THE EFFECT OF PROCESSING CONDITIONS ON THE VISCOELASTIC PROPERTIES OF POLYMER MATRIX COMPOSITES

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Abstract. *Viscoelastic material characterization is critical in designs that incorporate specified levels of damping and to the understanding of processing related problems. In this research, the effect of processing conditions on the viscoelastic properties of composite laminates was investigated. Laminates were produced using two different conditions - with and without the application of vacuum. The experimental investigation was conducted on subscale specimens loaded in flexure, using dynamic mechanical analysis (DMA) equipment. The influence of the applied vacuum on the measured viscoelastic properties was examined and discussed. The results presented demonstrate that DMA equipment offers good potential to study changes in viscoelastic properties of composite laminates, related to processing conditions.*

Keywords*: Composites, Dynamic Mechanical Analysis, Viscoelasticity, Processing.*

1. INTRODUCTION

Processing conditions are well known to affect considerably the mechanical properties of polymer matrix composites (Gao and Kim, 2001). Thus, vacuum bagging process is frequently applied to help consolidate the plies of laminates, to remove the excess of resin and to reduce voids. In addition, processing of high-performance parts often involves heat and external pressure, conditions that require the use of an autoclave. Voids are known to decrease strength, in particular when shear stresses are involved. Studies on the effect of processing conditions on the energy absorption of thermoset matrix composite tubes have been reported in the literature (Warrior et. al., 2003). These investigations have demonstrated the potential for tailoring the energy absorption properties of composite materials through controlled processing conditions.

A broad range of destructive and nondestructive testing methods is currently used to evaluate laminates. Among the destructive testing approaches, DMA is a very useful technique to study viscoelastic properties of materials and may be an efficient approach to evaluate processing related problems in composite laminates. Viscoelastic materials, such as polymer matrix composites, exhibit mechanical properties, which are between two ideal cases: elastic and viscous. In a viscoelastic material, the stress is a function of both strain and time (Papanicolaou *et al.*, 1999). Some of the important characteristics related to viscoelasticity are: creep, stress relaxation, and energy dissipation.

Nowadays, dynamic mechanical analysis (DMA) equipment are becoming more and more commonly seen in laboratories as a tool for viscoelastic materials characterization. Properties related to the material's ability to dissipate energy as heat (damping) or the ability to recover from deformation (elasticity) may be measured using this technique (Menard, 1999). DMA equipment allow measurements of modulus and damping over a wide range of frequencies and temperatures, providing important information about the cure of thermoset resins and aging of thermoplastics. This technique also offers great potential for investigating damping properties of composite materials. It provides fast and reliable results using a very small amount of material, which can, in many cases, be taken directly from the part. In addition, DMA test equipment allow precise temperature and atmosphere control (Melo and Radford, 2003).

In a typical DMA analysis, a periodic force or displacement is applied to a given specimen and the resulting displacement or force is measured. When a material displays a viscoelastic nature, the applied excitation and the measured response are out-of-phase (Melo, 2002). The storage modulus, *E*', is the elastic component of the modulus, while the loss modulus, *E*'', also referred to as the viscous or imaginary modulus, is the viscous component. The resultant of the two components is referred to as the complex modulus, *E** (Eq. 1). For a purely elastic material, stress and strain are in-phase and for a purely viscous material, stress and strain are 90º out-of-phase (Melo, 2002).

$$E^* = E' + iE''$$
$$E^* = E'\left(1 + i\tan\delta\right) \tag{1}$$

The tangent of the phase angle ($tan\ \delta$) is one of the most basic property measured in DMA testing. This property is an indicator of how efficiently the material dissipates energy through molecular rearrangements and internal friction. It is

defined as the ratio of the loss to the storage moduli and therefore is independent of geometry aspects (Eq. 2) (Menard, 1999).

$$\tan\delta = E''/E' \tag{2}$$

DMA is a very useful tool for investigating material properties related to temperature and/or frequency. In a typical DMA temperature-scan, the sample modulus decreases with the increase in temperature. This behavior is more pronounced over the glass transition, T_g, region, where the material changes from glassy to rubbery, and a considerable drop in modulus is observed, as the temperature of the polymeric material is increased. The drop in modulus is followed by a reduction in strength and a considerable increase in strain to failure (Melo, 2002).

The T_g region represents a major transition for the polymer matrix, where physical and mechanical properties changes drastically as the material goes from a hard glassy to a rubbery state. It defines the high end of the temperature range over which the polymer matrix can be used in structural applications, often referred to as the operating range of polymer matrix composites (Menard, 1999). Three methods are in current use for determining the T_g from DMA collected data (Fig. 1), depending upon the industry standards: the onset of the *E'* drop, the peak of the *E''* curve, or the peak of the tan δ curve. The values obtained from each of these methods may differ considerably from each other on the same run (Menard, 1999).

Vacuum assisted processing produces important modifications in composite materials' properties due to improved consolidation, removal of excess of resin and reduction in void content. DMA equipment may offer a great potential to study the effect of processing conditions on the viscoelastic properties of composites, as related to the application of vacuum. In the present investigation, DMA was used to study the effect of processing conditions on the viscoelastic properties of glass/epoxy, glass/polyester and glass/vinyl ester composites. Half of the laminates was produced using a vacuum assisted process, while the other half was produced without applied vacuum. Beam specimens were cut from all laminates and tested in 3-point bending mode. The influence of the processing conditions (with or without vacuum) on the viscoelastic properties of composite laminates was examined and discussed.

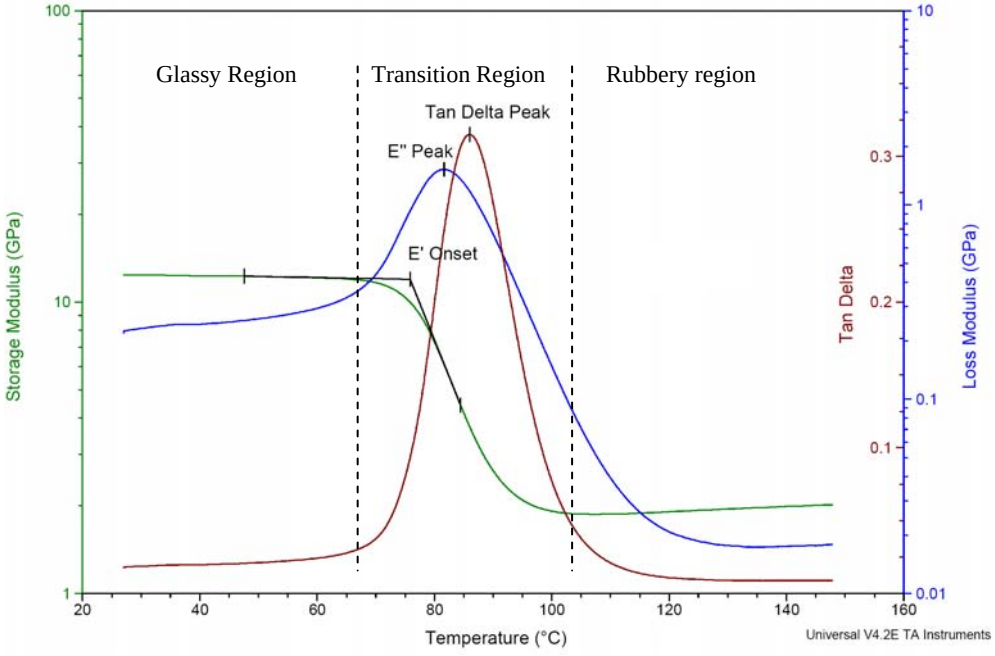

Figure 1. DMA measured properties related to temperature.

2. EXPERIMENTAL

2.1. Materials and test specimens

Composite laminates were fabricated using a balanced plain fabric E-glass (120 g/m^2) and three different resin systems: epoxy Araldite LY 1564 / Aradur 3416, polyester (orthophthalic) Novapol L-120, and vinyl ester Derakane 411-350. The epoxy system prepared with 34% Aradur 3416 hardener resulted in a gel time of about 100 minutes. The unsaturated polyester resin was prepared with 1 % MEKP initiator and 0.025 % of hydroquinone as cure retardant. The hydroquinone increased the resin gel time from 12 minutes to approximately 110 minutes. The vinyl ester resin used was prepared with 0.05% dimethylaniline (DMA) accelerator, 0.75% benzoyl peroxide powder (BPO) initiator, and

1.25 % styrene monomer as BPO solvent. This combination resulted in a gel time of about 90 minutes. All gel times were found adequate for the vacuum assisted process and thus, considered sufficient to study the effect of vacuum on the viscoelastic properties.

A 50 x 50 mm square cross section steel tube was used as mold. In this mandrel, a corner radius of 5 mm facilitated fabrication. For an ease removal of the tubes from the molds, cellophane paper was wrapped on all molds, in addition to a mold release wax applied directly to the mold surface and also, to the cellophane paper. All tubes were fabricated by mandrel wrapping of the fabric pre-impregnated with resin, which was positioned to produce a $[0/90]_n$ lay-up, with respect to the longitudinal axis of the tube. The fabric was cut in one continuous piece to produce a total of 18 layers of composite.

Four tubes were fabricated for each composite studied: Half of the tubes was fabricated under vacuum while, in the other half, vacuum was not applied (Fig. 2). With two tubes for each condition, the reproducibility of properties using the same process can be verified. After the lay-up was complete, the tubes fabricated without vacuum were kept rotating at 34 rpm in a custom-made apparatus for 12 h, thus avoiding resin flow to one side of the cross section, which would result in a non-uniform wall thickness. For vacuum processed tubes, one layer of peel ply and three layers of bleeder/breather were placed on top of the laminate before the vacuum bag. Vacuum was applied for 12 h. All tubes were allowed to cure for 24 h at ambient temperature before being removed from the molds. The epoxy/glass and vinyl ester/glass tubes were post-cured for 2 h at 100ºC.

2.2. Test specimens

To produce DMA test specimens, the tubes were first cut, using a diamond abrasive saw, into rectangular $[0/90]_{18}$ samples (70 x 16 mm). Laminate orientation was carefully controlled during the cutting procedure. After the initial cutting procedure, all specimens were sanded, square and flat, using metallographic preparation techniques. Six specimens were prepared from each tube. All specimens were conditioned following recommendations of ASTM D 5229/D 5229M – 92. Specimens' dimensions were determined following recommendations of ASTM D 5023 – 01. The final nominal dimensions were 62 x 13 x 2.3 mm (length x width x thickness) for specimens processed without vacuum and 62 x 13 x 1.5 mm for specimens processed under applied vacuum (Fig. 3).

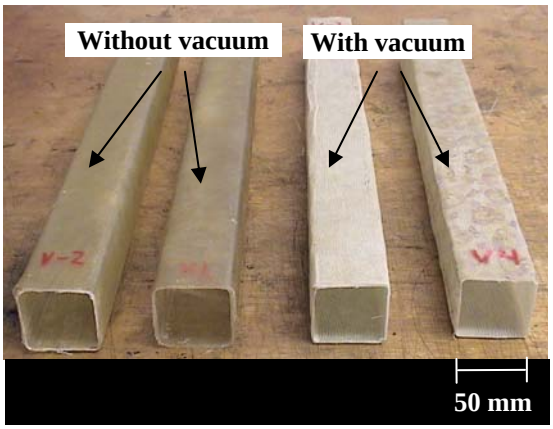

Figure 2. Square cross section composite tubes.

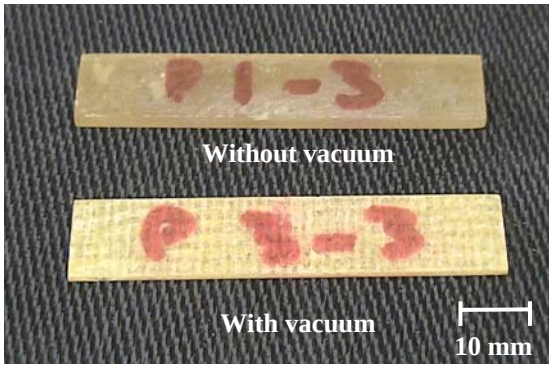

Figure 3. DMA 3-Point Bending test specimens.

2.3. DMA 3-Point Bending tests

DMA equipment offer different testing geometries including tension, compression, simple shear, and bending. The choice of the testing geometry is normally dictated by the type of information desired and by the stiffness of the material being tested. For fiber-reinforced materials, the bending mode is the most used geometry due to the high stiffness, which severely limits the strain in tensile mode evaluations (Melo, 2002).

In this investigation, dynamic measurements were carried out using a DMA Q800 analyzer from TA Instruments, in a three-point bending testing mode, with a 50.0 mm span (Fig. 4). Three-point bending was selected as the preferred testing geometry since clamped boundaries are reported to affect damping measurements, increasing the measured damping (Melo, 2002).

Figure 4. DMA 3-Point Bending Test

All dynamic tests were conducted using a heating rate of 2 ºC/min to ensure better temperature uniformity throughout the specimen. A small strain (0.1 %) was used throughout the measurements to maintain the material behavior within the linear viscoelastic region. The viscoelastic properties for epoxy/glass specimens were determined over the temperature range of 27 to 150 °C, from 27 to 200 ºC for polyester/glass and from 27 to 250 ºC for vinyl ester/glass. Storage and loss moduli, E' and E'', and $tan\ \delta$ were plotted as a function of temperature.

3. RESULTS AND DISCUSSION

The results of the dynamic measurements for beam specimens obtained from the two tubes fabricated without vacuum (WOV1 and WOV2) and from the two tubes processed under applied vacuum (WV1 and WV2), for all composites studied, are presented in Figs. 5 to 13 and Tables 1 to 3. All data was averaged from six different samples for each measured property.

In Figs 5 to 7, the temperature dependence of the storage moduli (E') for the epoxy/glass, polyester/glass and vinyl ester/glass is presented. The temperature dependence of the loss moduli (E'') for all materials is presented in Figs. 8 to 10. Finally, the tan δ measured as function of temperature is plotted in Figs. 11 to 13.

The mean values of the glass transition temperatures (T_g) for all materials tested, determined based on the E' onset, E'' peak and tan δ peak, are presented in Tables. 1 to 3. The tables also include E' values in the glassy and rubbery regions and the E' drop percentage, from the glassy to the rubbery region. Finally, the $tan\ \delta$ peak values are also shown.

It can be observed, based on data presented in Figs. 5 to 7 and Tables 1 to 3, that storage modulus was considerably higher for the vacuum assisted processed composites. Comparing to specimens processed without vacuum, storage modulus values of vacuum assisted processed specimens were increased by 62% for epoxy/glass, 76% for polyester/glass and 87% for vinyl ester/glass (Tabs. 1 to 3). Further, as the temperature is increased, the drop percentage in storage modulus, from the glassy to the rubbery region, was about 85 % for all composites produced without applied vacuum. For materials processed under applied vacuum, the drop in storage modulus was reduced to about 60 %, regardless of the resin system used. This effect was produced by the storage modulus over the rubbery region, which was significantly increased with applied vacuum. Thus, the applied vacuum removed the excess of resin and improved consolidation, which ultimately resulted in a higher storage modulus.

According to data presented, the difference in storage modulus measurements among specimens manufactured by the same process (WOV or WV) were not significant (Figs. 5 to 7 and Tabs. 1 to 3), indicating good reproducibility. Over the glassy region, the largest difference in storage modulus, for specimens of the same material and processed under the same conditions, was observed for vinyl ester/glass specimens processed without vacuum (18 % in the glassy region).

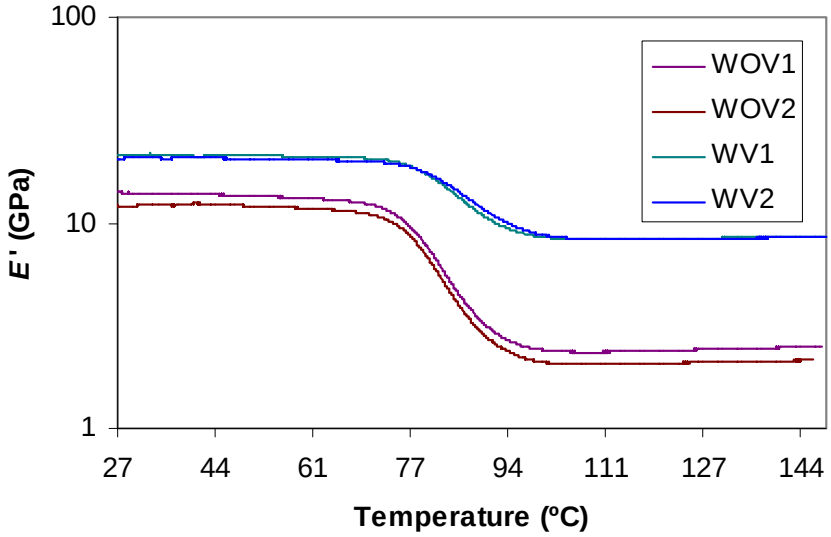

Figure 5. Temperature dependence of the storage moduli for epoxy/glass specimens

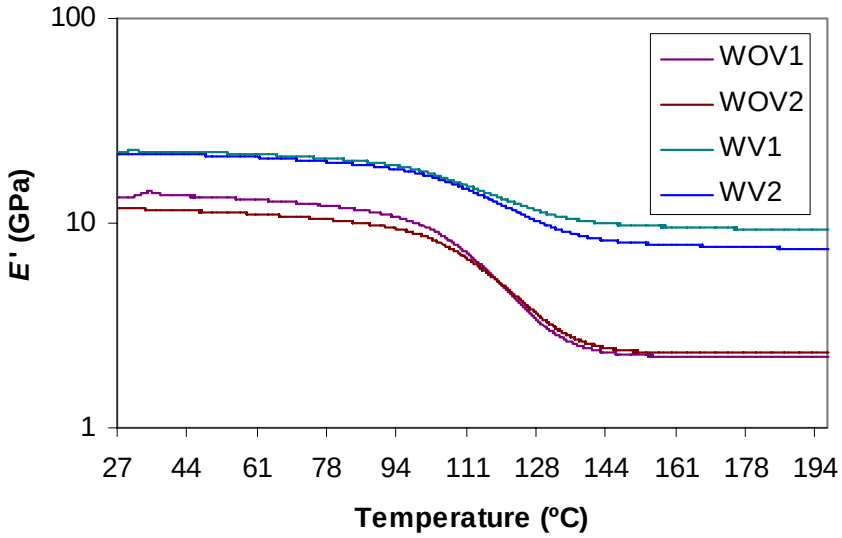

Figure 6. Temperature dependence of the storage moduli for polyester/glass specimens.

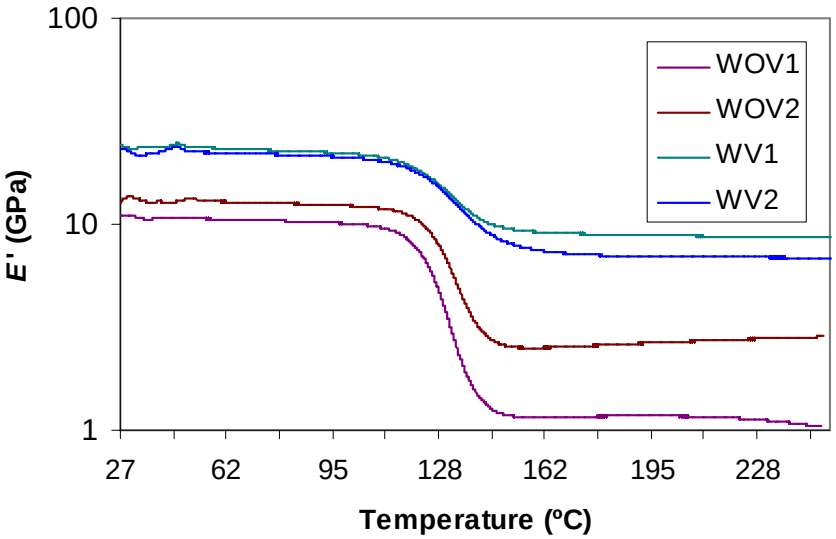

Figure 7. Temperature dependence of the storage moduli for vinyl ester/glass specimens.

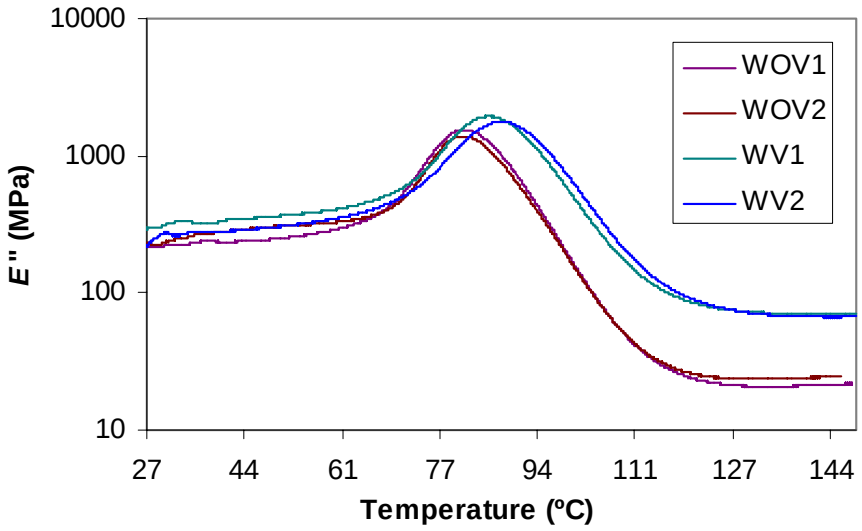

Figure 8. Temperature dependence of the loss moduli for epoxy/glass specimens.

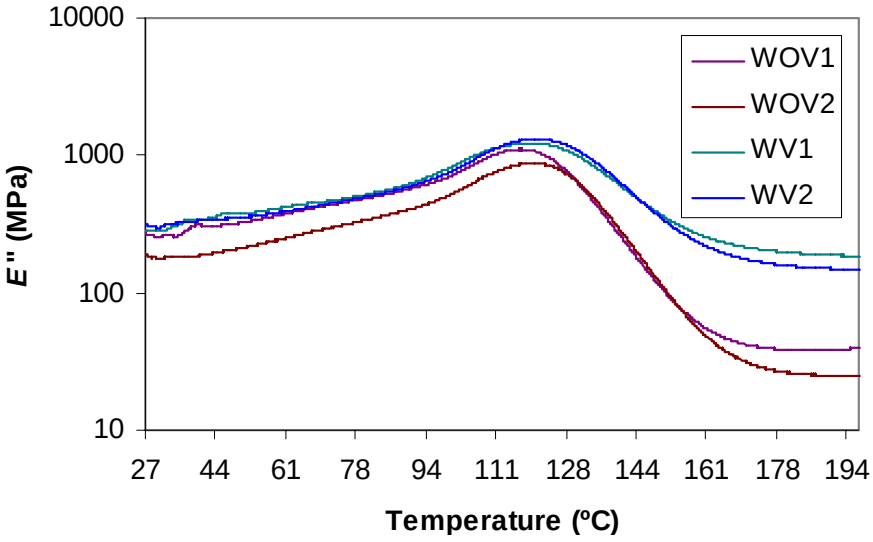

Figure 9. Temperature dependence of the loss moduli for polyester/glass specimens.

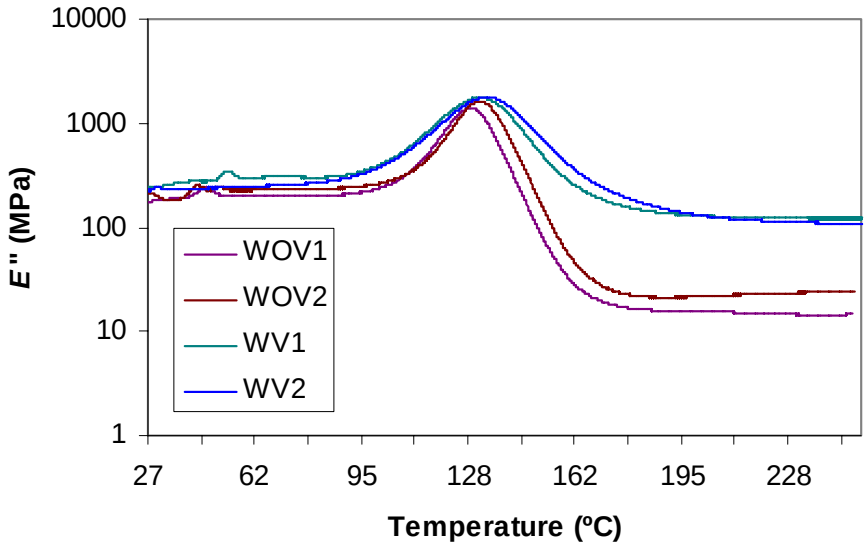

Figure 10. Temperature dependence of the loss moduli for vinyl ester/glass specimens.

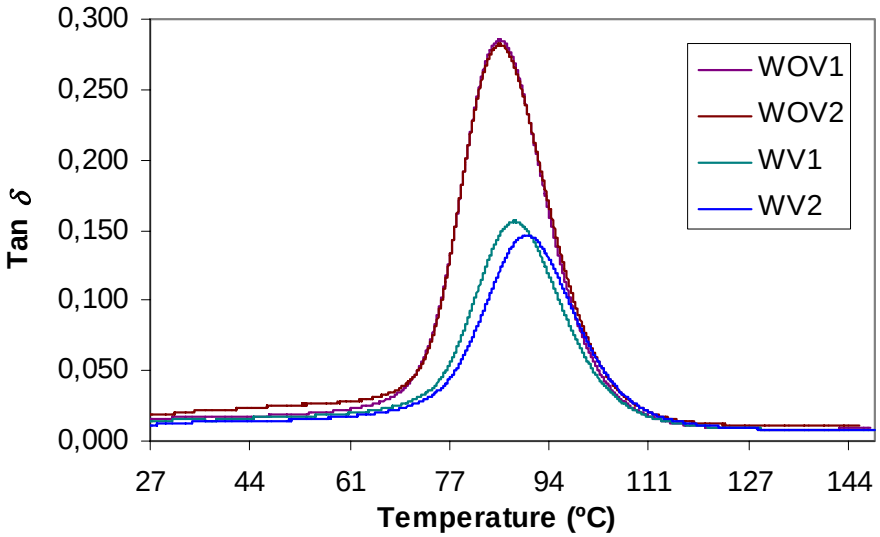

Figure 11. Temperature dependence of *tan δ* for epoxy/glass specimens.

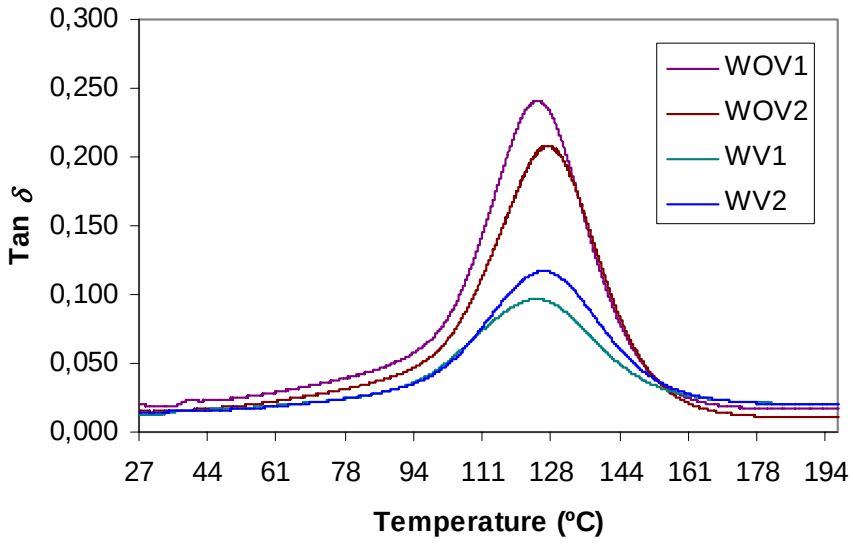

Figure 12. Temperature dependence of *tan δ* for polyester/glass specimens.

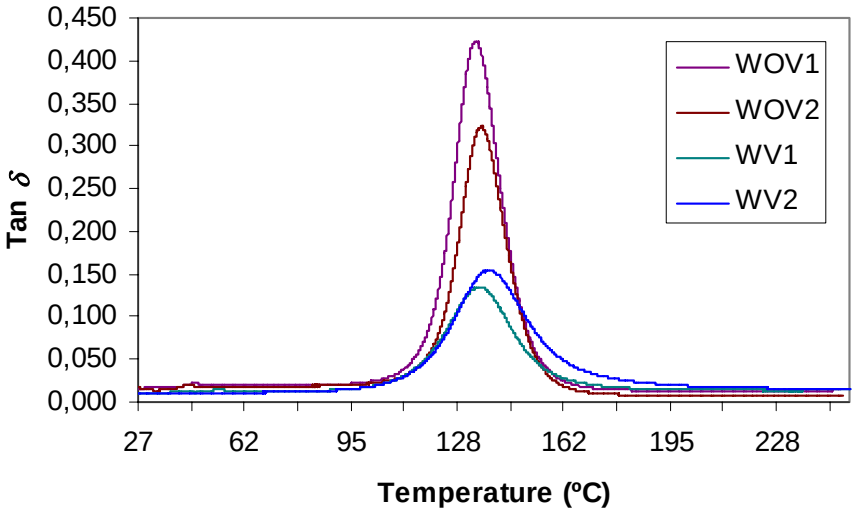

Figure 13. Temperature dependence of *tan δ* for vinyl ester/glass specimens.

Table 1. Viscoelastic properties for epoxy/glass specimens.

Beams	T_g (ºC)						E' (GPa)			Tan δ Peak
	E' Onset		E'' Peak		Tan δ Peak		Glassy (30 ºC)	Rubbery (110ºC)	E' drop (%)	
	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}				
WOV 1	75.4	0.5	81.6	0.7	85.7	0.7	13.8	2.3	83.0	0.285
WOV 2	77.4	0.5	83.3	0.4	87.7	0.4	12.1	2.0	83.1	0.282
WV 1	77.2	0.7	85.4	0.5	87.9	0.5	21.4	8.3	61.2	0.156
WV 2	78.3	0.2	87.6	0.3	89.9	0.4	20.6	8.3	59.7	0.146

$\bar{x}$ = sample mean (average); s_{n-1} = standard deviation

Table 2. Viscoelastic properties for polyester/glass specimens.

Beams	T_g (ºC)						E' (GPa)			Tan δ Peak
	E' Onset		E'' Peak		Tan δ Peak		Glassy (30 ºC)	Rubbery (160ºC)	E' drop (%)	
	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}				
WOV 1	102.4	1.0	117.9	0.6	126.0	1.7	13.4	2.2	83.2	0.241
WOV 2	103.0	3.90	120.1	1.1	126.1	0.8	11.8	2.3	80.2	0.208
WV 1	95.08	1.34	118.3	1.15	122.9	0.8	22.5	9.6	57.4	0.097
WV 2	99.03	1.96	118.6	0.99	123.6	0.7	21.8	7.8	64.1	0.117

$\bar{x}$ = sample mean (average); s_{n-1} = standard deviation

Table 3. Viscoelastic properties for vinyl ester/glass specimens.

Beams	T_g (ºC)						E' (GPa)			Tan δ Peak
	E' Onset		E'' Peak		Tan δ Peak		Glassy (30 ºC)	Rubbery (175ºC)	E' drop (%)	
	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}	$\bar{x}$	s_{n-1}				
WOV 1	122.1	0.9	128.8	0.3	133.6	0.4	11.0	1.2	89.4	0.423
WOV 2	123.6	0.9	131.3	0.7	134.9	0.6	13.4	2.6	80.8	0.323
WV 1	115.6	1.6	128.9	1.0	132.0	0.9	23.1	8.9	61.4	0.135
WV 2	117.3	0.8	131.0	0.7	135.1	0.5	22.6	7.1	68.7	0.155

$\bar{x}$ = sample mean (average); s_{n-1} = standard deviation

In Figs. 8 to 10, it is observed that, although the loss moduli were not affected by vacuum below the glass transition, the improved consolidation of vacuum processed laminates resulted in a higher loss modulus over the rubbery region. The same effect was also responsible for an increase in storage modulus. The measured data shown in Figs. 11 to 13 indicate that the *tan* δ peak for the beams processed without vacuum is higher than for the vacuum assisted processed beams. The application of vacuum led to a better consolidation of the laminate. In the T_g region, the reduction in storage modulus was more significant in specimens processed without applied vacuum (Tabs. 1 to 3). Since the loss modulus peak was not considerably affected by vacuum, the larger reduction in storage modulus of specimens produced without vacuum resulted in a larger *tan* δ peak.

According to data presented in Tabs. 1 to 3, the highest T_g, measured by the *tan* δ peak, was for the vinyl ester/glass (~ 133 ºC), followed by the polyester/glass (~ 124 ºC) and epoxy/glass (~ 88 ºC). T_g values for the same material, measured from specimens processed under different conditions were similar, indicating that this property was not affected by the use of vacuum during processing. For the materials studied in this investigation, the glass transition measured over the temperature range mentioned is a matrix dependent property and, therefore, was not expected to be affected by improved consolidation.

4. CONCLUSIONS

In this investigation, the effect of processing conditions on the viscoelastic properties of epoxy/glass, polyester/glass and vinyl ester/glass composites was evaluated. Laminates were produced using plain weave E-glass fabric under two different processing conditions: with and without vacuum. Beam specimens were tested in DMA three-point bending testing mode for the viscoelastic characterization.

Based on the experimental results, it can be concluded that:

- For specimens processed under applied vacuum, the storage modulus increased considerably: 62%, 76% and 87%, for epoxy/glass, polyester/glass and vinyl ester/glass, respectively. This increase was attributed to better consolidation of the laminate combined to a reduction in matrix volume fraction, due to the removal of part of the resin with the application of vacuum.
- The loss moduli were not affected by vacuum below the glass transition. However, the improved consolidation of vacuum processed laminates resulted in a higher loss modulus in the rubbery region.
- The *tan* δ peak for specimens processed without applied vacuum was higher when compared to the vacuum assisted processed samples. This was due to the significant reduction in storage modulus for specimens processed without vacuum, in the T_g region, and the fact that the loss modulus peak was not considerably affected by vacuum, over the same region. Then, the larger reduction in storage modulus of specimens processed without vacuum resulted in a larger *tan* δ peak.
- T_g values for the same material, measured from specimens processed under vacuum or without vacuum were very similar, indicating that this property was not affected by the use of vacuum during processing.

In summary, this research demonstrates that DMA equipment offers good potential to study changes in viscoelastic properties of composite laminates, as related to processing conditions.

5. ACKNOWLEDGEMENTS

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