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Characterization of thermally crosslinkable polyester films by thermomechanical analysis: a versatile and very sensitive technique for the evaluation of low crosslinking degree in polymers

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Abstract

Thermomechanical analysis (TMA) is an effective technique for the characterization of small samples such as thin films of micrometric thickness, allowing the determination of thermal events such as glass transition, softening temperature and thermal expansion. Here we describe use of the TMA technique to investigate the drying and curing properties of polyester thin films ranging from 40 to 70 μm thick. The main purpose of this study was to investigate the effects of residual solvent and crosslinking on the glass transition and softening temperatures of the polyester films subjected to thermal cycling. Despite the fact that the analysed films were thinner than 100 μm, TMA proved to be very sensitive to small changes in residual solvent content and to the effects of the degree of crosslinking on the glass transition and softening temperatures of the polymer films. The most important finding is the possibility of detecting very small degrees of crosslinking in an easy, fast and quantitative way. Other methods such as swelling were not sensitive enough to differentiate the crosslinked samples and data for thicker films are not comparable to the data for thin films.

Keywords: thermomechanical analysis; softening temperature; thermal properties; polyester films; polymer crosslinking

INTRODUCTION

In thermomechanical analysis (TMA), a probe is lowered onto the surface of a sample while the temperature is increased at a predetermined rate. The technique is based on the measurement of sample deformation under very low load as the temperature is increased and two main modes of deformation, defined by the probe/sample contact area and the applied load, can be performed: (i) expansion, when low forces are applied to large contact areas, and (ii) penetration, with small contact areas and high forces.[1–5] In general, a combination of expansion/penetration is observed. TMA has been used successfully for the measurement of several properties of polymers, such as the glass transition temperature,[1,3,4] softening temperature,[1,2,4] thermal expansion coefficient,[1,2,6] degree of crosslinking[1,2,7] and the average number of degrees of freedom of polymer segments between crosslinks.[8] A transition temperature is generally taken as a temperature at which the rate or direction of probe deflection changes abruptly.

The technique of TMA is particularly interesting for investigation of the thermomechanical properties of thin polymer films that would be difficult to analyse by other techniques. Thin polymer films used as coatings in several applications, e.g. for electrical insulation, protective layers and bonding films, are produced by casting, which can lead to variation in the properties depending on the residual high boiling solvents that plasticize the film, as well as on thermal treatments and other variables inherent to the process.

Polyester resins containing free hydroxyl groups are versatile materials used in several applications, notably for electrical wire insulation and protective coatings. The presence of side-chain hydroxyl groups improves the solubility of the resin and allows its crosslinking by reactions such as esterification/transesterification, urethane formation and reaction with organometallic compounds such tetra-*N*-butyl titanate. In particular, the transesterification reactions occur at temperatures above 170 °C. For polymer thin film coatings, these resins are usually cast from solutions in organic solvents. The majority of the volatile solvent is evaporated after an

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initial drying and the material is then subjected to heat treatment to eliminate the remaining solvent and cause crosslinking, producing a thermoset coating of high mechanical and chemical resistance. Residual high-boiling-point solvents may plasticize the film, altering its properties, notably decreasing its glass transition and softening temperatures.

The purpose of the present study was to investigate the use of the TMA technique to determine the behaviour of the glass transition and softening temperatures of crosslinkable polyester films when they are subjected to thermal cycles that simulate the industrial processing conditions of this kind of resin. The relationships between the heat treatment conditions and the resulting residual solvents and degree of crosslinking were established and correlated with the glass transition and softening temperatures. The resin was characterized by Fourier transform IR (FTIR) spectroscopy, TGA and DSC.

EXPERIMENTAL

Materials

A commercial saturated polyester resin containing 2% free hydroxyl groups (Brazil), determined by reaction with acetic anhydride (Brazil) followed by back titration of the excess acetic acid (Brazil), as described in ASTM D 4274-5, was employed. This polyester resin was synthesized mainly with phthalic anhydride (Brazil), ethylene glycol (Brazil), propylene glycol (Brazil) and glycerol (Brazil). It was dissolved in a mixture of xylol (Brazil) and cresol (70:30) (Germany), where xylol is the diluent (non-solvent) and cresol the solvent. Metal catalysts such as tin acetate and tetra-*N*-butyl titanate (USA) were present to increase the rate of the transesterification reaction during crosslinking.

Polymer characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded from a Perkin Elmer Spectrum 1000 spectrophotometer in the transmission mode. The samples were prepared by casting a dilute solution of the resin on KBr pellets. Prior to the analysis, the coated KBr pellet was dried in a vacuum oven to eliminate the solvent and/or to crosslink the polymer.

Differential scanning calorimetry (DSC)

DSC experiments were performed in a TA Instruments DSC-Q100 calorimeter with nitrogen as the carrier gas, flowing at *ca* 50 cm^3 min^{-1}. The glass transition temperature was determined as the temperature corresponding to half the change in heat capacity during transition ($T_g^{1/2}$). The samples for DSC were purified by precipitating the polymer dissolved in tetrahydrofuran (THF) (5 wt%) with methanol (10× the volume of the THF solution) three times, and drying in vacuum at 140 °C for 72 h. The samples were weighed (approximately 25 ± 4 mg) directly in aluminium pans. These samples were considered free of residual solvent.

Thermogravimetric analysis (TGA)

The TGA was carried out in a TA Instruments TGA-Q50 thermogravimetric analyser at a heating rate of 10 °C min^{-1} from ambient temperature (25 °C) to 900 °C in a nitrogen atmosphere with a flow rate of 60 cm^3 min^{-1}.

Thermomechanical analysis (TMA)

TMA tests were carried out in a Shimadzu TMA-50 thermomechanical analyser with a silicon probe of diameter 1 mm. For the cyclic TMA analysis, the probe position was changed to an unused area of the same test piece and a new cycle of heating and cooling was applied. TMA experiments were performed in two different ways: to study the effect of solvent loss on the thermomechanical properties, the samples were dried at 80 °C for 25 min and analysed by TMA from room temperature (*ca* 20 °C) to 180 °C, with an applied force of 1 g, while in the experiments designed to investigate the effect of crosslinking on thermomechanical properties the samples were dried at 140 °C for 24 h and analysed by TMA from room temperature (*ca* 20 °C) to 250 °C, with an applied force of 10 g. It was necessary to use different applied forces in these sets of experiments to obtain curves with controllable penetration of the probe, since the sample with residual solvent was much softer than the solvent-free sample. In both cases, the analysis was performed in a nitrogen atmosphere flowing at 20 cm^3 min^{-1}, at a heating rate of 20 °C min^{-1}.

Sample preparation for TMA

Rectangular pieces of aluminium foil dip-coated with the polyester resin solution in cresol:xylol (70:30) at a concentration of 27 wt% were dried by standing in air at room temperature for 15 min. The samples were then dried/pre-treated under three distinct conditions, the first two producing uncured test pieces, at 80 °C for 25 min and at 140 °C for 18 h under reduced pressure, for pieces with residual solvent and solvent-free, respectively. The third condition produced cured samples by treatment at 180 °C for 30 h. The 30–50 μm thick films supported on the aluminium were cut to a target size of 8.0 × 8.0 mm. A blank of aluminium foil alone was used to record the baseline and to eliminate the effect of the aluminium support on the TMA experiments. Crosslinking was confirmed by solubility tests in THF. For this purpose, small pieces of the sample film were immersed in THF in a test tube and agitated vigorously for at least 1 h. The sample was removed, dried and then weighed.

Swelling behaviour

Films of the polyester on an aluminium substrate as used for TMA measurements were immersed in THF for swelling after curing. The samples were weighed before and after for swelling determination.

RESULTS AND DISCUSSION

FTIR characterization

The FTIR spectra of the cured and uncured samples are shown in Fig. 1. No significant differences between spectra are observed. This was expected, since the extent of crosslinking of this kind of resin is very low and the new bonds appear at the same wavenumber as those of the characteristic bands of the resin. Crosslinking was confirmed by solubility tests in THF. Low crosslinking leads to soft gels.

DSC characterization

DSC measurements were performed in order to determine the glass transition temperature (T_g) of the dried uncured polyester resin. The DSC curve for the solvent-free sample is presented in

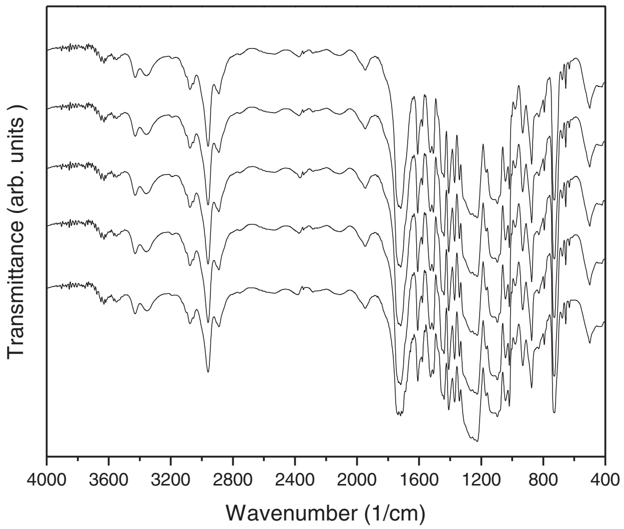

Figure 1. FTIR spectra of polyester films, uncured (top) and progressively crosslinked at 180 °C from top (second spectrum) down.

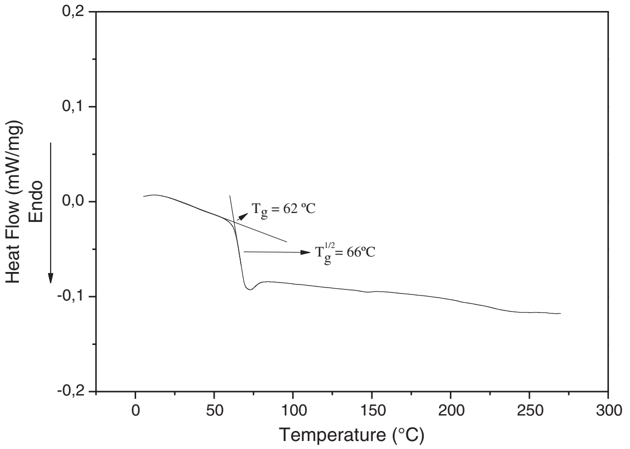

Figure 2. DSC trace for solid polyester resin.

Fig. 2. This trace shows the glass transition, in which the characteristic temperature was taken at the onset of baseline variation ($T_{\mathrm{g}} = 62$ °C) and at the half-variation point in heat flow (${T_{\mathrm{g}}}^{1/2} = 66$ °C).

TMA and TGA of polyester films

The results of TGA and TMA for samples with residual solvent and solvent-free samples are shown in Fig. 3. TGA was performed under the same conditions as TMA to assess the solvent loss during each thermal cycle. The thermal cycle was used to modify the samples in steps and thus enable the progressive change in the polymer film to be monitored during thermal treatment. The main goal was to differentiate the effect of residual solvent from the effect of thermal crosslinking.

Figures 3(a) and 3(b) show the TGA and TMA curves of the polyester samples with residual solvent (drying at 80 °C/25 min). The highest temperature reached in each cycle was 180 °C to avoid crosslinking, since transesterification occurs readily only above 170/180 °C. In the first cycle, there was a loss of 52.5 wt% due to solvent evaporation, followed by losses of 2.0 and 0.6 wt% in the second and third cycles, respectively. It is possible that some crosslinking took place, but this is unlikely because the amount of time spent at high temperatures, close to 180 °C, was very short, ensuring that the film was mainly thermoplastic throughout the three cycles. The TMA curves for these cycles (Fig. 3(b)) show a low T_{g} in the first cycle, before most of the solvent was lost, due to the plasticizing effect of the residual solvent. The T_{g} values in the second and third cycles were very close, around 70 °C, and the TMA curves practically coincided, showing that the thermal properties of the thermoplastic film are almost stable after the first heating cycle. The TMA curves in Fig. 3(b) were obtained with an applied load of 1 g (giving 1.25 N cm^{-2}) because the starting film was extremely soft and showed complete penetration in the initial stage of the first cycle of heating. The value determined for the glass transition temperature in the first cycle was 40 °C, lower than that determined by DSC, due to the plasticizing effect of the residual solvent (52.5 wt%), which was largely eliminated after the first cycle. The T_{g} determined in the second and third cycles was closer to that determined by DSC, around 67 °C.

Figures 3(a) and 3(b) show that just one cycle from 25 to 180 °C at a rate of 20 °C min^{-1} is sufficient to eliminate most of the solvent which can depress the glass transition temperature of the film.

Effect of thermal treatment (curing) using TMA (Figs 3(c) and 3(d))

In a general way, the processing of polyester resins cast from solution, such as those used in electrical applications, requires some form of heat treatment, to eliminate solvents and promote the curing of the resin. Here we used TMA to simulate cyclic thermal treatment, performing heating/measurement cycles, so that each cycle was used to characterize the material produced in the previous cycle of heating and cooling. A load of 10 g was used, to increase the sensitivity of TMA to small changes in the mechanical properties. Figures 3(c) and 3(d) show TGA and TMA curves for a 60 μm thick film of polyester dried at 140 °C for 24 h. The sample was subjected to five consecutive cycles of heating and cooling from room temperature to 250 °C. The table inset in Fig. 3(d) summarizes the TGA and TMA results, showing the glass transition temperature, softening temperature and weight loss for each cycle.

In the TMA curves in Fig. 3(d), it is possible to identify three events: (i) the glass transition around 70 °C, (ii) softening of the material around 182 °C in the first and second cycles and around 212 °C in the other cycles and (iii) the occurrence of complete penetration in the first and second cycles after 200 °C. In Fig. 3(c) we can see that the weight loss was very low in all thermal cycles, being 0.9 wt% in the first and less than 0.2 wt% in the subsequent cycles. The cumulative weight loss for the five cycles up to 250 °C was 1.44%. This loss was probably mainly due to elimination of small molecules in the crosslinking reaction. The glass transition temperatures are presented in the table inset in Fig. 3(d), alongside the corresponding penetration, the profiles of which are shown in more detail in the inset in the upper right corner of the figure. The T_{g} for the first cycle was 63 °C, while for the other cycles it was around 70 °C. The increase in the T_{g} value after the first cycle was due to the residual solvent loss during that cycle.

During the first and second cycles, the film is not completely cured, as shown by the complete penetration indicated by the plateau at the end of the cycle, above 200 °C, and by the lower softening temperatures observed. In the third, fourth and fifth cycles, the material displayed a plateau after T_{g}, with a well-defined softening temperature at around 212 °C, and no plateau at the end of

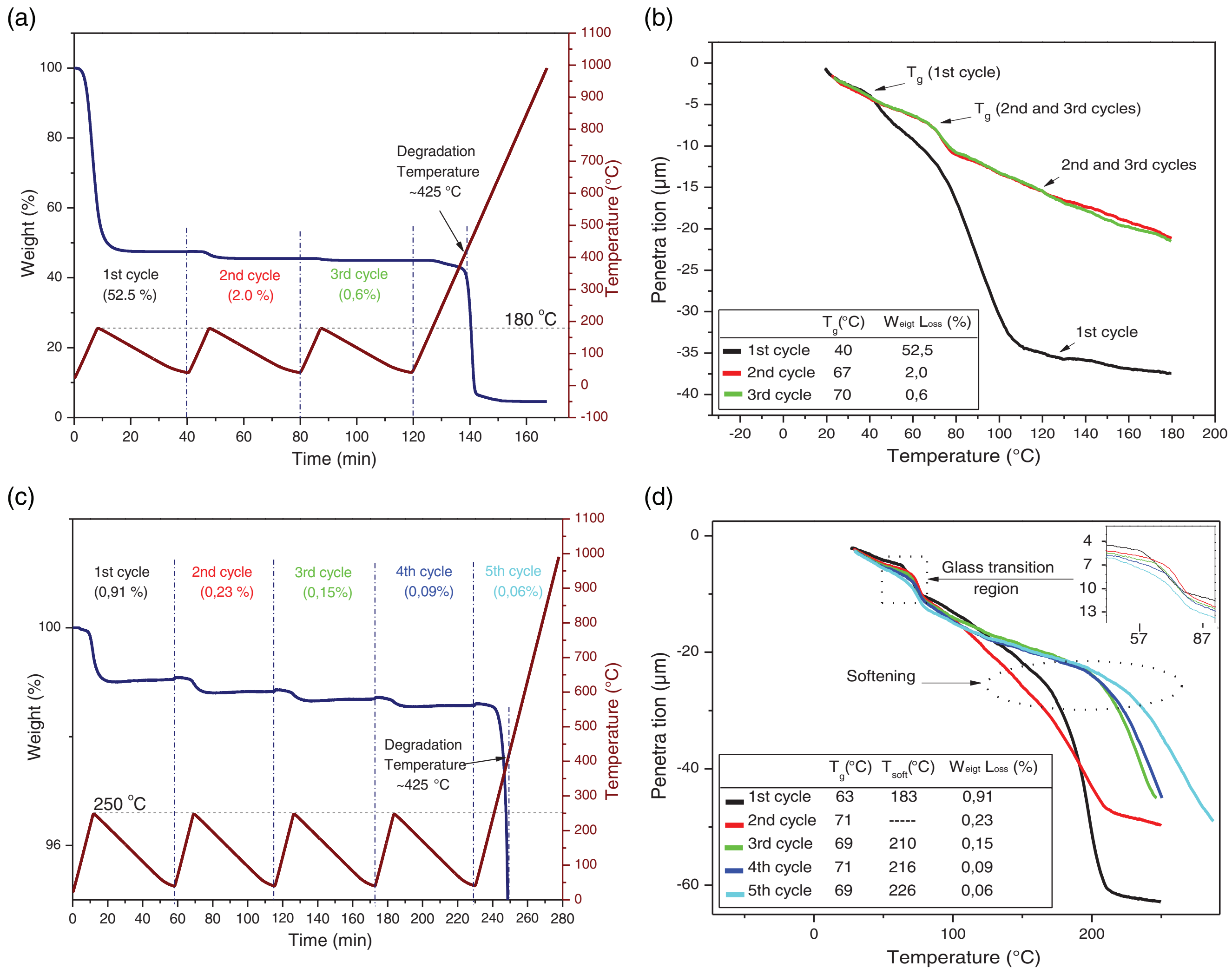

Figure 3. (a), (c) TGA and (b), (d) TMA curves for samples (a), (b) with residual solvents, dried under mild conditions (80 °C for 25 min), and (c), (d) solvent-free, dried under severe conditions (149 °C for 18 h at reduced pressure).

the cycle, which means that penetration of the sample was incomplete. These characteristics indicate that the film was crosslinked and that, with the heat treatment used, the crosslinking density reached a maximum after the third cycle.

The results for TMA penetration of the polymer film during crosslinking (see Fig. 3(d)) show that TMA is very sensitive even to small changes that cannot be detected by DSC or dynamic mechanical thermal analysis and that it shows a very good reproducibility over several cycles. The softening temperature can be determined with high precision.

Figure 3(d) also shows that the rate of penetration, observed as the slope of the curve after the glass transition, was very different for the thermoplastic (uncured) and thermoset (cured) films. For the thermoset, the rate of penetration (before softening) was quite low and the softening temperature was observed at higher temperatures. This effect was due to the rubbery state of the material, where chain movement is more restricted owing to chain crosslinking. The slope of this plateau is related to the degree of cure of the material, which makes TMA an attractive technique for determining the degree of crosslinking of thermally crosslinkable materials.

The solubility tests showed mass losses less than 5%, which can be considered negligible for the studied system. These results confirm that the samples studied by TMA were in fact crosslinked after thermal treatment.

Swelling experiment data were not conclusive due to the fact that very small mass variation was involved because the crosslinked degrees of the studied samples are very close and also because the high surface area of the samples and the high THF volatility make a reliable swelling measurement very difficult. Despite the fact that swelling is the most traditional method to measure crosslinking degree, our experiments showed that for small variation in crosslinking and for thin films it is not practical. This confirms the potential of the method described here not only due to its high sensitivity for small variation in crosslinking degree but also due to its high reliability.

CONCLUSIONS

The glass transition temperature (T_g) determined by TMA was close to that determined by DSC. The effects of residual solvents were observed by means of the TMA technique.

The T_g of the solvent-free material was not affected by the degree of crosslinking over several cycles of curing, but was affected by the presence of residual high-boiling-point solvents, which act as plasticizers. Crosslinking was detected by TMA and seems to be manifested in the rate of penetration after T_g, in the value of the softening temperature and in the incomplete penetration of the sample during the TMA experiment. The softening temperature, which is difficult or impossible to determine by other techniques, was easily detected by TMA. Four events were observed in the TMA experiment in polyester films: (i) the vitreous state where a plateau is observed, (ii) the glass–rubber transition, (iii) a linear increase of the penetration for the thermoplastic samples or a plateau for the crosslinked ones (restricted flow region) and (iv) the softening temperature for the crosslinked samples and complete penetration for the thermoplastic materials. TMA can be performed in cycles to simulate curing and to characterize polymer films, and is an interesting tool for process optimization based on cyclic heating and cooling. The high sensitivity of TMA to crosslinking shows its potential to perform the characterization of this kind of material even at very low levels of crosslinking on a quantitative basis.

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