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Supported dynamic mechanical thermal analysis: an easy, powerful and very sensitive technique to assess thermal properties of polymer, coating and even nanocoating

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Abstract

A dynamic mechanical thermal analysis (DMTA) performed on stacked coated supports or on samples sandwiched between rigid supports (carbon or glass fibers, metal or glass plates, …) is described.

The choice of a dual cantilever deformation favors the shear strain of the less stiff material between the more rigid supports. A theoretical model demonstrates that the less stiff material response is mainly recorded and moreover amplified. An exceptional sensitivity to the soft material is therefore observed.

This method does not require any special sample (only stacking of coated supports or sample sandwiching) whilst it enables to characterize in situ polymer coating, even nanocoating. This characterization is of prime interest in technological coating developments such as paints, fiber sizings, glues, … This possible measurement of thermal transitions peculiar to nanocoatings also opens more fundamental studies as the probing of interface influence on thermal transitions.

Keywords: Dynamic mechanical analysis; Coating study; Interphase thermal transitions

1. Introduction

dynamic mechanical thermal analyses (DMTA) of supported samples were extensively carried out on thermosets. The fluid, too soft and tacky character of their precursor before cure explains the need of a support. So, the use of a torsional braid analyses (TBA), proposed by Gillham [1], brought out evidence of gelation and vitrification times by a rheological method. However, the supported DMTA (SDMTA) was also reported for other materials like thermoplastic [2] or organic compounds [3] and the support can be either fabrics [2,4], either meshes [5], either metal spring [6] or metal sheets [7–9].

Shearing and bending deformations are reported to give a viscoelastic response of the matrix on its more rigid support. An extended and recent review presented by Prime [10] summarizes the state-of-the-art.

In most of those studies, it is to be noticed that the support was necessary for the measurability. However, the authors noted that it increases the difficulty of quantitative modulus measurements of the coating and that it may interfere on the viscoelastic response of the polymer because of an interface influence or an interphase formation [5,11,12]. Therefore, the authors recommend the choice of an inert support [2,4] and of thick coatings [7].

Conversely, Thomason [13] changed this drawback into an advantage because he used SDMTA on very thin coatings impregnated onto fibers in order to study the support effect on the coating thermal transitions. In other words, he used this technique to investigate the interphase viscoelastic properties. His study was based on a technique developed by Miller [14], in which a spring is filled with fiber sample and where a cyclic two points flexural strain method is used. This sample preparation allowed the investigation of the sizing of glass fibers even when the thickness of those coatings is roughly estimated as low as several tens nanometers.

In this paper, we report another SDMTA method. It is based on a dual cantilever deformation performed either on films sandwiched in between plates, either on stacked coated supports for instance bundles of commercial coated fibers. This sample configuration allows the measurement of very thin coatings.

Moreover, unlike Miller's method, the sample preparation is easy to apply regardless the supports (not only fibers but also metal, glass plates or silicon wafers are suitable)

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and regardless the sample forms (powder or films sandwiched between two plates, or even coatings on their support are suitable). Because a signal is recorded by this method regardless the coating thickness (from above 1 mm and down to about 1 nm), it opens more fundamental research like the study of the viscoelastic properties of the interphases by study of nanocoatings.

We report here the main studies we carried out thanks to this technique in order to highlight its interest and its versatility. Its reproducibility, validity and sensitivity are also discussed.

2. Materials

Supports

- When plates are used they are cut in order to obtain 60 mm × 6 mm rectangle sheets.
  The copper plates were cut in a 1/4 mm-thick copper sheet and were washed in methylene chloride.
  The glass plates were cut in 0.15 mm-thick optical glass slides from Vel.
  The Si wafers are cut into Si wafers supplied by A.C.M. (diameter of 3″, ⟨1.0.0⟩ oriented, n-type, P doped, thickness 200 μm,). After cutting, the plates were cleaned by a piranha solution: immersion for 20 min in a freshly made solution (50/50 (V/V)) of sulphuric acid (98%, Merck) and Hydrogen peroxide (27%, Vel). This procedure is known to efficiently [15,16] remove the organic contaminants and to produce a highly hydrophilic surface by leaving on the silicon substrate a hydroxylated layer.
- The fibers were mainly studied as received. They were covered with their proprietary coating.
  The following fibers are studied:
  - AS4, 6K were supplied by Hercules, YKMM/5000 by Donnay, M40JB by Toray, T300S by Union Carbide, P55S by Amoco, HTA 5131 by Tenax, for the carbon fibers.
  - The glass fibers (BVR510, R40TX5-2400, R40JX7-2400, R43 and R16EX3-2400) were supplied by Owens Corning.
- The washed studied fibers were AS-4 Carbon fibers obtained from Hercules. They were washed in Soxhlets extractor in order to remove processing aids, sizing and contaminants. 80 h of extraction in methylchloride followed by 48 h of extraction in methanol were carried out. 10 g of fibers were washed into 100 ml of solvent. They were then hung and dried for 24 h in room air and for 2 h under vacuum at room temperature. The wash procedure is described in more detail elsewhere [17,18].

Polymers

Polystyrene PS (LACQRENE) was supplied by Elf Atochem and named LACQRENE.

Polyethylene terephthalate PET (E47) was supplied by ICI.

Poly(meta-xylylene adipamide), PAmxD,6 named ‘PARA0000’ was supplied by Solvay.

The nitrocellulose was supplied by PB Clermont.

The bismaleimide resin (HX1601) was supplied by Hexcel.

The self assembled monolayers

The self assembled monolayer was deposited onto an oxidized Si wafer. Octadecyltrimethoxysilane (98%) (OTMS) supplied by A.B.C.R. was self assembled from a 10 mM toluene solution at room temperature for 48 h. The wafers were then rinsed in chloroform, held in a chloroform ultrasonic bath for 10 min. Finally, they were dried under an argon flow.

3. Method

The RSA II mechanical spectrometer from Rheometrics, Inc. was used. A dual cantilever deformation mode was applied to the supported samples. However, a shear deformation mode of the less stiff material was favored by its sandwiching in between a more rigid material (the support) as demonstrated further.

Therefore, when fibers were studied, fibers bundles were looped in 100 mm-long loop, 10 turns for the carbon fibers and 5 turns for the glass fibers, giving after flattening of the loop a stacking of, respectively, 120,000 fibers (bundles of 6000 carbon fibers) and 12,000 fibers (bundles of 1200 glass fibers) and an actual sample length of about 50 mm. Whilst, when coating deposited on glass plates or metal plates were studied, respectively, three and five plates were stacked. For the study of the self assembled monolayer deposited onto Si wafers, three coated wafers plates were studied. However, two uncoated cleaned wafer plates were inserted in between in order to keep a controlled coating thickness of around 2 nm. To keep the sample cohesion and to facilitate the grip within the jaws, three lead rings were used to clamp the so-obtained samples. Those ring devices were set where the jaws grip the sample as shown in Fig. 1. They prevent the sample sliding reported in a similar procedure as ours described by Ahlstrom [19]. This assembly procedure allows an easier sample preparation than the Miller's method did because it does not need threading.

Experimental parameters were: frequency of 10 Hz, strain amplitude of 0.1%, temperature range: from −100 to 300°C. As a rule, five measurements were recorded every 3°C after thermal stabilization of 0.3 min in between.

The better expected temperature resolution is therefore around 3°C.

Dual cantilever DMTA analysis does not aim at an absolute modulus measurements because the modulus were calculated from the force generated by the sample at a given amount of strain and from the size of the sample.

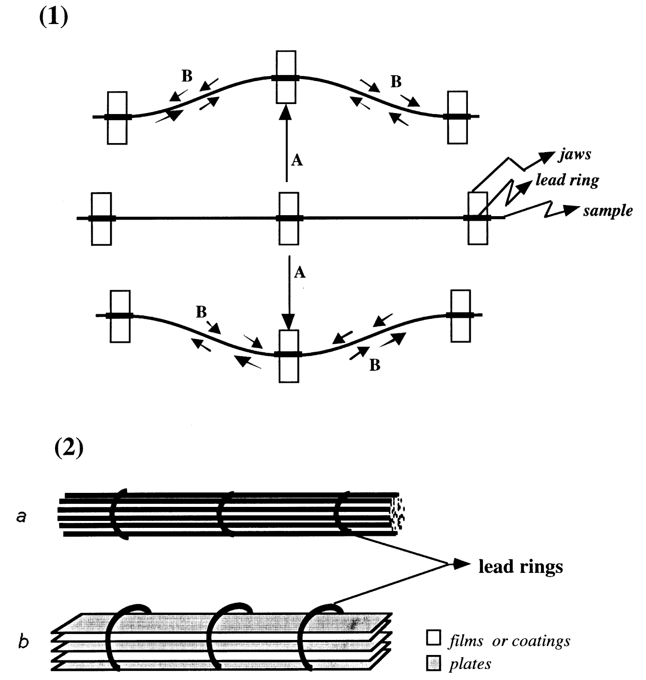

Fig. 1. Schema of the sample fixture geometry and deformation. 1/the sample deformation and the applied stresses were drawn. (A) is the periodic imposed force inducing periodic strain, (B) is the shear strain induced into the sample). 2/the sample geometry is presented (a) for coated fibers, (b) for sandwiched films or for coated plates.

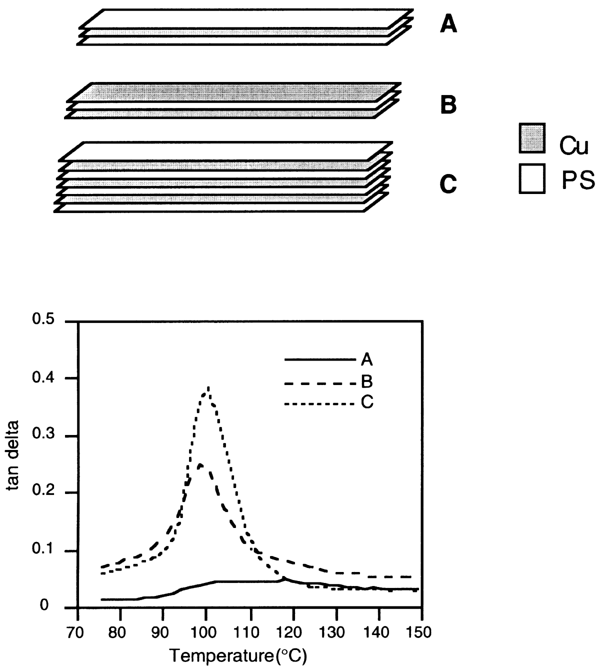

Fig. 2. Sample modeling: (A) two sheets of PS sandwiching a copper plate; (B) a sheet of PS between two copper plates; (C) a tripled stacking of PS-copper stacking covered by an additional PS sheet, giving two sandwiched Ps sheets and two external PS layers and their respective tan δ responses recorded in SDMTA analysis.

This size input in the modulus calculation is particularly critical because the modulus variation related to discrepancies in the dimension depends on the cube of the length and of the thickness and obviously may vary the modulus by a large error. In the here reported SDMTA mode, the sample dimensions could not be accurately measured out at all (complex sample geometry, heterogeneous samples, voids into the samples), and, hence, only rough sample dimensions were input (i.e. $50 \times 2\ \text{mm}^2$). Moreover, in dual cantilever mode, the calculation method assumes that the sample strain instantaneously changes in strain from a finite strain to zero strain at the end of the clamp. This discontinuity impossible in practice must be corrected by the experimental determination of an apparent length [20].

In our particular composite sample, the actual deformation mode is a complex mixture of various pure modes applied on a complex sample configuration and therefore, only relative value of modulus are anyway measured out by this method.

For all those reasons, in our particular composite case, because only relative values of G' and G'' can be measured out, we deliberately decided to suppress G' and G'' figures in the reported figures in order to avoid unreliability. Nevertheless, the transition temperatures of the coating, the properties targeted by the dynamic mechanical analyses can clearly be assigned to modulus changes (fall or increase) or to their tan δ ratio.

The DSC analyses were carried out under a nitrogen atmosphere thanks to a Mettler Toledo DSC 821$^{\text{e}}$. The DSC instrument was calibrated with metal standards (indium-lead). The sample weight was of about 10 mg. The samples were heated at 10°C/min from 40 to 300°C with a holding time of 2 min at 300°C in order to achieve a complete melting. The samples were then cooled and reheated at the same rate and over the same temperature range.

4. Results and discussion

4.1. Selectivity, sensitivity of the technique: a theoretical explanation

The more surprising aspects of the method were its selectivity to the less stiff material and its sensitivity.

In order to explain its selectivity and sensitivity, a modeling of its principles was undertaken. First of all, the studied sample was simplified using a PS/copper plate sandwich. Three samples presented in Fig. 2 were studied: they are an assembly of one, two or three copper layers, with variously inserted PS films (see Fig. 2). Those three samples led to only two types of behavior:

- For two sheets of PS sandwiching a copper plate (Fig. 2A), *bending* of the PS sheets did not give important response. A wide and weak peak was only observed.

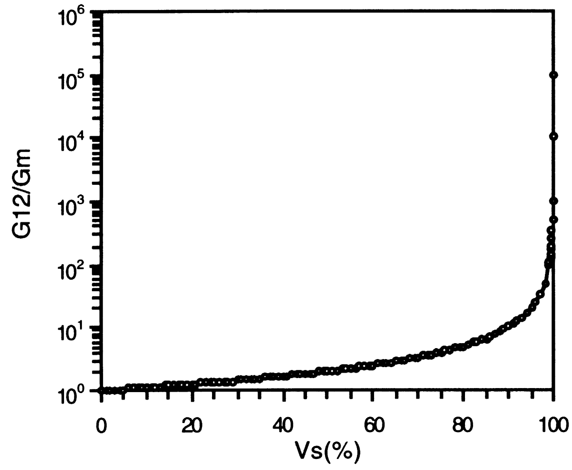

Fig. 3. Amplifier factor $(1 - V_s)^{-1}$ versus the percentage V_s of support in the studied composite.

- For a sheet of PS between two plates (Fig. 2B), the response was quite different: a tan δ peak at the glass transition temperature of the PS was clearly observed. In comparison with Fig. 2A, the bending of the sandwich favors in this sample configuration an additional *shear strain.*
- For the mixed case (Fig. 2C), the response of the two PS films strained in shear between the copper plates dominated and is even higher than case (B) one because of the two sheared films. Nevertheless, the bending of both external PS films did not affect the tan δ peak position, it was still recorded at the PS glass transition temperature within the method temperature resolution.

This model demonstrates the essential role of a shear strain for such a recording. Therefore, the G_{12} shear modulus of this model was calculated. It can be expressed for such a model composite by the well-known micromechanical expression [21] (which is a series-connected model) given in Eq. (1):

$$\frac{1}{G_{12}} = \frac{V_m}{G_m} + \frac{V_s}{G_s} \tag{1}$$

where G_m is the shear modulus of the coating G_s the shear modulus of the support V_s the support volume V_m the coating volume and $V_m + V_s = 1$. Eq. (1) could be rewritten in Eq. (2)

$$G_{12} = \frac{G_m}{1 - V_s\left(1 - \frac{G_m}{G_s}\right)} \tag{2}$$

Because G_m of the film deposited onto the support is a few orders lower than G_s of the support. Eq. (2) can be rewritten considering $G_m/G_s \ll 1$.

$$G_{12} = \frac{G_m}{1 - V_s} \tag{3}$$

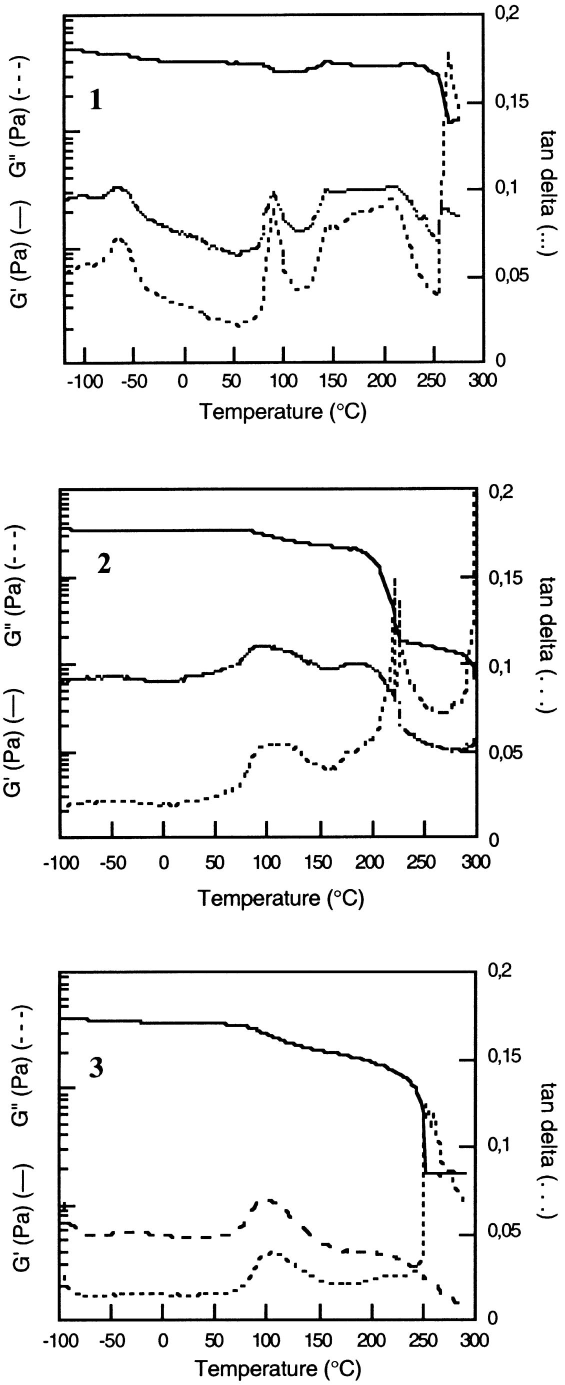

Fig. 4. SDMTA viscoelastic responses versus the temperature on: (1) heating; (2) cooling; and (3) reheating for the same amorphous PET.

This simplified relation shows clearly that the shear modulus of the composite sample is mainly and straight a function of the film shear modulus (G_m) multiplied by a factor $1/(1 - V_s)$.

Therefore, within this model, the film shear modulus variations are directly detected on the measured composite modulus by a variation of G_{12}. It explains the measurability of the film modulus changes, although a composite sample is studied. Moreover, it demonstrates that an exceptional

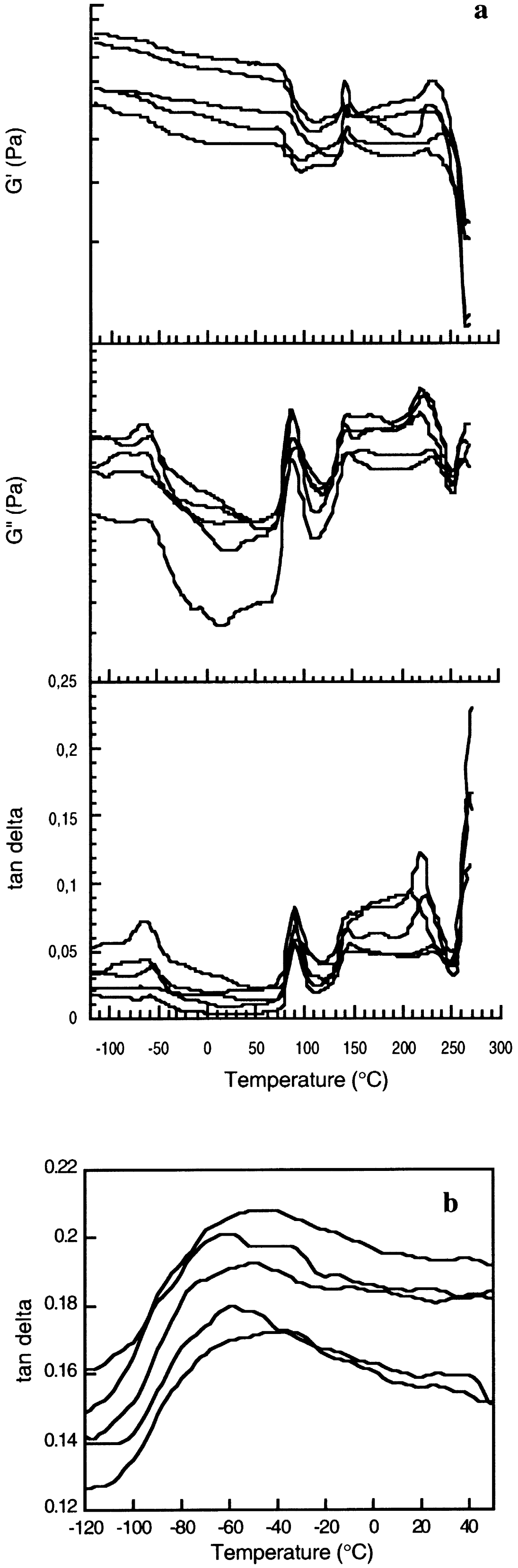

Fig. 5. Comparisons of five SDMTA viscoelastic responses recorded for a PET sample (a) and of five SDMTA recordings of AS-4 carbon fiber sizing (b). The responses are vertically shifted for readability criterions.

sensitivity of the technique on very thin matrix layer must exist because G_{12} is a function of G_m multiplied by the enhancing factor $1/(1 - V_s)$. This factor amplifies the measured modulus at increasing support content. Fig. 3 presents the evolution of this factor versus V_s.

4.2. Validation of the method

Thereafter, the comparison of the transitions recorded by this technique with more classical analysis methods was carried out in order to check its validity. A polyethyleneterephthalate (PET) was therefore studied at the same time by SDMTA (supported film samples), by classical DMTA (bulky bar samples studied as same frequency) and at last by DSC.

Fig. 4 presents the viscoelastic responses of the copper plates/PET films sandwich. If the bulky bar samples only enables by classical DMTA the recording of the secondary transitions (T_β) at around −50°C and of the glass transition at around 90°C, the sandwiched sample gives more information thanks to the supporting plates.

On the amorphous sample presented in Fig. 4(1), the following observations can be done:

- A secondary transition (T_β) is observed before T_g at around −60°C.
- The T_g is recorded at 90°C.
- The crystallization is observed at around 140°C (increases in G', G'').
- Further crystallization phenomena are recorded at around 210°C
- The melting starts at 255°C (decrease in G').

Moreover, the presence of a support enables to study a cooling scan under controlled temperatures as presented in Fig. 4(2). The crystallization on cooling starts at around 230°C and exhibits a G'' maximum at around 180°C, finally the T_g is again recorded at 90°C.

On reheating the T_g is observed in Fig. 4(3) at the same temperature and the melting starts at 250°C. No crystallization phenomena were anymore observed because the sample was fully crystallized during the cooling ramp.

All those recorded data are in good agreement to the transition temperatures measured out by DSC (first heating: $T_g = 80°C$, $T_{ch} = 150°C$ and $T_m = 260°C$; on cooling: $T_{cc} = 175°C$; second heating: $T_g = 80°C$, $T_{ch} = 160°C$, $T_m = 250°C$).

Similar comparisons performed on a polyamide also gave good agreement between transition temperatures.

4.3. Reproducibility of the method

The same samples were for two different sample types (respectively, plates or fibers as supports) scanned five times in order to show that the reproducibility of the method is satisfactorily good. A PET "sandwich" samples (copper/PET layers) is firstly studied. G', G'' and $\tan\delta$ were

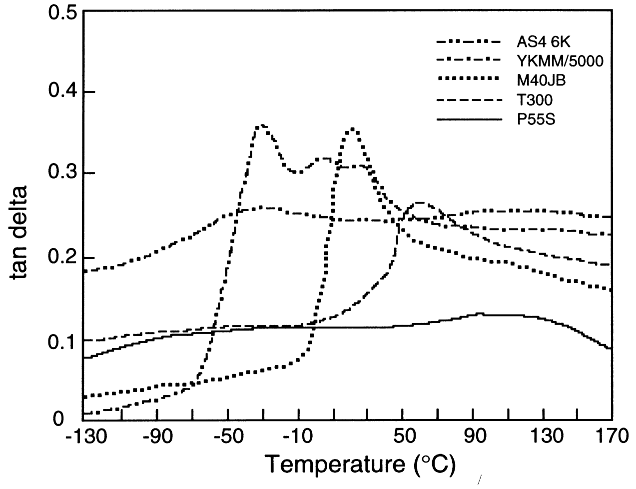

Fig. 6. Viscoelastic fingerprints of various carbon fibers recorded versus the temperature by DMTA.

recorded and given in Fig. 5a. Secondly, Fig. 5b presents the tan δ of as-received AS-4 carbon fibers (fiber with their proprietary coating). The same good reproducibility was obtained on those samples but also on all other samples further studied.

4.4. Versatility of the method

From the comparison of thermal studies carried out by DSC, DMTA and SDMTA and reported heretofore in details, the validity and reproducibility of the new technique was ascertained.

In this paragraph, we want to highlight the strong points of the method. Obviously, first of all, the in situ study of coating encounters a technological demand for developments and quality controls in coating manufactures such as paints, glue, fiber sizing, hair gel, … Moreover, a more fundamental interest could be focused on showing how the interface presence could affect those coating thermal transitions and hence on probing the interface effect.

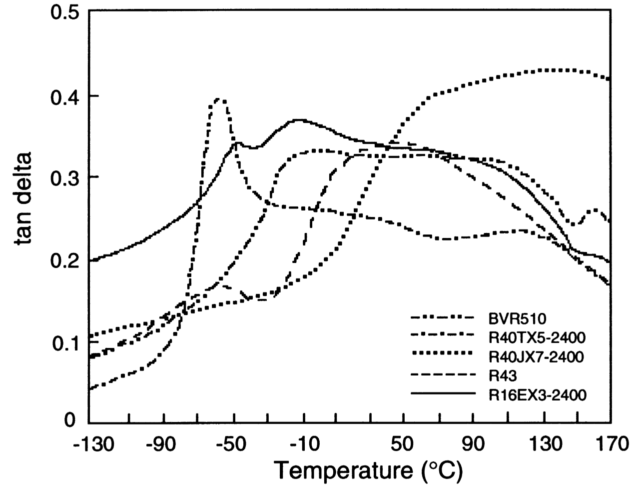

Fig. 7. Viscoelastic fingerprints of various glass fibers, recorded versus the temperature by DMTA.

4.4.1. Study of coatings

The thermal study of coatings is a difficult problem. Usually, various strategies are attempted [22,23]: the removal of the coating, the study of thicker coating or better, the development of more sensitive techniques were aimed at. SDMTA is a powerful sensitive technique fulfilling the latter expectation. Indeed, it allows the in situ study of coatings like fiber sizing and so on.

4.4.1.1. Study of fiber sizings. Figs. 6 and 7 present the viscoelastic responses (tan δ) recorded, respectively, for various carbon and glass fibers. Those responses are fingerprints of proprietary coatings and can be used in quality control procedures or for thermal oxidation, aging,… explorations. So, Fig. 8 shows how much the fingerprint could vary along a commercial glass fiber roll while Fig. 9 shows how much the sizing removal by solvent washes leads to a tan δ response vanishing. By this decrease, it was shown that the cleaning of AS-4 fibers is

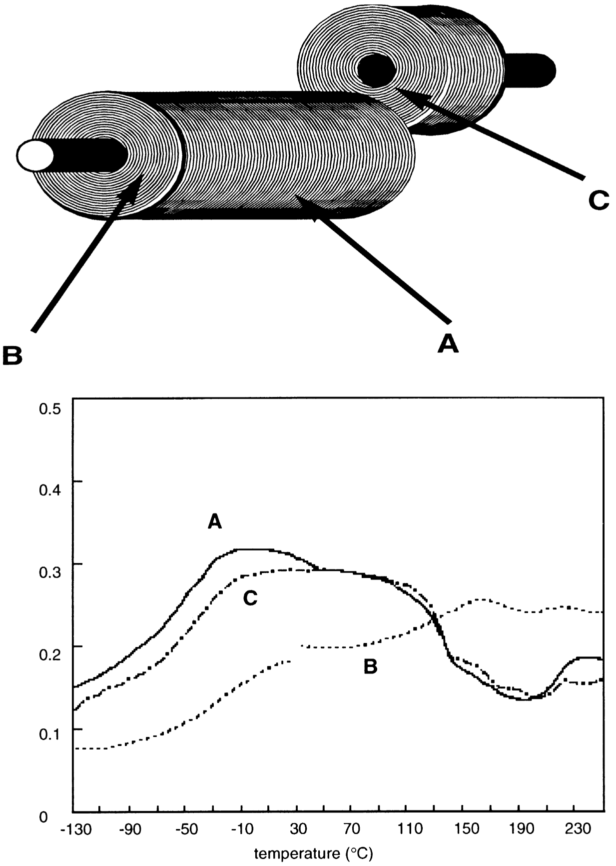

Fig. 8. Viscoelastic fingerprint (tan δ) of glass fibers sampled in the same commercial roll, recorded by DMTA versus the temperature: (a) fibers sampled in the external layer of the roll; (b) fibers sampled at the lateral end of the roll; (c) fibers sampled near the axis of the roll.

favored by a methylchloride extraction followed by a methanol extraction and is not in the reverse order [17].

Finally, Fig. 10 allows to demonstrate an aging of fiber sizing. Fig. 10a shows that the epoxy sizing of HTA fibers exhibits a T_g at around 20°C, cures beyond 250–270°C (increases in G', G''). After cure up to 300°C, a T_g of 220°C on a second heating was observed (not shown). Fig. 10b demonstrates that an aging of this sizing can be observed after 2 years because, despite a T_g of around 20°C, curing is not observed anymore on first heating. A T_g of only 90°C was observed (not shown) on second heating and confirms the change in curing.

4.4.1.2. Study of electropolymerized PAN on its cathode. The viscoelastic study of PAN electrografted onto copper and of ungrafted PAN films lied on the same metal emphasized by SDMTA a deeply different behavior between both polymers. While, ungrafted films were paracrystalline, the grafted PAN chains were observed amorphous and presented an irreversible transformation into polyimine above 225°C. A reversible transition previous to this transformation was assigned to crystallization. This study was reported in great details in a previous paper [24].

4.4.1.3. Study of nanocoating. Because very thin coatings like fiber sizing or electropolymerized PAN were successfully studied by this SDMTA technique, it was decided to check its ability to analyze a nanocoating deposited with a controlled thickness. The study of octadecyltrimethoxysilane (OTMS) self assembled onto oxidized Si wafers was chosen because it gives [25,26] a coating of a controlled thickness of about 2 nm. Fig. 11 presents the response of this grafted OTMS and clearly shows a transition with a maximum in tan δ and G'' at 17°C as well as probably a melting point at 37°C (drops in G', G''). This melting point is not so far from the 29–30 and 32–34°C reported for the ungrafted octadecane and nanodecane, respectively.

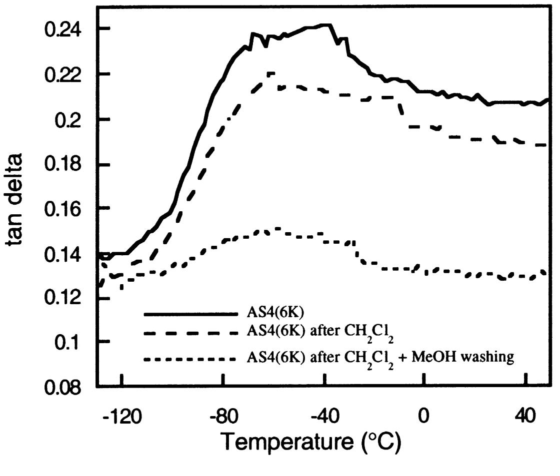

Fig. 9. Viscoelastic fingerprint (tan δ) of AS-4 6K carbon fibers before and after washing by methylchloride and subsequently by methanol.

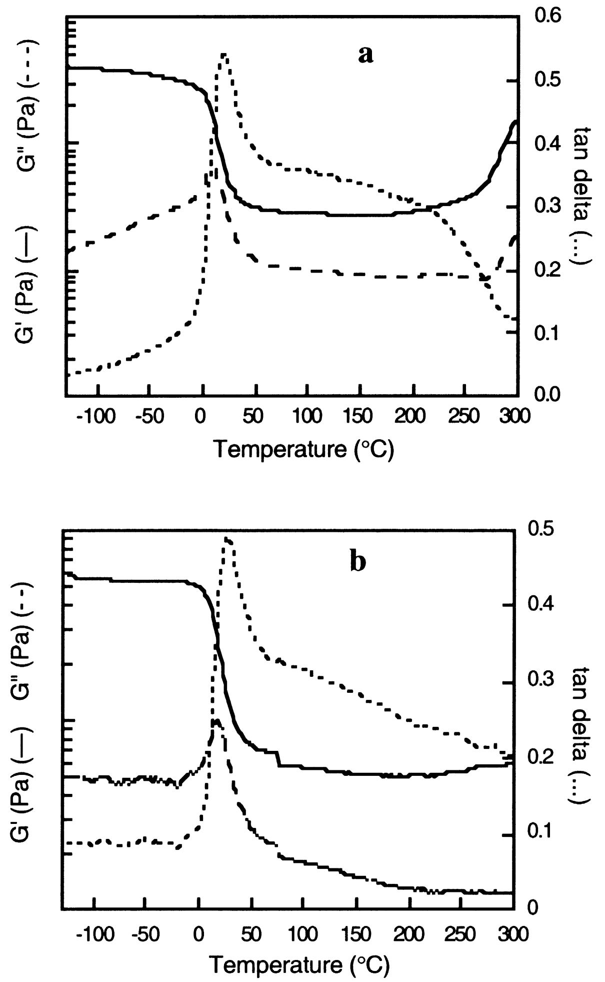

Fig. 10. Viscoelastic fingerprint of an HTA 5131 carbon fibers from Tenax fiber (first heatings are presented for both samples): (a) on the freshly received fibers; (b) on the aged fibers (same lot after two years without particular caution to prevent aging).

4.4.2. Study of polymer-support interactions

The ability of the SDMTA technique to explore coatings, ranging from 1 nm to 1 mm and more, opened a possible comparison of the viscoelastic responses of same coatings on same substrates, differing only by the thickness.

This comparison is very interesting because it enables to investigate experimentally the perturbations of the viscoelastic properties of a polymer near a wall. This topics was firstly theoretically developed and found an important experimental development since 1994 in many teams [27–32].

Nevertheless, most of those studies failed to produce conclusive results because the study was carried out on a film deposited onto a substrate with the other film surface free (uncapped supported films) and the observed perturbations cannot univocally be ascribed as due to the substrate because the presence of another

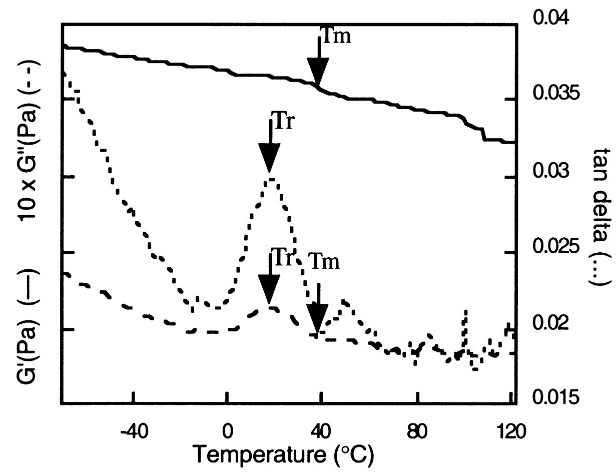

Fig. 11. Viscoelastic responses of a octadecyltrimethoxysilane grafted onto a silicon oxidized wafers recorded versus temperature by SDMTA.

dominating interface with air. Only Forrest et al. [32] studied capped supported films. In our particular case, because the sample is sandwiched in between substrates, it could also solve this experimental problem.

Fig. 12 presents the tan δ transitions of thin matrix coatings on washed fiber bundles when the fiber/matrix ratio w/w varies from 35/65 to 95/05. A T_g shift to higher temperatures is observed when the PS coating is thinner. A T_g shift from 102°C for the thickest to 125°C for the thinnest is observed in Fig. 12.

An important fundamental study based on the T_g measurements of thinner and thinner coatings on C-fibers bundles was performed. Those results will be reported extensively elsewhere [33,34]. The main ones can be nevertheless summarized as follows: A shift of the T_g of a monodisperse polystyrene (PS, $M_n = 1000$) T_g from 87 to 105°C was observed. While, when the grafting of PS ($M_n = 1000$) onto the carbon fiber surface through a covalent link was promoted, the T_g was displaced up to 152°C.

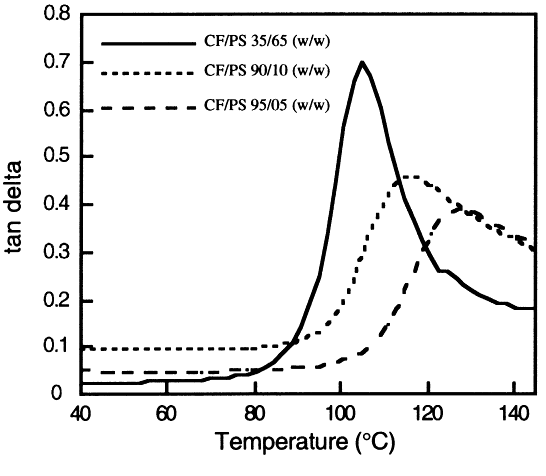

Fig. 12. Viscoelastic response (tan δ) change versus temperature for various PS/carbon fibers volume ratio. (Thickening of the coating on the left).

4.4.3. Study of polymers

At last, it is important to mention the possible study of polymer by this method when other method fails.

4.4.3.1. Intractable polymers. Nitrocellulose is a polymer which ignites spontaneously upon heating, preventing any thermal analysis by classical techniques.

SDMTA enables its glass transition measurement. The measurement was made possible due to the small amount necessary and to the confinement of the sample. A T_g was observed at 190°C immediately followed by its thermal degradation.

4.4.3.2. Study of plasticizing effect. The flow exhibited at room temperature by an amorphous polymer plasticized at high level does not allow any T_g study on the whole mixture scale by classical DMTA, given the difficulty which arises from its manipulation (the sample is not free-standing) and from its positioning in the apparatus. The here proposed technique bypasses this problem thanks to the support and even allows measuring pure plasticizers' T_g, as reported by De Groote [35].

It is, however, very important when using this supported method to keep in mind the possible influence of the support on the analysis results. Generally, the choice of an inert support and of thick coating decreases this influence. However, attention has to be paid to possible artifacts as the last example illustrates it.

4.4.3.3. Observation of a catalytic effect due to the substrate. The study of a bismaleimide (BMI) resin carried out onto copper plates revealed very short gelation time (27 min at 140°C). The catalytic effect of the copper oxide present on the copper plates was demonstrated by the comparison of the gelation times measured out onto glass plates with and without additional copper oxide amounts. A longer gelation time (100 min at 140°C) is clearly observed when glass plates in absence of any copper oxide amounts were used as supports.

5. Conclusions

A particular sample configuration and mounting procedure is described. It favors the viscoelastic DMTA response of a softer material deposited onto a rigid support.

The advantages of the technique are as follows:

- *Sensitivity.* The demonstrated selectivity to the softer material and the deduced amplified response lead that a few mg or coating as thin as a few nanometers are suitable. A 2 nm-thick coating was successfully studied.

- *Easiness.* The sample preparation is very direct and not restricting: fibers, hair, copper plates, glass plates and even silicon wafers are suitable supports while thermosets precursors, liquid, oil, powder, micrometer films, molten polymer are easy to study. The sample preparation only consists in a stacking or a sandwiching.
- *Main interests.* It enables direct in situ characterization of coating on their supports. Its interest in paints, glue, fiber sizing characterization is obvious because it allows to study very easily an interface influence. The possible study of coating as thin as the nanometer has opened the fundamental study of a polymer near a wall by this technique. It will be reported extensively elsewhere [33,34].

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