observed after the initial linear stage. Water absorption curves for the four adhesives exposed to the different test solutions showed that the adhesives absorbed more water upon exposure to distilled water than when exposed to different sodium chloride solutions. In all cases, water absorption curves for the adhesives exposed to distilled water were found lying above the curves for those immersed in different concentrations of NaCl solutions. The higher the concentration of the NaCl solution, the less water absorbed by the adhesives. Among all of the four adhesives, regardless of the test solutions used, adhesive C absorbed most water, followed by adhesives A, D and B.

The logarithm of the fractional percentage of water uptake in adhesive C, $\log[M_t(\%)/M_\infty(\%)]$, is plotted as a function of the logarithm of time in Fig. 5. Using the relationship given in Equation 1 [14], it can be determined whether or not water absorption by the adhesives occurs according to Fickian diffusion behaviour. A computer curve-fitting software (Cricket graph version 1.3) was used to determine the best fit line for the data, and calculate the slope of the best fit line. The values of n determined for the four adhesives are shown in Table II. In all cases, the values of n were found to be greater than 0.5, and less than 1. It is considered that water absorption in the four adhesives occurred according to non-Fickian or anomalous diffusion behaviour [14]. Water absorption curves of $M_t(\%)$ versus $t^{1/2}$ are shown in Figs 6–9. Sigmoidal water absorption curves were obtained for adhesives A, B, and D after they were immersed in five different solutions, respectively, for 49 days. For adhesive C,

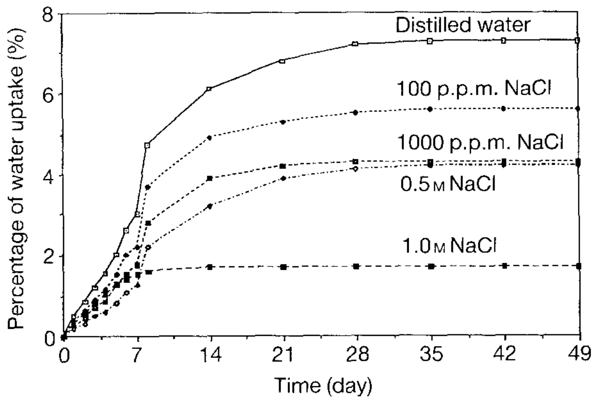

Figure 1 Water-absorption curves for adhesive A immersed in different solutions.

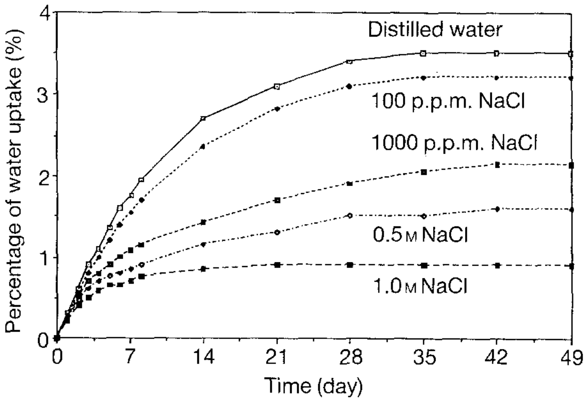

Figure 2 Water-absorption curves for adhesive B immersed in different solutions.

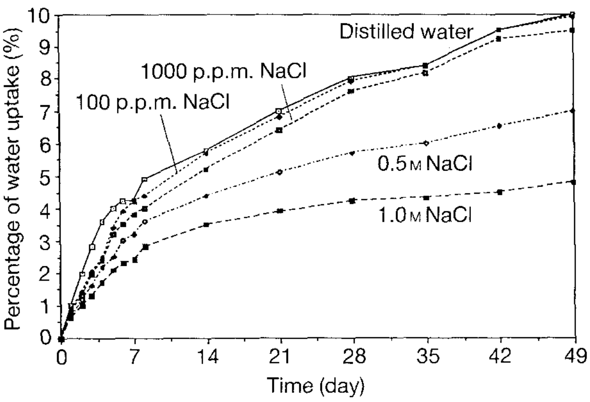

Figure 3 Water-absorption curves for adhesive C immersed in different solutions.

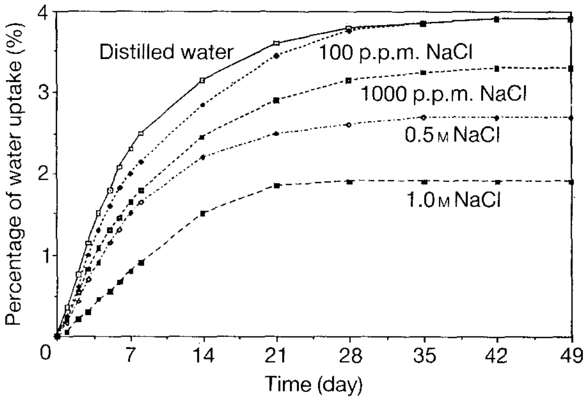

Figure 4 Water-absorption curves for adhesive D immersed in different solutions.

TABLE II Values of n determined for adhesives immersed in different solutions

Adhesive	n				
	Water	100 p.p.m. NaCl	1000 p.p.m. NaCl	0.5 M NaCl	1.0 M NaCl
A	0.729	0.748	0.787	0.879	0.625
B	0.604	0.605	0.504	0.513	0.612
C	0.521	0.600	0.609	0.558	0.507
D	0.563	0.639	0.646	0.642	0.847

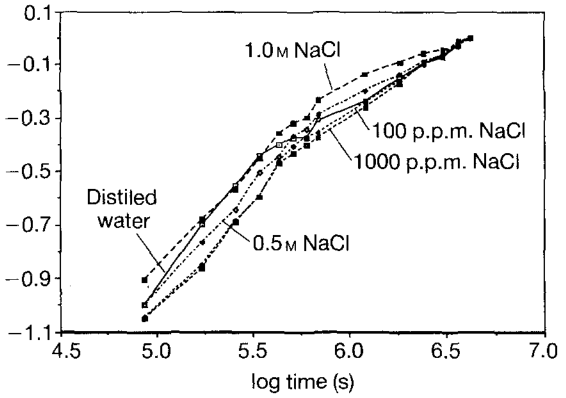

Figure 5 Evaluation of water-absorption behaviour for adhesive C immersed in different solutions.

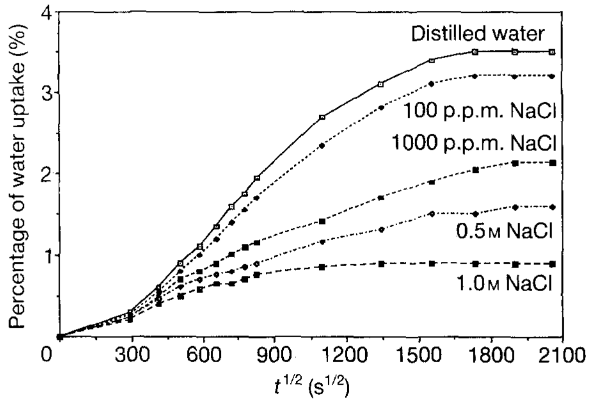

Figure 7 Curves of M_t(%) versus $t^{1/2}$ for adhesive B immersed in different solutions.

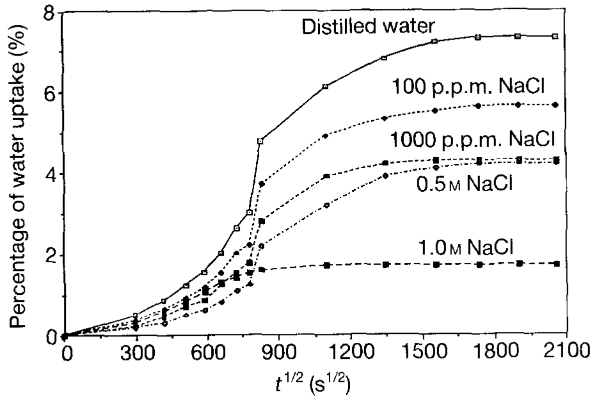

Figure 6 Curves of M_t(%) versus $t^{1/2}$ for adhesive A immersed in different solutions.

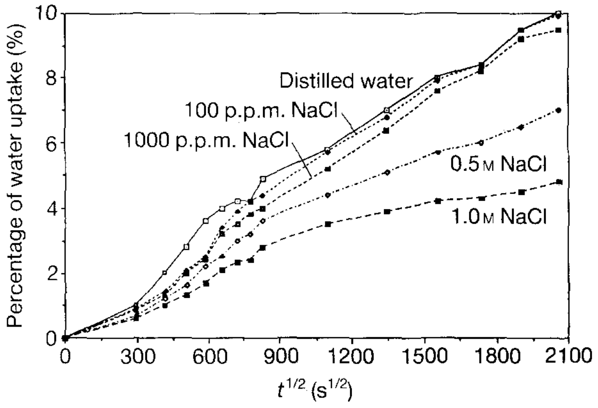

Figure 8 Curves of M_t(%) versus $t^{1/2}$ for adhesive C immersed in different solutions.

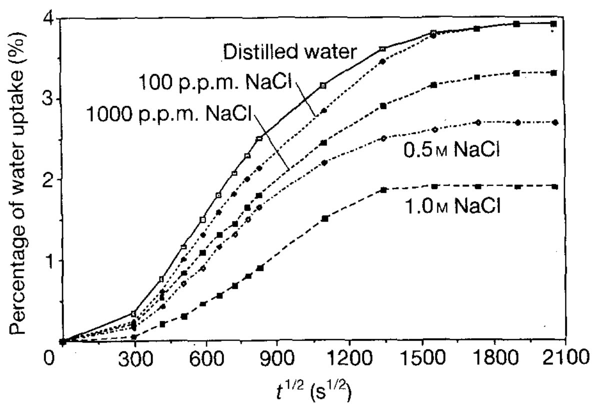

Figure 9 Curves of M_t(%) versus $t^{1/2}$ for adhesive D immersed in different solutions.

pseudo-Fickian water absorption curves were obtained.

4. Discussion

The shape of the water absorption curves (M_t(%) versus t) is similar to that obtained by Bellenger *et al.* [31] for water absorption in other epoxy adhesives with different formations. It is believed that during the initial linear stage of water uptake, water penetrates into the adhesive matrix by diffusion, and by capillary action along the pre-existing cracks and microvoids. When the adhesive absorbs water from the bulk solution, water-soluble substances (inorganic fillers) inside the adhesive matrix dissolve in water, thereby producing more voids or pores within the adhesive matrix. Porosity in the adhesive caused by the dissolution of water-soluble substances increases the water absorptiveness of the adhesive. Moreover, plasticization or swelling of the adhesive occurs after a sufficient amount of water is absorbed into the adhesive. Cracks or crazes that govern the capillary action of water absorption may form inside the adhesive during swelling. As a result, a further gradual increase in the percentage of water uptake occurs in the adhesive after the initial linear stage of water absorption. The adhesives are considered saturated with water at the steady state after reaching the stage of gradual water uptake. Water absorption curves for the adhesives exposed to the five test solutions show that the adhesives absorb a larger amount of water upon exposure to distilled water than when exposed to different sodium chloride solutions. The higher the concentration of the NaCl solution, the less water absorbed by the adhesives. This behaviour affirms that the absorption of water in the adhesives follows the reverse osmosis mechanism. When water is absorbed by the adhesive from the bulk solution, an electrolyte is produced upon dissolution of the internal water-soluble substances (inorganic fillers). Because of osmosis, water from the bulk solution is driven into the adhesive matrix to dilute the electrolyte. The attempt by water to dilute the electrolyte eventually sets up osmotic pressures that are capable of producing swelling and microcavities in the adhesive. The formation of microcavities in the adhesive and the swelling effect can increase the rate of water transport, and hence the effective water-diffusion coefficient of the adhesive. However, in the cases where the bulk sodium chloride solution is more concentrated than the electrolyte produced inside the adhesive matrix, reverse osmosis occurs. The absorbed water is driven out from the adhesive matrix during reverse osmosis, thereby balancing the concentration difference between the internal electrolyte and the bulk NaCl solution. As a result, a decrease in the amount of water uptake by the adhesive can be predicted.

Among the four adhesives exposed to the different test solutions during the experiment, adhesive C absorbed most water, followed by adhesives A, D, and B. The water equilibrium concentration, $M_\infty(\%)$, increases primarily with the concentration of water-soluble fillers, namely calcium carbonate and calcium silicate, incorporated in the adhesive matrix. From Table I, it follows that adhesive C contains a filler mixture of calcium carbonate (15%–20%), calcium oxide (5%–10%), silicon dioxide (5%–10%) and talc clay (10%–20%). This filler composition produces a very porous matrix for the adhesive, and provides a high content of calcium carbonate to dissolve in water during water immersion. Adhesive A contains the second highest concentration of calcium carbonate (less than 16%–17% of the total adhesive composition when mixed with silica), followed by adhesive D (5% of calcium carbonate and calcium silicate), and adhesive B (0% calcium carbonate, 0.6%–2.4% of porous-type cabasal silica). The consistency between the composition and content of the fillers and the amount of water uptake affirms that the mechanism of water absorption in the adhesives is primarily governed by the capillary action of water absorption through cracks and voids, and osmosis. The larger the amount of water-soluble fillers existing in the adhesive matrix, the greater will be the porosity of the adhesive due to the material dissolution in the absorbed water. As a result, the rates of the capillary action and osmosis increase together with the water absorptiveness of the adhesive.

Sigmoidal water absorption curves ($M_t(\%)$ versus $t^{1/2}$) were obtained for adhesives, A, B and D after they were immersed in different solutions for 49 days. For adhesive C immersed in the five test solutions, pseudo-Fickian water absorption curves were obtained. These results, together with the values of n determined using Equation 1, reveal that water absorption in all the adhesives occurs according to non-Fickian or anomalous diffusion behaviour [14, 24]. According to Alfrey *et al.* [14], pseudo-Fickian water absorption occurs only when the value of n is less than 0.5. However, the values of n obtained for adhesive C are greater than 0.5, and less than 1 (in fact close to 0.5). The apparent inconsistency arising in these results is caused by using the percentages of water uptake at day 49 as the equilibrium water concentrations $M_\infty(\%)$, in calculating the fraction of $M_t(\%)/M_\infty(\%)$. Adhesive C was not saturated with water after 7 weeks immersion in the different test solutions (Figs 1–4). Hence, the water concentrations, $M_t(\%)$, at the seventh week were chosen as the equilibrium water contents, $M_\infty(\%)$, in determining the values of n. Lower values of $M_\infty(\%)$ produce greater fractions of $M_t(\%)/M_\infty(\%)$, thereby resulting in higher values of n. In agreement with the points of view of Shirrell [26], Ishai [27], and Wong and Broutman [29], non-Fickian water absorption behaviour in adhesives A, B, C, and D is possibly caused by (i) adhesive degradation (dissolution of the water soluble fillers); (ii) adhesive cracking; and (iii) molecular relaxation (swelling).

5. Conclusions

1. The amount of water uptake in the adhesives increases with the content of water-soluble fillers, such as calcium carbonate and calcium silicate, incorporated in the adhesive matrix. Hence, the rank of adhesives according to the average amount of water uptake is

$$\underset{\text{(highest)}}{C} > A > D > \underset{\text{(lowest)}}{B}$$

2. Because of reverse osmosis, the amount of water absorbed in the adhesive decreases with the concentration of the bulk NaCl solution.
3. Water absorption in the adhesives investigated occurs according to the non-Fickian water diffusion behaviour.
4. Water penetrates in the adhesive matrix by diffusion, osmosis and capillary action.

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