On the hybrid character of glass fibres surface networks

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The structure of organomineral coatings on glass fibres surface is a function of numerous parameters. Among them, the molecular parameters of organosilane coupling agents in aqueous solution are of great importance [1]. The understanding of hydrolysis and condensation mechanisms, the influence of the pH, temperature, concentration and the nature of the organic ligand are keys for the control of the structure [2–4]. It is now well accepted that the structure resulting from the deposition from an aqueous solution of 1,4 γ-aminopropyltriethoxysilane consists in a three-dimensional graded cross-linked network [5, 6]. The crosslinking density increases as the glass surface is reached and the outer layers are thought to be physisorbed. The situation still remains uncertain in the case of more complex industrial sizings, although it is assumed that the silane migrates to the interface providing an interfacial region which is similar to that obtained from the pure coupling agents solutions [7]. The silane may act as a surfactant for the colloidal polymer particles in the sizing emulsion. The evolution of the structure in the course of a thermohydrolytic treatment has not been discussed so far, although changes in the mechanical behaviour of the fibres [8–10] and in the mechanical properties and the structure of interfacial zones in composites materials [11, 12] have been reported. The first steps of interfacial zones formation can be described by the dissolution of the outer physisorbed layers of the structure in the reacting comonomers, and the consecutive diffusion in the preformed inorganic–organic network [3]. An attempt to apply general concepts from the chemistry of hybrid materials to the formation and properties of glass-fibers sizings and glass fibers-polymer interfaces can thus be proposed by considering the simultaneous reactions of organic and inorganic components. Apart from an analogy between the sizing treatment of glass fibers and the strengthening of silica glass by means of hybrid inorganic–organic coatings [13], the application of concepts from the chemistry of hybrid materials in the field of glass fibers sizings and their interfaces with a polymer has remained to our knowledge purely conceptual, suffering from a lack of experimental data. In fact, due to the geometry of these systems, the dimensions involved and the necessity to perform *in situ* measurements, the experimentation still remains difficult. In the early eighties, Miller [l4] developped a technique based on dynamical mechanical analysis which enables to characterize coatings directly on glass fibers strands. Using this technique, we report here an experimental observation of the hybrid character of glass fibers sizings via the evolution of their structure in the course of a thermo-hydrolytic treatment.

The loss factor was computed on a Rheometrics RSAII apparatus every 2 degrees between −150 and 200 °C. Three different kinds of E-glass fibers from Vetrotex Co. differing by their surface treatments have been considered:

– a water-based sizing treatment corresponding to the deposition of an aqueous solution of an anti-static agent only,

– a silane-based treatment corresponding to the deposition of γ-aminopropyltriethoxy-silane from a 1 wt.% aqueous solution of silane,

– an industrial sizing referred to as P122 by Vetrotex Co., known as an universal sizing. The coupling agent included in the sizing formulation is the γ-APS. Other components such as lubricant and film-former were also included.

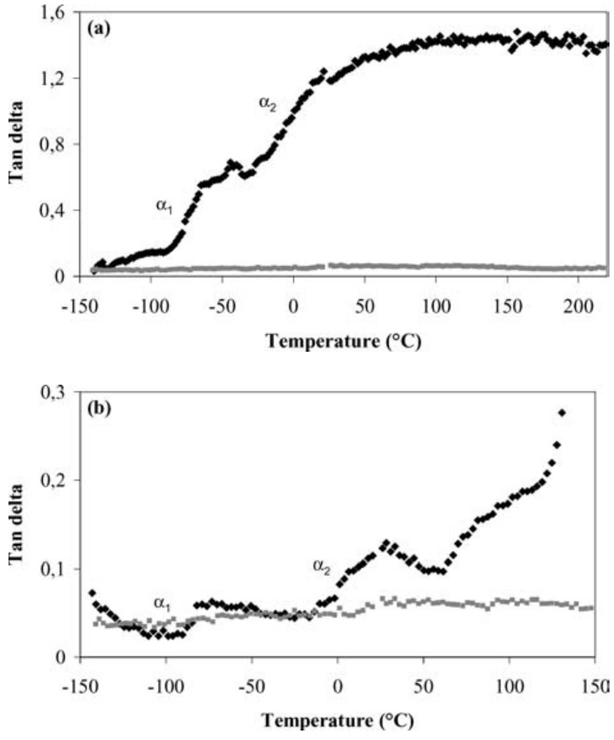

Figure 1 Loss factor of γ-APS (a) and P122 (b) sized E-glass fibers determined by dynamical mechanical analysis in bending at 1 Hz. Untreated glass fibers loss factor in grey.

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TABLE I Temperatures (°C) corresponding to the beginning of the relaxations of γ-APS and P122 sized E-glass fibers, A.R. and after 24 and 72 hr at 60 °C and 98% R.H.

	γ-APS			P122	
	A.R	24 hr	72 hr	A.R	72 hr
α_1 Relaxation	−88	−8	66	−90	−102
α_2 Relaxation	−32	40	105	−16	−8

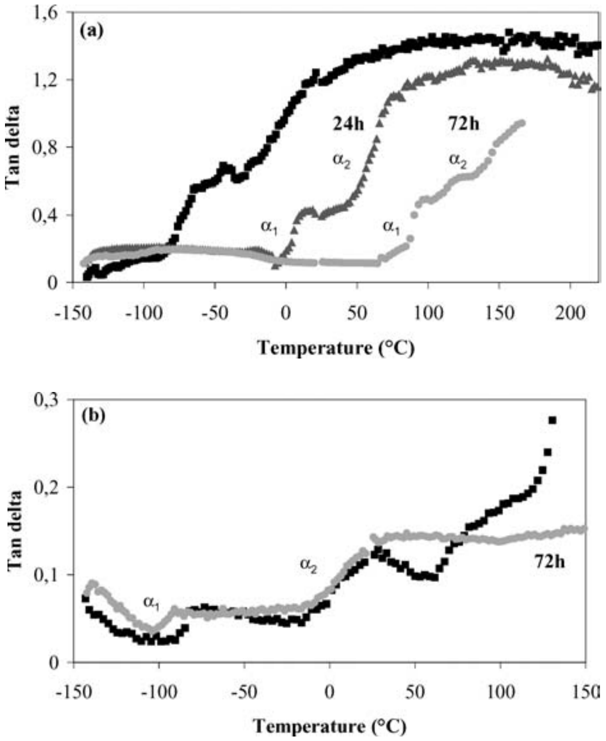

Figure 2 Lost factor of γ-APS (a) and P122 (b) sized E-glass fibers determined by dynamical mechanical analysis in bending at 1 Hz. A.R. in black, after 24 and 72 hr at 60 °C and 98% R.H. in grey.

The evolution of the loss factor as a function of temperature is presented Fig. 1. Measurements made on untreated fibers lead to the conclusion that pure glass does not show any relaxation in the temperature range considered. The loss factor of the γ-APS-based coating characterized by two main relaxations referred to as α_1 and α_2 on Fig. 1a is representative of a graded cross-linked network. Care has to be taken however since the interpretation of the data can be biased by possible hydrolysis or condensation of the network during the experiment. The low temperature α_1 relaxation may be attributed to R-SiOX groups who are free enough to move [15]. Similar relaxations are observed in Fig. 1b for an universal sizing. Temperatures corresponding to the beginning of each relaxation computed Table I are of the same order for both coatings, confirming the similarities between a silane-based model sizing versus a polymer/silane based industrial sizing [7].

Both structures were tested after a thermo-hydrolytic treatment at 60 °C and 98% RH. Fig. 2a shows an important translation of both α_1 and α_2 relaxations toward higher temperatures for the γ-APS network. This reduction in mobility may be attributed to a condensation of the remaining silanol species into siloxane bonds. From Fig. 2b, the behavior of the polymer/silane-based sizing is significantly different: α_1 and α_2 relaxations are considerably less translated, indicating an important stability of the network as compared to the pure silane. This stability may be attributed to the organic nature of polymer/γ-APS bonds [4]. One should also note the decrease of the α_1 relaxation temperature reported Table I, indicating a plasticization of the network. The presumed condensation observed for the network resulting from the deposition of an aqueous solution of organosilane is not observed for the polymer/silane-based coating. The different structures observed after a thermo-hydrolytic treatment as well as the nature of the mechanisms involved are related to the hybrid character of glass-fibers surface networks. The extrapolation of such behaviors to interfacial zones in composite materials could provide new highlights for the design of hydrolytic resistant interfaces.

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