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THE ADHESION THEORIES APPLIED TO ADHESIVELY BONDED JOINTS OF FIBER REINFORCED POLYMER COMPOSITE ELEMENTS

BY

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Abstract. The adhesive bonding is one of the most suitable joining technique for structures made of composite materials. Adhesive bonding of fiber reinforced polymer (FRP) composite products is utilised in various applications such as: strengthening techniques, reparing the surface of different FRP elements and as a general alternative, when mechanical fastenings are not suitable.

The adhesion between the adhesive and the adherents arises from the fact that all materials have attraction forces acting between their atoms and molecules. The bond strength depends on the intensity of the attraction forces and on the interaction between the adhesive and the surfaces of the adherents. This paper presents a review of the existing adhesion theories suitable for FRP composite products. Also, varios research programs related to the adhesion mecanisms between FRP elements are presented in this paper.

Keywords: adhesive; adherent; polymeric composite materials; bonding; surface treatments.

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1. Introduction

In some structural applications of the fibre reinforced polymer (FRP) composites, the elements have to be connected. The structural connections can be obtained by using either mechanical methods, using different types of fastenings, or by adhesive bonding. The latter is more appropriate for FRP composite elements since they usually exhibit different mechanical properties along their principal axes and also, because the mechanical methods tend to produce stress concentrations near the position of the fastening elements (Adams & Wake, 1984).

The adhesion between the adhesive and the FRP composite elements can be explained by using suitable adhesion theories. Although the findings of various experts in the field of adhesion are still divergent on the share that each type of interfacial connection has in obtaining a higher bond strength at the interface level, the evaluation and the interpretation of the bonding characteristics, based on the principles of the adhesion theories, may improve the bond performances.

There are two categories of adhesives that are currently used for civil engineering applications, structural and non-structural adhesives. The structural adhesives are those that can be used to obtain load-carrying joints. Based on their chemical composition they can be classified in thermosetting or thermoplastic resins and elastomeric compounds (Baldan, 2004). The non-structural adhesives are used to connect elements that are not subjected to significant loads. The adhesion theories are referring to the adhesives that are suited for structural applications.

The first adhesion theories refer to mechanical interlocking, physical adsorption, chemical bonding and diffusion. However, due to the development of various methods for FRP composite elements surface characterisation, other adhesion theories were postulated in relation to the chemical and physical phenomena's that characterize the FRP surfaces (Adams *et al.*, 1997; Baldan, 2004; Ebnesajjad & Landrock, 2009).

This paper presents the most important adhesion theories that can describe the adhesion mechanisms of FRP products. Also, various experimental programs relating to the adhesion theories are presented and discussed.

2. Mechanical Theory

The Mechanical Theory states that the degree of adhesion that can be obtained for a bonded joint is directly linked to the porosity and to the surface roughness of the substrates. According to this theory, the adhesive must uniformly fill the cavities of the adherents' surface, so that an intimate and continuously contact is obtained (Packham, 2003).

The adhesive displaces the air which is entrapped in the cavities of the surface area and creates anchorage spots. Therefore, it is concluded that the intensity of the adhesion force is based on the adhesive capability to penetrate the surface roughness of the adherents. The mechanism of the Mechanical Theory is illustrated in Fig.1.

Fig. 1 − The mechanical coupling between the adherents and the adhesive surface.

Parker & Waghore (1982) have studied the mechanical interlocking effect for single lap joints (SLJ) made of carbon fibre reinforced polymer (CFRP) products and five types of epoxy adhesives. For the experimental program, three types of specimen series were instrumented. The CFRP materials corresponding to the first series have been prepared by solvent wiping. The CFRP materials from the second series have been hand abraded, while the ones from the third series have been grit blasted. The samples have been unidirectionally loaded in tension until failure occurred. The authors concluded that the only parameter that improved the ultimate loads was the degree of surface preparation. Thus, grit blasting is suitable for obtaining superior bond strength but in the same time, the blasting parameters should be provided for each type of FRP product, since over abraded surfaces may lead to moisture entrapment and to insufficient curing conditions.

Maeva *et al.* (2004) pointed out that a strong adhesion is obtained if the adhesive has two main properties. The first is related to its capacity to wet the substrate and the second states that the adhesive should have adequate rheological characteristics in order to penetrate the surfaces of the adherents in a reasonable time. Thus, the roughness degree of the FRP elements should be compatible to the adhesive's viscosity.

An important challenge in any blasting technique is to obtain a constant roughening degree across the entire bond area. As shown in the work of Parker and Waghore (1982), the X-ray photoelectron spectroscopy (XPS) revealed that the hand abraded surface techniques do not provide the same level of homogeneity as the blasting techniques. For FRP elements, the over processing of surfaces can alter the specimens' cleanliness and the curing conditions of the adhesive, while in case of insufficient processed surfaces, the mechanical interlocking will be altered.

Ebnesajjad (2008) suggested that the adhesion properties could be enhanced by increasing the surface roughness through four different interlocking mechanisms: the mechanical interlocking effect, the surface cleanliness, the increased surface reactivity and the increased specific surface. However, these interlocking mechanisms are not universally applicable, since strong bonds may also be achieved for adherents with smooth surfaces.

3. Electrostatic Theory

This theory was originally proposed by Deryaguin *et al.* which postulated that all adhesion phenomena may be explained by the charge transfer across the interface. The authors state that the most important argument of the electrostatic theory is the electrical discharge that occurs when flexible FRP elements are peeled off from rigid substrates (Deryaguin *et al.,* 1978, 1987). The Electrostatic Theory states that the adhesion effect is triggered by the transfer between the adhesive and the substrate which is enabled by the difference in the electronic band structure (Oltean, 2011).

The attraction forces occur between surfaces with different electric charges and significantly improve the delamination strength. The contribution of the electrostatic forces to the bond strength increases with the charge density (Baldan, 2004). The mechanism of the Electrostatic Theory is presented in Fig.2.

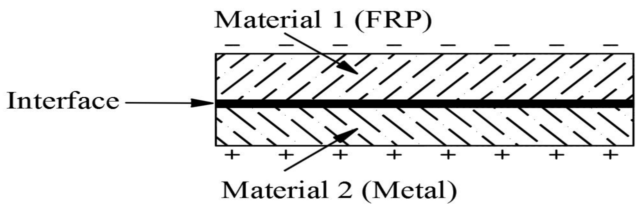

Fig. 2 – The electrical double layer (electrostatic mechanism) at the FRP-Metal interface (Baldan, 2004).

4. Diffusion Theory

The Diffusion Theory was first proposed by Voyutskii and states that the adhesion is developed through the diffusion of molecules in between the adhesive and the adherents (Voyutskii *et. al,* 1963). The phases of diffusion as illustrated by Fourche (1995) are presented in Fig. 3.

The diffusion theory indicates that two polymers that are maintained in contact with a constant pressure, will diffuse together following Flick's laws of diffusion (Baldan, 2012). Thus, the interpenetration depth x, may be calculated using Eq. 1.

$$x \approx \exp\left(-\frac{E}{2RT}\right)t^{1/2}, \tag{1}$$

where: E is the diffusion activation energy, t – contact time, R – molar gas constant and T – temperature.

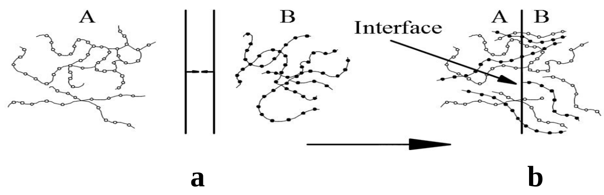

Fig. 3 − The diffusion theory of adhesion: *a* – inter-diffusion of adhesive; *b* – substrate molecules (Fourche, 1995).

Wake (1978) suggested that the fundamental of the diffusion theory is the thermodynamic compatibility between the constitutive materials. This means that for most of the FRP elements which are bonded with epoxy adhesives, the theory is not valid. Generally, the theory is applicable in bonding of autohesion polymers, bonding of rubbery polymers, and in the solvent-welding of thermoplastics (Baldan, 2004).

5. Thermodynamic theory of adhesion

The thermodynamic theory of adhesion states that the adhesion is the result of the surface forces that appear between two materials that are maintained in contact (Groll & Ţăranu, 2003). According to Comyn, (2006) if two materials which are electrically neutral are maintained at a relative small distance one to another, a physical attraction between them will arise. The process which establishes the contact between the adhesive and the adherents is called wetting. The wetting of the adherents surface is possible if the adhesive has a lower surface tension than the critical surface tension of the adherents. An example of adhesive wetting and spreading across smooth and rough adherents' surfaces is presented in Fig. 4.

Most of the available structural adhesives tend to create strong bonds when metallic elements are jointed but their performance is lower in the case of FRP composite elements (Ebenesjad, 2008). The surface energy of FRP elements is usually lower than the one of the adhesives and various treatment methods are required to enhance the adhesion.

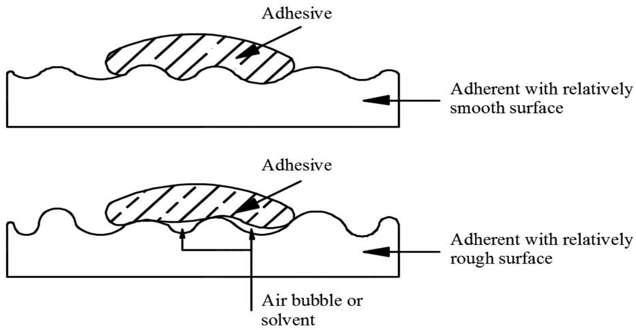

Fig. 4 – Adhesive wetting and spreading across smooth/rough adherents' surfaces.

The parameter that mainly describes the surface wetting is the contact angle Θ which appears between the adhesive (or a control liquid) and the adherent surface. Habernicht, (2009) suggested that good bonding results are obtained if the angle Θ is maintained below 30º. Examples of satisfactory and unsatisfactory contact angles are presented in Fig. 5.

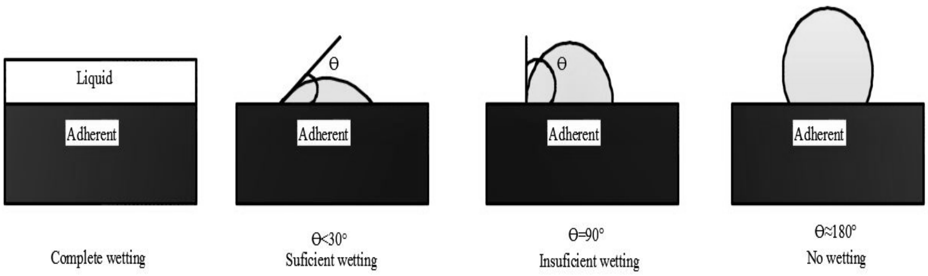

Fig. 5 – Contact angle Θ for different wetting cases (Oltean, 2011).

The spreading of the adhesive on the interface is influenced by the roughness of the adherents and by the value of angle Θ. The spreading pressure, π_e is the pressure needed to lower the adherents surface free energy. The latter may be expressed by

$$\pi_e = \gamma_S - \gamma_{SV} , \tag{2}$$

where: γ_S is the surface free energy of the adherent in vacuum and γ_{SV} – surface free energy in equilibrium with the saturated vapors. The forces acting on the liquid drop on the adherent surface are presented in Fig. 6 (Comyn, 2006).

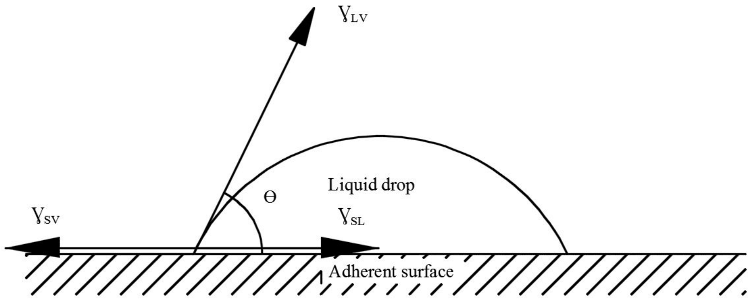

Fig. 6 – Liquid drop on the adherent surface. Forces acting in equilibrium state (Comyn, 2006).

The variation of π_e confirms the supposition of Habernicht, (2009) regarding the contact angle Θ and may be neglected if Θ > 10º. The wettability of the adherent surface is checked by the equilibrium of the forces presented in Fig. 6. When the surface free energy is lowered by the replacement of the solid-vapor (S-V) surface, by a solid-liquid (S-L) and an liquid-vapor surface together, Eq. 3 becomes valid

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} , \tag{3}$$

where: γ_{LV} is the surface free energy of liquid adhesive in equilibrium with the saturated vapors and γ_{SL} – surface free energy between the liquid adhesive and the solid substrate.

On the other hand, when the free energy could not be lowered, no wetting will occur and Eq. 4 becomes valid

$$\gamma_{SV} + \gamma_{LV} < \gamma_{SL} . \tag{4}$$

6. Chemical Bonding

The chemical bonding theory states that the formation of the adhesion forces is due to the chemical connections. The theory was postulated by Bilkerman, (1968) and relates the chemical bonding mechanism to four types of interactions: covalent bonds, hydrogen bonds, Lifshitz-van der Waals forces and acid-based interactions. The particular interaction of a given adhesive bond is given by the chemical composition of the interface.

The chemical bonding mechanism is specific for FRP adherents. The adhesion is formed between the adhesive chemical group and the adherents ones. Baldan (2004), suggested that the bond strength and the failure modes are, in most cases, influenced by the chemical reaction at the interface layer. The coupling agents and the surface oxidative treatment methods are used to enhance the properties of the chemical bonds for FRP adherents.

7. Conclusion

The adhesion theories are described by the means of two mecanisms of atraction, the chemical atraction and the mechanical atraction since it has been concluded that the diffusion forces are of minor importance. The effectiveness of the adhesive bonding of FRP products is influnced by some variables, including the surface preparation techniques, the surface roughness, the surface tension, the polymeric composition of the adhesive, the curing characteristics of the adhesive and the joint geometrical characteristics.

In the case of FRP adherents, it is difficult to ascribe the adhesive bonding to one particular mechanism. Generally, a combination of the two adhesion mecahanisms is responsible for insuring the bond effect.

The adhesion is a surface physico-chemical phenomenon. Thus, the first aim in an adhesively bonded joint is to prepare the substrate surface so that the compatibility between the adhesive and the adherents is assured.

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TEORII DE ADERENŢĂ APLICATE ÎMBINĂRILOR ADEZIVE ALE ELEMENTELOR COMPOZITE POLIMERICE ARMATE CU FIBRE

(Rezumat)

Îmbinarea adezivă este cea mai indicată metodă de asamblare a elementelor realizate din materiale compozite. În cazul compozitelor polimerice armate cu fibre (CPAF), îmbinările adezive sunt utilizate în diverse aplicaţii inginereşti, cum ar fi: consolidări structurale, reparaţii ale suprafeţelor elementelor de construcţii de tip CPAF şi îmbinări structurale atunci când îmbinările mecanice nu sunt fezabile.

Fenomenul de adeziune dintre adezivi şi aderenţi este datorat forţelor de atracţie dintre atomii si moleculele materialelor. Rezistenţa mecanică a îmbinării adezive depinde atât de intensitatea forţelor de atracţie cât şi de interacţiunea dintre adeziv şi suprafeţele de contact ale aderenţilor. Această lucrare prezintă o analiză cuprinzătoare a teoriilor de adeziune existente ce sunt adecvate pentru explicitarea îmbinării elementelor de construcţii realizate din CPAF. De asemenea, mai sunt discutate in cuprinsul lucrării, diverse programe experimentale ce tratează mecanismele de adeziune specifice elementelor de tip CPAF.