polymer

Electrokinetic approach of adhesion between polyester fibres and latex matrices

C. Campagne, E. Devaux*, A. Perwuelz, C. Cazé

Laboratoire de Génie et Matériaux Textiles (GEMTEX), UPRES EA2461, Ecole Nationale Supérieure des Arts et Industries Textiles (ENSAIT), BP 30329, 59056 Roubaix Cedex 01, France

Abstract

The adhesive interaction between salt-treated polyester fibres and elastomeric matrices has been studied. Two types of approaches have been used to predict the impact of the salt treatment on the interaction between both jointing partners. First of all ξ-potential measurements have been used to characterize the interactions between fibre and matrix. Changes in the surface composition of salt-treated fibres were investigated by electrokinetic measurements using the streaming potential. Zeta potential of latex were determined using the electrophoresis method. The second approach is the characterization of adhesion by the interfacial shear strength determined from the single-fibre pull out test. We compared results issued from the two methods used during this study. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Fibre–matrix adhesion; Zeta potential; Micromechanical tests

1. Introduction

The mechanical behaviour of a composite material depends on the nature of the reinforcing fibres and on the matrix used as binder between these fibres. The principal role of the matrix is to transmit the mechanical stresses of one fibre to the others. The quality of a composite material then depends mainly on the quality of the stress transfer in the vicinity of the interface between the fibres and the matrix. This interfacial stress transfer can be characterized by using micromechanical tests, which consist most of the time in monofilament composite materials processing. According to the respective mechanical behaviour of fibre and matrix, various tests will be used: fragmentation is well adapted for the systems where the matrix has a low elastic modulus and where the fibre has a purely elastic behaviour [1–4]. The pull-out is the oldest experimental technique used and consists in the extraction of a fibre embedded in a polymeric resin [5]. The fibre can be extracted out of the matrix which can be a block of resin, a disc or a droplet [6, 7]. These various characterization techniques of interfacial adhesion have known many improvements and adaptations in order to take into account the particular behaviours of various composite systems [8–10].

The theoretical interpretation of experimental results is also the object of numerous works [11–13]. However, none of the adhesion theories currently existing is sufficient to explain all the phenomena involved in the adhesion between fibres and a matrix in a composite material. In this paper, we present an approach allowing to interpret adhesion by means of electrokinetic measurements of colloidal latex solutions on various polyester fibres. Thus, the zeta potential ξ of colloidal aqueous solutions and of fibre surfaces are measured and the results are compared with interfacial shear stress measurement carried out with the pull-out test.

The equilibrium between the attractive forces of Van der Waals and the repulsive electrostatic forces governs the dispersion and the stability of suspensions and emulsions during time. The zeta potential represents the electrostatic potential of the particles. The zeta potential is not the superficial potential of the particle, but it is often representative of it, because it is measured at a few Angstroms of the surface. The latex coating a fibre can then be considered as the application of the heterocoagulation theory [14]. Indeed, during the latex coating, coagulation occurs between the fibre and the latex, which is a colloidal dispersion. The electrokinetic approach making it possible to study the interactions which can contribute to

* Corresponding author. Tel.: +33-320-258-983; fax: +33-320-272-597.
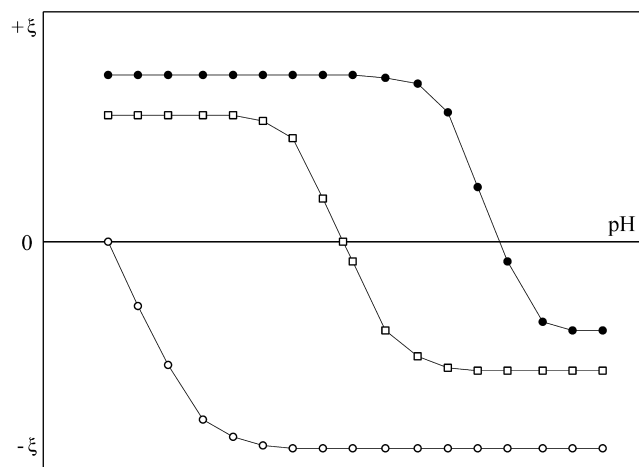 *E-mail address:* eric.devaux@ensait.fr (E. Devaux).

Fig. 1. Representation of zeta potential ξ of a solid as a function of pH: (●) alkaline dissociable functional groups; acid and alkaline dissociable functional groups; (○) acid dissociable functional groups.

adhesion was proposed by Häbler and Jacobasch [15]. The latter has showed that measurements of zeta potential can be used to characterize the interactions between two materials. Bismarck [16] investigated the interactions between a carbon fibre treated with oxygen plasma discharges and a polycarbonate matrix. Zeta potential measurements were carried out on each of two materials as a function of pH. Whatever the type of analysed fibre, the zeta potential decreases with pH, then remains constant from a certain value of pH. There exists a difference between the plates of the curves for matrix and for fibre. The more this variation $\Delta\xi$ will be important, the better will be the interaction between the two materials. Zeta potential measurements also make it possible to study the surface acido-basic properties of the polymer [17,18]. Generally, the presence of acid or basic functional groups promotes a shape of curve ξ versus pH such as that presented in Fig. 1. The increase in negative zeta potential with increasing values of pH is due to the increase in the dissociation of superficial acid groups. In the case of basic groups on the surface, the positive electric charge increases with the reduction in pH. The non-
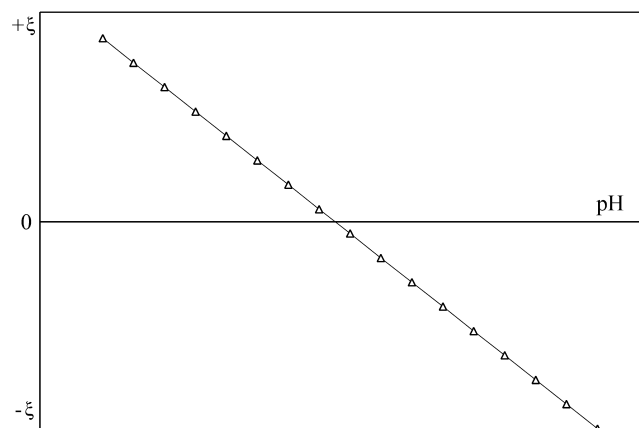

Fig. 2. Representation of zeta potential ξ of a solid as a function of pH: non-polar surface without dissociable functional groups.

polar polymers lead to a curve ξ versus pH without plate because of the lack of dissociable groups (see Fig. 2).

For our investigations, two techniques were used for the determination of zeta potential: the electrophoresis technique for the colloidal aqueous solutions, and the streaming potential technique for fibres.

Concerning the zeta potential measurement for colloidal aqueous solutions, the phenomenon usually studied is electrophoresis, i.e. the movement of charged particles in suspension in a liquid and under the influence of an electric field. The negatively charged particles will move towards the anode and the particles charged positively towards cathode. The force of friction undergone by the particles tends to be opposed to this movement. When equilibrium between these two opposite forces is reached, the particles move with a constant speed. The zeta potential is deduced from electrophoretic mobility following the law of Henry (see Eq. (1))

$$U_E = \frac{2\varepsilon\xi}{3\eta}f(K\alpha) \tag{1}$$

where U_E is the electrophoretic mobility, ξ the zeta potential, ε the permittivity, η the viscosity of the medium, and $K\alpha$ a factor corresponding to the relationship between the thickness of the double ionic layer and the diameter of the suspended particle. Most of the time, the determination of zeta potential by the electrophoresis method is carried out in an aqueous medium with a low concentration of electrolyte (lower than 10^{-3} mol l^{-1}): $f(K\alpha)$ equals 1.5 according to the approximation of Smoluchowski [19]. Eq. (1) then becomes:

$$U_E = \frac{\varepsilon\xi}{\eta} \tag{2}$$

For the small particles in a low permittivity medium, and according to the approximation of Hückel, $f(K\alpha)$ equals 1.

The zeta potential measurement of reinforcing fibres rises from that of their streaming potential. The principle of streaming potential measurement is based on the displacement of an electrolyte solution in a capillary where the wall is electrically charged. The electrostatic interaction between the charge of the interface and the ions in solution involves a concentration in contra-ions and depletion in co-ions in the capillary. Thus, at the capillary exit, the composition of the solution is slightly modified. That results in the establishment of an electric potential different to that of the entrance. The imbalance of composition of the solution at the capillary exit depends on the quantity of charged sites in the column on one hand (density and quantity of matter), and on the difference in pressure between the entrance and the exit in the capillary on the other hand (flow rate). Measurement consists in determining the voltage/pressure correlation for definite physicochemical conditions.

The fundamental equations associating the mechanical forces and the electric forces were derived for the first time by Helmholtz and Smoluchowski [19]. The zeta potential ξ

is calculated from Eq. (3) as

$$\xi = \frac{E}{\Delta p} \frac{\eta}{\varepsilon \varepsilon_0} \frac{L}{Q} \frac{1}{R} \tag{3}$$

where E is the streaming potential, Δp is the difference of hydrodynamic pressure through the liquid, η is the liquid viscosity, ε is the liquid permittivity, ε_0 is the permittivity of the open space, L is the capillary length, Q is the capillary section, and R the electric resistance through the tube. The term L/Q can be considered as a cell conductivity and can be replaced by the term RX_S when the cell is filled with a known solution of electrolytes with a conductance X_S. Eq. (3) then becomes:

$$\xi = \frac{E}{\Delta p} \frac{\eta}{\varepsilon \varepsilon_0} X_S \tag{4}$$

The potential difference E is measured at the extremities of the column under stages of increasing pressure P applied during 1–10 min in the two directions of flow. The parameters acquired are the pressure (P) and voltage (E) at the extremities of the column, the solution conductivity (γ) and the device temperature (T). The liquid used in our case is an aqueous solution of electrolyte whose various parameters η, X_S and ε_0 are known. Zeta potential ξ is calculated by the following equation

$$\xi = 13.55 \times 10^4 \frac{E}{\Delta p} C \gamma \tag{5}$$

where ξ and E are expressed in mV, P in mbar and γ in S cm^{-2}. Constant C gathers the medium permittivity and the solution viscosity, both dependent on temperature. The phenomenological law can be then written as:

$$C = 16.32 - 0.35197T + 0.00351T^2 \tag{6}$$

The variations of pressure and voltage are recorded at the extremities of the cell, and curves such as that presented in Fig. 3 are obtained. The zeta potential measurement of the fibre surface is carried out with approximately 1 g of material. The sample is introduced and maintained in the
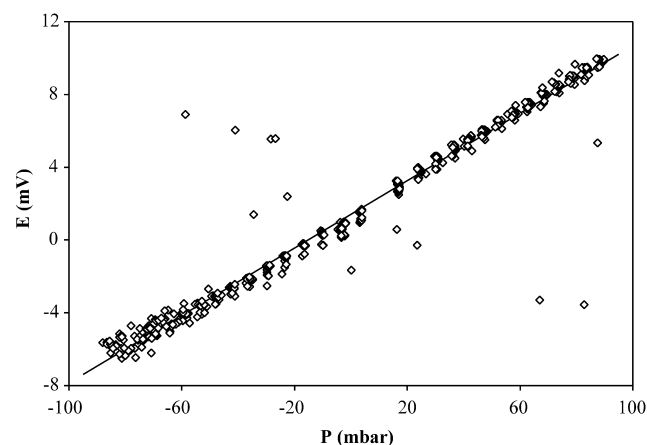

Fig. 3. Standard curve of the voltage as a function of pressure at the extremities of the capillary tube.

electrolyte solution (sodium chloride) during one or two hours in order to reach equilibrium before the measurement itself. We carried out five measurements on each sample.

2. Materials and experimental techniques

The matrix used in this work is a mixture of two latex intended for the chemical bonding of non-woven materials containing polymeric fibres. The first latex (named latex A) consists in microspheres of modified acrylic polymer, which can self-reticule forming a very hard film, and having an exceptional resistance to water and to chemical agents. It also has the properties of the acrylic emulsions, in particular the light resistance, stability and permanence in time. The synthetic latex, or colloidal dispersion of generally spherical polymer particles, are primarily produced by radical polymerization in aqueous emulsion. The acrylic latex used is obtained by radical copolymerization of methyl methacrylate and of ethyl acrylate. The self-reticulation of the majority of latex is obtained owing to the presence of N-methylol groups. Then, the reticulation reaction is done by the formation of ether or methylene bridges. It can be supposed that the self-reticulation of this acrylic latex is carried out because of these groups. The emulsion is stabilized by anionic surfactants. An important reticulation density can be possibly obtained by the addition of a melamine formaldehyde resin contained in the colloidal dispersion. This last compound can condense on itself by the intermediate of the N-methylol groups. The high glass transition temperature of this latex (45 °C) is due to the presence of methyl methacrylate groups.

The second latex is a colloidal aqueous dispersion of a self-reticulating copolymer of butadiene, acrylonitrile and N-methylol acrylamide. This colloidal dispersion, called latex P, contains self-reticulating groups. The surfactants have an anionic nature. The acrylonitrile rate is approximately 30%. This reticulated latex resists to oils, greases, fuels and various solvents; moreover, it shows a good behaviour in water. Its elasticity modulus is 36 MPa. It has a strong resistance to abrasion and good mechanical properties. The polymer in the colloidal solution contains chemical groups which allow the reticulation without addition of others reticulation components, and without the use of a high temperature (130–150 °C). This latex is self-reticulating due to the N-methylol acrylamide groups which allow the formation of ether or methylene bridges. The two latex will be studied either pure, or in mixture with 75% of latex P and 25% of latex A. These last proportions correspond actually to the formulations industrially used for the chemical bonding of the non-woven materials. This formulation gives a product whose elasticity modulus equals 794 MPa.

The polyethylene terephtalate fibres (PET) used come from an industrial production and are coated at exit of die. The polymer average molar mass lies between 15,000 and 20,000 g mol^{-1}. In order to control precisely their surface

quality, the fibres are preliminarily washed by immersion in petrol ether then in methanol in an ultrasound tank. Various coatings are then applied to fibres in order to improve their interaction with latex. To increase these interactions, it can be interesting to decrease the barrier of potential which surrounds the particles in solution. The latter could approach the fibres and be adsorbed on their surface due to Van der Waals interactions. Some investigations showed that the introduction of inorganic salt in the latex dispersion made it actually possible to lower this barrier, but generated most of the time a latex coagulation which is unfavourable for adhesion with fibres [20,21]. However, these studies showed that the pretreatment of fibres with inorganic salts also led to a decrease of the potential barrier and thus increased the fibres/latex interactions. The influence of a divalent salt ($CaCl_2$) on the fibre surface was studied. An aqueous solution containing 10 g l^{-1} of calcium chloride was prepared. The fibres were then immersed in this solution for 5 min.

The apparatus used for the measurement of zeta potential of latex is a Zetasizer 3000 supplied by the Malvern company. The zeta potential is determined by an electrophoretic method. The suspended particles in their medium are placed in an electric field and move towards the anode or cathode according to their electric charge. During this displacement, they carry along with them a fine layer of ions and solvent. Surface separating the stationary medium and the particle surrounded by its ions and solvent layer is called hydrodynamic surface of friction. The zeta potential is then defined as the potential of this surface. Thus, by measuring the displacement speed of the particle in an electric field of known intensity, his zeta potential can be calculated. Five measurements were made on each sample.

The zeta potential of fibres is measured by means of an apparatus provided by the company Zetacad (see Fig. 4). The sample is maintained in the column (1) and filters of porosity 70 μm (2) maintain the fibres in this column. Electrodes of Ag/AgCl (3) are laid out on both sides of the

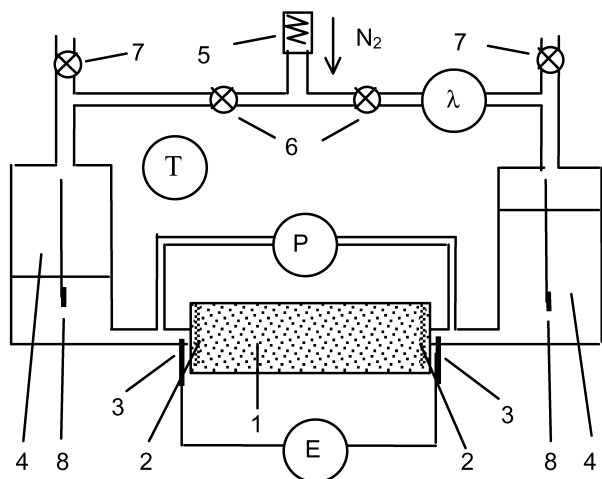filters. The electrolyte (1 l) is moved between the containers (4) under nitrogen pressure (0–500 mbar) by means of an admission valve (5). The direction of displacement is ordered by a set of valves of circulation and venting (6 and 7). The inversion of direction is caused by level sensors in Ag immersed in the solution (8).

The evaluation of adhesion between the polyester fibres and the latex matrix was carried out using a micromechanical test derived from the microdrop test [22,23]. During this test, the value of the debonding force is obtained directly. However, for a given matrix–fibre combination, significant dispersion of the experimental results can be related to the position of the microdrop on equipment or to the measurement of the fibre diameter [7]. Variations in chemical, physical or morphological nature along fibre can also affect the results of measurements which use only very small dimensions [24,25]. It can be noticed in addition that the use of slightly blunted blades to avoid accidentally cutting the fibre during a test causes a not easily controllable stress state in the contact zone of the drop. These many disadvantages led us to modify this test in order to limit the dispersion of our experimental results. A 0.1 mm thick aluminium cap was pierced at its centre by a laser beam, thus obtaining a circular opening of roughly 100 μm diameter. A polyester fibre was introduced into the hole, then the latex resin was injected around the fibre. The system was maintained on its support until complete reticulation of the latex (150 °C during 15 min). The composite was then transferred to a tensile testing machine and the fibre was extracted from the matrix at a speed of 1 mm min^{-1} (see Fig. 5). The embedded lengths L were measured after the interface debonding. The average shear stress τ_a was calculated by dividing the debonding force by the surface (see Eq. (7)).

$$\tau_a = \frac{F}{2\pi r_f L} \tag{7}$$

where F is the maximal force measured at the time of interfacial debonding and r_f is the polyester fibre radius. The experimental results were then treated according to the analysis developed by Greszczuk [26], consisting of reporting the evolution of τ_a as a function of L. Many improvements of this analysis are available in the literature, but it remains reliable if one uses it only for the comparison of different composite systems. The repartition of the force along the embedded part of the fibre is determined as ($x = 0$

Fig. 4. General diagram of the device for the measurement of zeta potential of fibre surface.
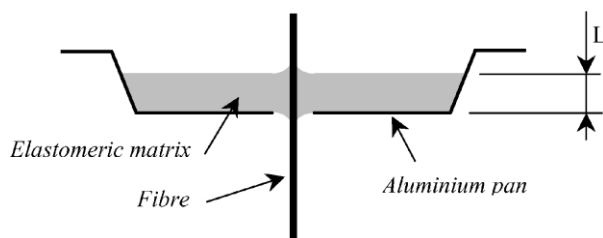

Fig. 5. Experimental device for the pull-out of a fibre embedded in a latex.

at the emergence point of the fibre)

$$F(x) = C_1 \sinh(\alpha x) + C_2 \cosh(\alpha x) \qquad (8)$$

where C_1 and C_2 are constants determined by the following limiting conditions

$$\begin{cases} F(0) = -F \\ F(L) = 0 \end{cases} \qquad (9)$$

α is a constant for each composite system, defined as

$$\alpha = \sqrt{\frac{2G_i}{b_i r_f E_f}} \qquad (10)$$

where G_i is the shear modulus of the interphase, E_f is the fibre elastic modulus, and b_i is the thickness of the interphase involved in the trial processing. In terms of interfacial shear stress, Eq. (8) can be written as:

$$\tau(x) = \frac{F\alpha}{2\pi r_f} \left[\frac{\cosh(\alpha x)}{\tanh(\alpha L)} - \sinh(\alpha x) \right] \qquad (11)$$

The maximum value of the interfacial shear stress, τ_{max}, is determined when $x = 0$:

$$\tau_{max} = \frac{\alpha F}{2\pi r_f \tanh(\alpha L)} \Rightarrow \tau_a = \frac{\tau_{max} \tanh(\alpha L)}{\alpha L} \qquad (12)$$

Because of the difficulty of determining accurately the values of G_i and b_i, τ_{max} and α are determined by using the latter equation with a non-linear regression between two parameters (τ_{max} and α). The mathematical regression is carried out with all of the debonding force's values. Extrapolating the curves to a zero embedded length allows obtaining the value of τ_{max}.

Greszczuk's analysis uses a very basic stress criterion which describes only partially the fracture behaviour of the interface. Other analyses use energy criteria, such as the one proposed by Gent and Liu [27]. A simple analysis of linear mechanics of fracture (energy released during the propagation of the interfacial crack = elastic energy of deformation stored in the elastomeric matrix) lead to the following relation between the debonding force F and the energy of interfacial rupture G_i

$$F^2 = 4\pi A r_f E_m G_i \qquad (13)$$

where E_m is the elastic modulus of the elastomeric matrix considered as purely elastic, r_f is the fibre radius, and A is the cross-section area of the block of matrix considered in which is really stored the deformation energy (cylindrical part of radius R). Relation (13) does not really give the dependence of F as a function of the embedded length L. It can only be applied for a zero embedded length. After extrapolation of F with $L = 0$, G_i is determined from Eq. (13), considering that only the matrix cylinder present in the cap hole is submitted to the strain (in our case, the hole has a diameter of 100 μm, which corresponds to a value of R of approximately 50 μm). According to Gent and Liu however, the work spent by friction along the interfacial

fracture zone at the time of debonding becomes significant and must be taken into account because the embedded length is greater than R. The increment of debonding force due to the friction is then

$$\partial F = 2\pi r_f \mu p \, \partial X \qquad (14)$$

where μ is the friction coefficient of the fibre–matrix interface, p is the compressive stress and X is the length where decohesion occurred. P is given by the following Eq. (15)

$$p = \frac{F_t}{3\pi R^2} \qquad (15)$$

with F_t the total debonding force including the friction. After integration of Eqs. (15) and (16) is obtained:

$$F_t = F \exp\left(\frac{2\mu r_f X}{3R^2}\right) = 2\sqrt{\pi A r_f E_m G_i} \exp\left(\frac{2\mu r_f X}{3R^2}\right) \qquad (16)$$

So, after total interfacial debonding, X can be replaced by the embedded length L in order to obtain a relation taking into account a dependence of the force as a function of L. This force increases in an exponential way versus L. Both analyses of Greszczuk and Gent et al. were used to characterise our composite systems.

3. Experimental results

3.1. Zeta potential of the colloidal latex solutions

The samples for the measurement of zeta potential are particles dispersed in a liquid. The main objective of this preparation is to preserve the original quality of the surface during the dilution process. Initially, the colloidal aqueous solutions are filtered. The solution collected is then diluted (one drop in 30 ml of distilled water). Measurements have been carried out on the latex A, P and on the mixture in proportion 75% P/25% A with pH 8. Table 1 presents the values of zeta potential of the various colloidal solutions. It is noted that latex A has the highest value of zeta potential in absolute value ($\xi = -55$ mV). Fig. 6 represents the evolution of zeta potential of latex A solution as a function of various concentrations of divalent salt addition ($CaCl_2$). A considerable reduction in ξ (in absolute value) is recorded as a small quantity of divalent salt is added to the mixture. For a concentration higher than 10^{-1} mol l^{-1}, the salt addition in the colloidal solution involves a constant value

Table 1
Values of zeta potential of the colloidal solutions of latex A, P, and 75% P/25% A

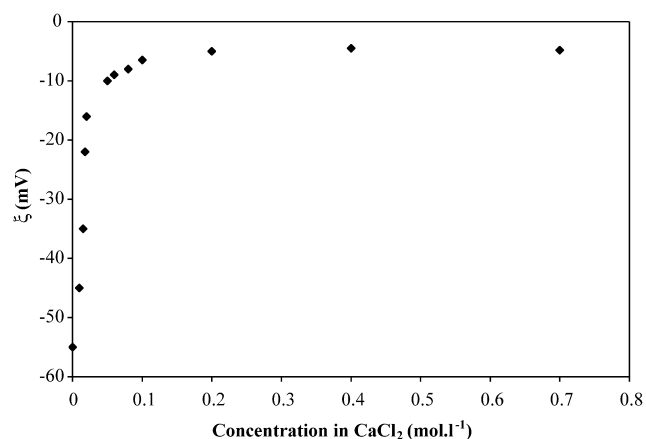| Type of latex	ξ (mV)
Latex A	-55 ± 1
Latex P	-50 ± 0.5
Latex 75% P/25% A	-45 ± 1

Fig. 6. Evolution of zeta potential of latex A as a function of the addition of $CaCl_2$ with various concentrations.

of the zeta potential ($\xi = -5$ mV). This shows that the latex A solution never flocculates, whatever the salt concentration. The suspension is thus indifferent to the effect of electrolyte. The ions do not interact with the particles surface of the latex solution and they are only attracted towards surface by electrostatic effect. The potential decreases in an exponential way by screen effect. An addition of 10 gl^{-1} of divalent salt $CaCl_2$ in a colloidal solution corresponds to a concentration of 9×10^{-2} moll^{-1}. With this salt concentration, latex A shows a zeta potential about -7 mV and does not coagulate.

Latex P flocculates when a small quantity of salt is added, and this whatever its concentration. The ions react here chemically by effect of adsorption or complexation with the particles of the colloidal solution. A chemical mechanism is then added to the screen effect. The initial electric charge is neutralized and a flocculation occurs.

The latex A and P present almost identical zeta potentials (-55 and -50 mV, respectively) for a same value of pH, but they do not behave in the same way after the addition of a divalent salt. Zeta potential measurements were also carried out on the mixture of latex A and P (in respective proportion of 25 and 75%) as a function of the divalent salt $CaCl_2$ concentration. The values are presented in Table 2. The zeta potential decreases as a function of the added salt concentration. From a salt concentration of

Table 2
Values of zeta potential of the mixture of latex 75% P/25% A as a function of the divalent salt concentration $CaCl_2$ addition

>Divalent salt $CaCl_2$ concentration (moll^{-1})	ξ (mV)
0	-45
0.01	-31
0.02	-19
0.05	-12
0.06	-8
0.08	Flocculation
0.10	Flocculation

8×10^{-2} moll^{-1}, the initial charge of the latex particles is neutralized.

3.2. Zeta potential of the polyester fibres surface

Uncoated PET fibres were used for the determination of their zeta potential of surface. These fibres were also treated with an aqueous calcium chloride solution (10 gl^{-1}). The solution of electrolyte used for the different measurements is sodium chloride with a concentration of 10^{-3} moll^{-1}. This solution passes through a fibre stopper (0.75 g) located in a cylindrical tube made of glass under a pressure ranging between 20 and 100 mbar. An electric potential (streaming potential) is measured between Ag/AgCl electrodes located in the tube containing the sample. The study of ξ of polyester fibres as a function of pH was carried out while varying the pH solution of NaCl from 3 to 10 by adding drops of solutions of HCl or KOH with a concentration of 0.1 moll^{-1}. For each pH value, the PET fibres to be analysed are equilibrized in their solution of electrolyte while making circulate under constant pressure this solution from one tank to another during 2 h.

Fig. 7 represents the zeta potential of the surface of polyester fibres (uncoated and treated by calcium chloride) as a function of pH. The shape of these two curves lets appear a plate in the alkaline area. The formation of the double electric layer thus is mainly caused by the dissociation of acid functional groups. An extrapolation of these curves to $\xi = 0$ (isoelectric point) also makes it possible to distinguish acidity or alkalinity of a solid surface if dissociation of the superficial groups is the principal mechanism of the double electric layer formation. A low value of the isoelectric point indicates an acid character of surface. As shown by the curves of Fig. 7, the PET fibres studied present at their surface dissociable acid functional groups. ξ curve as a function of pH for the uncoated PET presents a plate in the alkaline area corresponding to $|\xi| = 19$ mV. The same fibre treated with an inorganic salt also presents a plate, but the absolute value of its zeta
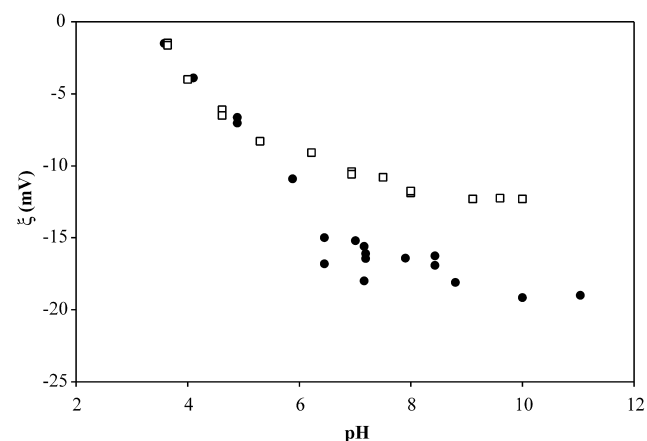

Fig. 7. Evolution of zeta potential of uncoated PET fibres (●) and treated by $CaCl_2$ (□) in an electrolytic solution of NaCl as a function of pH.

potential is decreased ($|\xi| = 12$ mV). The cations Ca^{2+} adsorbed on the fibre surface thus decreased zeta potential of 7 mV. It is noted in addition that the sign of zeta potential of fibres is identical to that of the aqueous colloidal solutions.

3.3. Pull-out tests of polyester fibres in latex

The pull-out tests were carried out with the uncoated polyester fibres and treated by $CaCl_2$ embedded in the latex P on one hand, and in the industrial mixture of 75% latex P and 25% latex A on the other hand. The tests with latex A alone could not be carried out because of the too high rigidity of this material after reticulation: whatever the embedded length L in the sample, a fibre breakage was always observed before that of the interface. In a general way, the values of τ_{max} obtained after Greszczuk analysis are always much higher when the polymeric matrix is more rigid.

The experimental results obtained with the latex P are presented on Fig. 8. The latter are discussed according to the analysis developed by Greszczuk, and the curves are extrapolated to a zero embedded length. It is noted that the values of τ_{max} obtained are, respectively, 3 MPa in the case of uncoated fibre and 6 MPa when the fibre is treated with $CaCl_2$. In the case of the mixture of latex with 75% of P and 25% of A, the results are presented on Fig. 9. The values of τ_{max} pass from 18 to 23 MPa when the fibre is treated with a divalent salt.

The analysis according to Gent and Liu, respectively, gives G_i values of 12 and 65 J m^{-2} for the polyester fibre untreated or treated by $CaCl_2$ embedded in the latex P on one hand, and of 16 and 26 J m^{-2} for the same fibres on the other hand in the latex mixture on the other hand. These values confirm the influence of the superficial treatment on the interfacial adhesion.
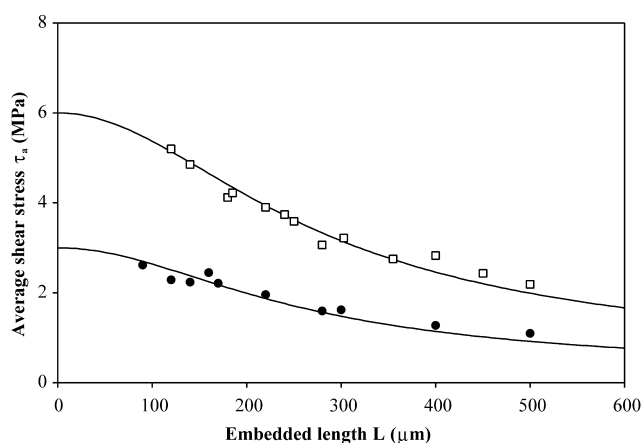

Fig. 8. Experimental results of the pull-out tests Greszczuk analyses for the uncoated polyester fibres (●) and treated with $CaCl_2$ (□) embedded in the latex P.
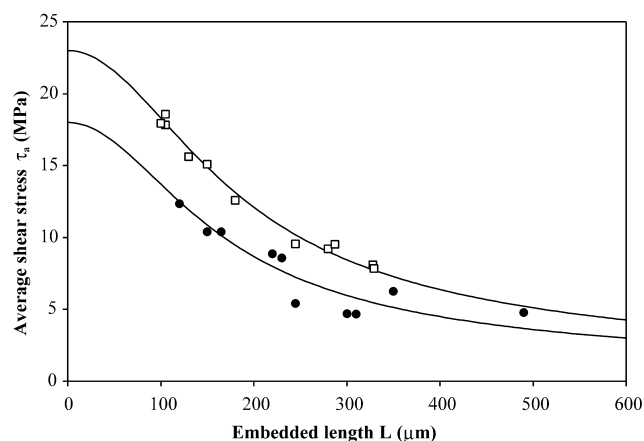

Fig. 9. Experimental results of the pull-out tests Greszczuk analyses for the uncoated polyester fibres (●) and treated with $CaCl_2$ (□) embedded in the mixture with 75% of latex P and 25% of latex A.

4. Discussion

The latex 75% P/25% A at pH 8 has a zeta potential of -45 mV (see Table 2). For the same value of pH, the uncoated polyester fibre has a zeta potential of -19 mV, whereas the fibre treated by $CaCl_2$ shows a zeta potential of -12 mV (see Fig. 7). Thus, the difference between the values of zeta potentials for fibres and latex for same a pH is 26 mV with uncoated fibre and of 33 mV with treated fibre. The difference $\Delta\xi$ is thus more significant when the fibre is covered with a divalent salt. Bismarck [16] stipulates that larger $\Delta\xi$ is, the better will be the interaction between the two materials studied. By comparing these values of $\Delta\xi$ with the values of τ_{max} obtained after the pull-out tests (respectively, 18 MPa with the uncoated fibre and 23 MPa after treatment with $CaCl_2$), it is noted that this condition is actually checked. The results indicate that treating the PET fibre with an inorganic salt favours adhesion. This better interaction results in a higher value of $\Delta\xi$ for this system, and shows that the electric repulsion is definitely less significant than for the system with an uncoated fibre. The energy barrier to bring closer the latex particles to fibre will thus be decreased, and the interaction with latex may be increased, depending on the mechanism of charge-building at the solid/liquid interface.

The results presented in Table 2 show that the colloidal solution 75% P/25% A coagulates in the presence of inorganic salt when the concentration reaches 8.10^{-2} mol l^{-1}. However, the local salt concentration on fibre after treatment is probably much higher than that in solution. It is thus very probable that the latex comes to be adsorbed then to coagulate on the PET fibre treated by $CaCl_2$ thus improving the adhesion of matrix on the reinforcing fibre.

The same observations can be carried out when the uncoated PET fibre or treated is embedded in the latex P alone. However, because of its lower rigidity compared with that of the mixture 75% P/25% A, the values of τ_{max}

obtained after decohesion are definitely lower than in the case of the mixture. Thus, $\Delta\xi$ takes the value 31 mV in the case of the uncoated polyester fibre with a value of τ_{max} equalling 3 MPa. Moreover, $\Delta\xi$ reaches 38 mV when the fibre is treated by $CaCl_2$ with a maximal interfacial shear stress of 6 MPa. It is noted thus that for this system as for the precedent, an increase in $\Delta\xi$ leads to an increase in τ_{max}.

5. Conclusion

The use of polyester fibres as reinforcement for composite materials is in general limited because of the low surface polarity of PET. This characteristic involves in most of the cases a poor interfacial adhesion, which is prejudicial to the global mechanical behaviour of the material. So, in this study, we evaluated the action of salts with cations on the interaction between polyester fibres and the matrix. Measurements of the ξ–pH dependence show changes in surface chemistry of salt-treated PET fibres. This method is an appropriate tool to characterize surface modifications of fibres with latex. The higher the difference between ξ values of the matrix and the fibre, the higher the adhesive strength between them.

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