

Dynamic Mechanical Properties for Polyurethane Elastomers Applied in Elastomeric Mortar

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ABSTRACT: Dynamic mechanical properties of a polyurethane (PU) elastomer and a mortar processed with the same elastomer (modified polytetramethylene ether glycol (PTMEG)) were studied. The results obtained showed that the liquid aromatic amine ETHACURE[®] 300, used as cure agent, can be used to substitute the aromatic amine MOCA[®], which is usually used as cure agent in high performance elastomers. The resulting mortar produced with ETHACURE[®] 300 presents similar dynamic-mechanical thermal properties

when compared with MOCA[®]. However, dynamic-mechanical thermal analysis studies showed that the mortar developed with ETHACURE[®] 300 presents some advantages such as the low values of $\tan \delta$, indicating a good capacity of recovery of the strain after retreating an applied force. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: dynamic mechanical thermal analysis; ETHACURE[®]; 300; polyurethane elastomer

INTRODUCTION

Nowadays, polymeric lips have been applied in some joint parts of viaducts, bridges, and industrial floors.^{1,2} These components have been traditionally used with epoxy resin bases and, more recently, with urethane bases.^{3,4} Therefore, when compared with the polymeric lips obtained from epoxy bases, the elastomeric one can be considered advantageous due mainly to its elongation benefits, since the elastomeric materials can generate an elongation higher than 100% when compared with the thermoset resins.^{3,4} This property allows the lip to accompany the movements executed by concrete structures along its useful life.

The knowledge of the dynamic mechanical behavior of the polymeric lips is very important and can be achieved on small-scale simulations, accompanying the suffered variations in the structure without actually destroying part of it when making the samples.⁵ For this kind of study, the dynamic-mechanical thermal analysis (DMTA) is very useful.

Polymers always present viscoelastic behavior, that is, they have both properties like viscous and elastic materials. Elastomeric materials recover

instantaneously their dimensions and the original form, after removing of the deformation loads, can promote a reduction of two or three times when compared with the original length. On the other hand, a viscous material flows under the action of an external force, without recovering the original dimensions when the force is removed.⁶

Due to the viscoelastic behavior of polymers, the characterization of its mechanical behavior should be done in an appropriate time and temperature scale. At very low temperatures (approximately -30°C), the polymeric material presents a glass behavior characterized by its rigidity. In the glass region, its modulus does not vary significantly with temperature or time because the thermal energy is not sufficient enough to promote any translation and rotation of the polymeric chain segments; in other words, they are frozen in fixed average positions. On increasing the temperature, a glass transition can be observed and it will be characterized by a significant change in the mechanical properties of the polymer (the storage modulus of the elastomers in some cases can be reduced to about three times). This change can be attributed to the movement of the polymeric segments and chains which causes a softening in the polymer and both, a consequent reduction of the storage modulus (E') and an increase in the loss modulus (E'').³ Finally, in a higher temperature region, the polymer acquires a rubbery type behavior.

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TABLE I
Composition in Mass of the Elastomeric Mortar from
AEPTMEG/E300 (%)

| | Component | Mass (%) |
|--------|---|----------|
| Part A | Talc no. 325 + Quartz no. 200 | 61.00 |
| | Prepolymer PTMEG/TDI NCO = 4.30% | 30.00 |
| | Carbon black no. 125 | 1.00 |
| | Toluene | 5.00 |
| Part B | Aromatic diamine ETHACURE [®] 300 | 3.00 |

The glass and rubbery transition domains characterize the viscoelastic behavior of the polymer and determine how the elastomers can be applied. DMTA allows to determine: (a) the dynamic or storage modulus (E'); parameter that indicates the stiffness of the material or the stored energy and (b) the loss modulus (E''), that shows the dissipated energy, that is, the energy dissipated in the molecular rearrangements, which lead to a permanent and no reversible deformation. The ratio E''/E' indicates the loss tangent or the mechanical reduction, $\tan \delta$, also named as damping factor, is responsible to give information on the relative contributions of the viscous and elastic components of viscoelastic materials.² Materials with a $\tan \delta$ value less than 1 exhibit more elastic behavior and they may have relatively high storage modulus.

This article aims to study the dynamic-mechanical behavior of a polymeric mortar with elastomeric characteristics, constituted by an urethane prepolymer, mineral fillers, pigment, solvent, and an amine cure agent. Another objective of this work is to check the substitution of the aromatic amine (solid) MOCA[®], globally used in the obtaining of high performance elastomers, by a liquid aromatic amine, ETHACURE[®] 300. MOCA[®] is solid at room temperature, inadequate for field works, and a cancer cause agent.^{7,8}

EXPERIMENTAL

Obtaining of the polyurethane prepolymer

The polyurethane prepolymer was prepared through the reaction between excess of a diisocyanate with a polyether polyol. The diisocyanate used in this work was diisocyanate-toluene 80/20 (TDI 80/20) composed by a mixture of its isomers 2,4 (80% w/w) and 2,6 (20% w/w), manufactured by Isopol (Dow Chemical). The polyol used was the polytetramethylene ether glycol (PTMEG), manufactured by BASF (USA), under the trademark poly THF 1000, with an average molar weight of 1000 g mol^{-1} .⁶

The mixture was prepared in the molar ratio of 1.67 : 1 (TDI 80/20:PTMEG), aiming to obtain a free isocyanate content (%NCO) of 4.30%. In this way,

500 parts of prepolymer had 388 parts of PTMEG and 112 parts of TDI 80/20. The reaction was carried out in a glass reactor, under inert atmosphere or under vacuum. Initially, the reactor was loaded with the PTMEG and the temperature was maintained in the range from 50 to 55°C. After this, the 112 parts of TDI 80/20 were slowly added into the reactor and the temperature was raised up to 70°C, and kept constant during approximately 2 h. The content of NCO (%) was determined according to the ASTM D 4274 norm.⁹ The theoretical free isocyanate content (%NCO) is 4.30% and the experimental value obtained after 120 min was 4.33%. Then, the content into the reactor was transferred to a container and closed, under dry nitrogen atmosphere. This specimen was denominated as PTMEG/TDI.

Obtaining of the elastomeric mortar

Table I and Figure 1 display the formulation and the scheme of the elastomeric mortar. As depicted in this table, two separate parts (A and B) were prepared and mixed in the moment of the application.

During the production of Part A, the urethane prepolymer PTMEG/TDI component was quickly heated up before to be processed in an oven at 100°C and the mixture with the mineral fillers (quartz and talc) was made by using a spatula. In this work, quartz (200 mesh) and talc (325 mesh) were initially mixed between then and after this, dried at 100°C during a 100-h period. It is recommended that the fillers have their moisture content measured by using a Karl-Fischer titration technique, considering as appropriate values lower than 0.05%.⁸ This recommendation is due to the fact that water in the fillers can react with functional terminal NCO groups of the prepolymer chains producing polyurea which is associated to the liberation of CO₂, causing bubbles in the final product. These bubbles will convert the final elastomer in foam, therefore, damaging the elastomeric mortar.⁴

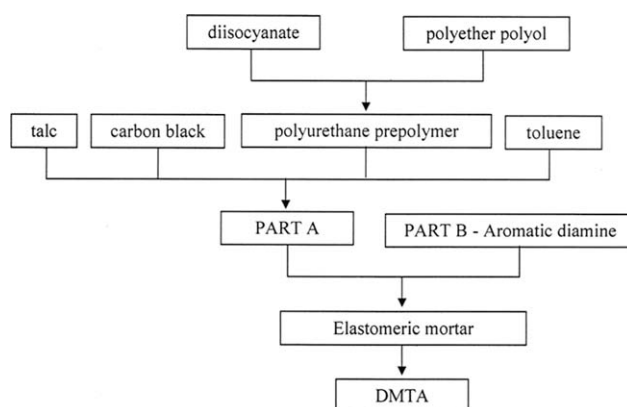


Figure 1 Scheme of mortar processing.

Reduction of moisture is an essential step in the production of high performance polyurethane systems. The inherent reactivity of moisture with isocyanates and isocyanate prepolymers degrades significantly the performance of polyurethane coatings, sealants, and elastomers. Additives will effectively control the effects of moisture in the application of two component urethane systems. For this reason a moisture scavenger for urethane systems was used in formulations.

After 5 min of addition of the fillers to PTMEG/TDI, 50% of the necessary amount of toluene (Merck®-Solvesso degree P.U., humidity smaller than 0.075% Merck®) was added, together with carbon black, to facilitate the mixing of the fillers and the pigment. After approximately 10 min, the mixture was completed with the addition of the solvent, stirred for 10 min, and transferred to a container under dry nitrogen atmosphere. The container was tightly closed and named as Part A. Part B was arising from the aromatic diamine ETHACURE® 300, manufactured by Albermale.

Preparation of the polyurethane elastomers samples and elastomeric mortars

In order to perform the DMTA characterization, polyurethane elastomer (based on MOCA® and in ETHACURE® 300) and elastomeric mortar samples were obtained from the reaction between the components of each system, immediately followed by molding in the form of plates.¹⁰

Samples of polyurethane elastomers

The samples of polyurethane elastomers were obtained by reaction between prepolymer, PTMEG/TDI with the cure agents aromatic diamine ETHACURE® 300, and MOCA®. To prepare the samples, it is necessary to consider the stoichiometry of the reaction between the prepolymer with terminal $-NCO$ groups, and the cure agent with $-NH_2$ groups. Table II presents the mole ratio and used quantities of monomers.

The content parts of ETHACURE® 300, for 100 parts of prepolymer PTMEG/TDI, were calculated using the following expression¹⁰:

$$PPH = \frac{SR \times EqW \times \%NCO}{42}$$

where PPH is parts per hundred, SR is NCO/OH ratio. The hard segment content of polymer was calculated as the mass fraction of diol and diisocyanate in the material. EqW is equivalent weight of cure agent, M_{NCO} (molecular weight of NCO) = 42 g mol⁻¹, %NCO is free reactive NCO content of prepolymer used. For example, if SR = 0.95; EqW

TABLE II
Polyurethane Prepolymer and Elastomer Raw Material Mole Ratio

| Materials | Mole ratio | Free NCO content (m/m, %) |
|---|------------|---------------------------|
| PTMEG | 1.00 | |
| TDI (80/20) | 1.67 | |
| PU prepolymer (PTMEG/TDI) | 1.00 | 4.30 |
| MOCA | 1.05 | |
| ETHACURE Elastomer (PU prepolymer/MOCA-based) | 1.05 | 0.05 |
| Elastomer (PU prepolymer/ethacure-based) | | 0.05 |

ETHACURE® 300 = 107 g mol⁻¹ and %NCO = 4.30, the PPH can be calculated as:

$$PPH = \frac{[(0.95)(107)(4.30)]}{42} = 10.5$$

It means that for 100 parts of prepolymer PTMEG/TDI, 10.5 parts of ETHACURE® 300 are needed.

The adopted procedure was the following: 200 parts of prepolymer PTMEG/TDI were weighted in a 500-mL beaker and heated up to 80°C; the beaker was kept in a desiccator coupled with a vacuum pump, on a heating mantle, to maintain that temperature for 30 min. After this period, the content in the beaker was immediately mixed with 21 parts of ETHACURE® 300 at 25°C, with a wood spatula.

The sample obtained from MOCA® was prepared in a similar route, but since this reagent is in solid state in the room temperature, the previous heating up to 110°C was necessary prior to its addition. After heating, 200 parts of the prepolymer at 80°C were weighted and mixed with 26 parts of MOCA® at 100°C, with a stoichiometry of 95% based on the best mechanical behavior reasons.¹⁰ The quantity of 26 parts of MOCA® is needed due to the different equivalent weight of this cure agent.

The samples were transferred to appropriate molds immediately after the mixing. The precure was accomplished isothermally in an oven at 70°C, during 16 h, and the postcure in 7 days at room temperature.¹⁰ After this cure period the samples were characterized by thermal analyses.

Elastomeric mortar samples

The elastomeric mortar samples were obtained by mixing components A and B, according to a stoichiometry of 95%, or, according to Table I, in the approximate A/B ratio = 32/1. Then, 200 parts of Component A and 6.2 parts of the Component B were mixed with a wood spatula during around 5 min, forming a homogeneous mixture. The precure of the

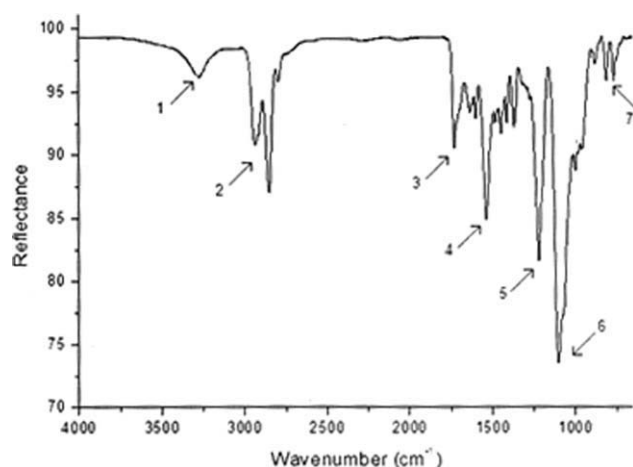


Figure 2 FT-IR spectra from the polyurethane loaded with quartz.

mortar was accomplished in an oven at 70°C, during 16 h, and the postcure in 7 days at room temperature.¹

Dynamic mechanical thermal analysis

DMTA analyses were carried out in a TA Instruments TA 2100 analyzer and module DMA-983, at room temperature (25°C) and relative humidity of (55 ± 10)%. Samples with dimensions of 60 × 10 × 2 mm³ were used and fixed by vertical serrated claws, with constant pressure springs, manual torque, and a distance among the claws equal to 20 mm. Before DMTA analysis, the samples were dried and maintained in desiccators at room temperature.

During this analysis, the samples into the DMTA, were cooled down to -130°C, using a liquid nitrogen, maintained in this isotherm during 3 min and heated up to 60°C (at 3°C/min). For this, they were used as DMTA parameters: 1 Hz frequency, 0.80 mm oscillation amplitude, 0.5 length correction, and 0.5 Poisson constant. The determinations were made twice in the case of the elastomers, and three times in the case of the mortar and the average values were used.

FT-IR analyses

The infrared spectrum was acquired using Perkin-Elmer system 100 FTIR spectrophotometer, at a resolution of 4 cm⁻¹. The spectra were taken in reflection mode in the region 650–4000 cm⁻¹.

RESULTS AND DISCUSSION

Viscoelastic behavior for the polyurethane elastomers systems

The symbol M was used to represent the PTMEG/TDI/MOCA[®] elastomer and the EC for PTMEG/TDI / ETHACURE[®] 300 component.

TABLE III
Characteristics of IR Bands Associated with Polyurethane¹¹

| Band | Frequency (cm ⁻¹) | PU associated bands |
|------|-------------------------------|---|
| 1 | 3273 | 3150–3600 cm ⁻¹ (NH stretching) |
| 2 | 2939, 2861 | 2800–3000 cm ⁻¹ (CH stretching) |
| 3 | 1724 | 1600–1760 cm ⁻¹ (amide I: C=O stretching) |
| 4 | 1541 | 1540 cm ⁻¹ (amide II: δ _{N-H} + ν _{C-N} + ν _{C-C}) |
| 5 | 1229 | 1226–1292 cm ⁻¹ (amide III: ν _{C-N}) |
| 6 | 1106 | 1105 cm ⁻¹ (C–O–C ether stretching) |
| 7 | 769 | 766 cm ⁻¹ (amide IV) |

The mid infrared spectra of the polyurethane loaded with quartz in between the range 4000–650 cm⁻¹ were classified into seven characteristic bands, around 3300, 2900, 1700, 1540, 1230, 1100, and 780 cm⁻¹, with reference to the polyurethane spectra. Unfortunately, the quartz added to the PU was not active in the ATR analysis, probably due to its granulated form. This result was confirmed by individual analysis of quartz and PU. Figure 2 shows the main FT-IR bands numbered from 1 to 7 and Table III presents a classification of these bands associating with polyurethane. Seymour et al.¹² reported that the C–H stretching vibration of urethane bonds, in poly(ether-urethanes), may appear as two bands.

Figures 3 and 4 show the variation of the storage modulus (E'), the loss modulus (E'') (right ordinate), and the loss tangent ($\tan \delta$) (left ordinate) as a function of the temperature, respectively, for EC and M. As can be observed from these figures, the behavior of E' show a linear portion in the region between -130 and -60°C, where the variation of the modulus is less intense. This area is denominated "glass

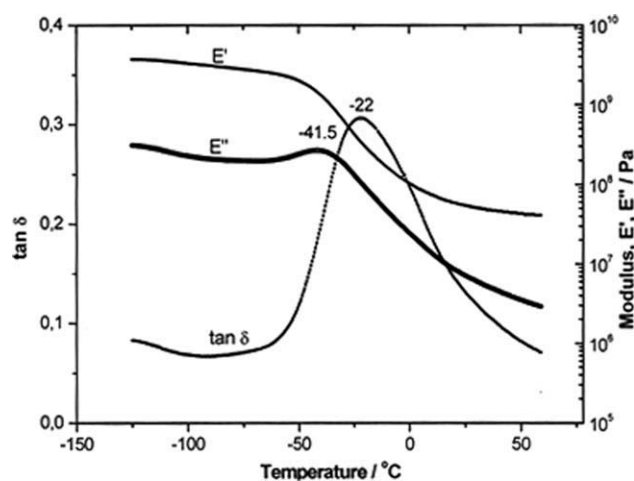


Figure 3 Curves of the storage modulus (E'), the loss modulus (E'') and the $\tan \delta$ as a function of temperature for elastomer EC. Heating rate: 3°C/min, frequency: 1 Hz, and oscillation amplitude: 0.80 mm.

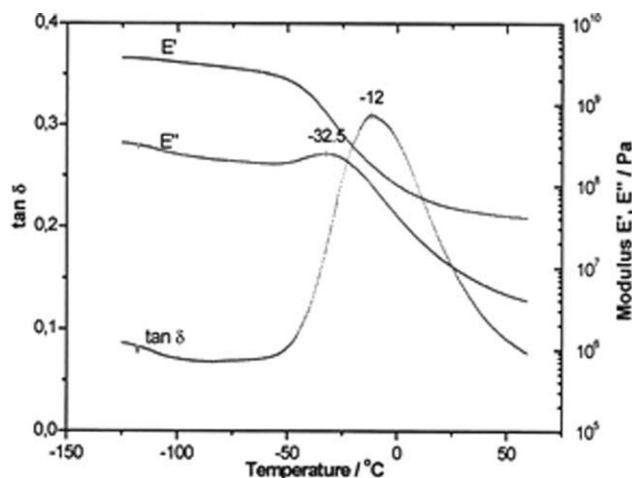


Figure 4 Curves of the storage modulus (E'), the loss modulus (E'') and the $\tan \delta$ as function of temperature for elastomer M. Heating ratio: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and oscillation width 0.80 mm.

area" and can be characterized by the low mobility of the polymeric chains. A similar effect can be found in the literature for other kinds of elastomeric materials, as observed in Refs. 9, 13–15.

With the increase of the temperature, a steeper fall in the E' modulus is also observed, characterizing the glassy-transition region, that is, the change of the glassy state into rubbery state, with reduction of the elastic component. Simultaneously, the increase of the polymeric chains mobility causes an increase in the energy dissipation that is reflected in the increase of E'' modulus. After all chains acquire mobility (rubbery behavior), the value of E'' present a balance range, in this case larger than before the transition, originating a peak in E'' curve and, therefore, in $\tan \delta$ behavior. According to the literature, the maximum of E'' or $\tan \delta$ values can be used to define the glass transition temperature, T_g .^{16,17} In this study, the T_g values were obtained using the maximum of E'' for comparison among the elastomers, being observed that the T_g values are -41.5°C for EC and -32.5°C for M, so EC presents higher mobility of the polymeric segments at lower temperatures than M. According to the literature, the relaxation peaks observed is due to a segmental motion in the main polymer chains associated to rotational motion of side groups.^{16,17}

The behavior observed in both cases, EC and M, is typically those observed by the elastomers that the glass transition temperature is below the room temperature; their storage modulus are usually very low at this condition. At this point, they resemble an amorphous material that is heated above the glass transition temperature. However, differently from the amorphous materials, elastomers exhibit relatively low values of $\tan \delta$ at temperatures above the

glass transition. This indicates that while it is necessary a small force to deform the material, its recovery will be good once the applied force is removed, as it happens in the rehearsals of uniaxial traction of elastomers. When the temperature is decreased, the material passes through glass transition and its behavior is the same that a rigid material.¹⁷ In the case of reticulated elastomers, under high temperatures, the storage modulus is low, but measurable, not presenting a second decline, as it happens with thermoplastic elastomers due to the softening or melting.^{10,12}

Figure 5 shows E' curves for both studied elastomers (EC and M), where can be observed that in temperatures below 0°C , the M elastomer presents higher E' values when compared with the other one, indicating more rigid structure and, therefore, larger modulus of elasticity to the bending/tensile loads, while above 0°C the difference is minimum, presenting very low and similar storage modulus.

The contribution of the viscous component or, in other words, the portion of the material that will flow under tension conditions (stress) is represented by E'' , and it is associated to the creep and tension relaxation. The $\tan \delta$ value expressed by E''/E' ratio is not dimensional and it supplies a convenient way to compare polymers, while E' and E'' are subjected to alterations caused by the composition geometry and processing conditions, $\tan \delta$ can be seen as a viscoelasticity index or the reduction capacity.¹²

Figure 6 shows the variation of loss modulus (E'') and $\tan \delta$ curves for the two elastomeric systems. From this figure can be observed that the peaks in the $\tan \delta$ curves present similar values in both cases; however, for EC the peak starts at lower temperatures (approximately -40°C). In theory, EC has a

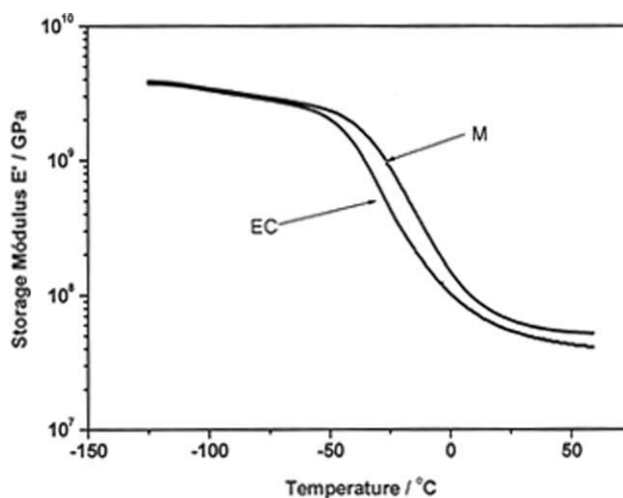


Figure 5 Curves of the storage modulus (E') of elastomers EC and M as a function of the temperature. Heating rate: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and width of oscillation 0.80 mm.

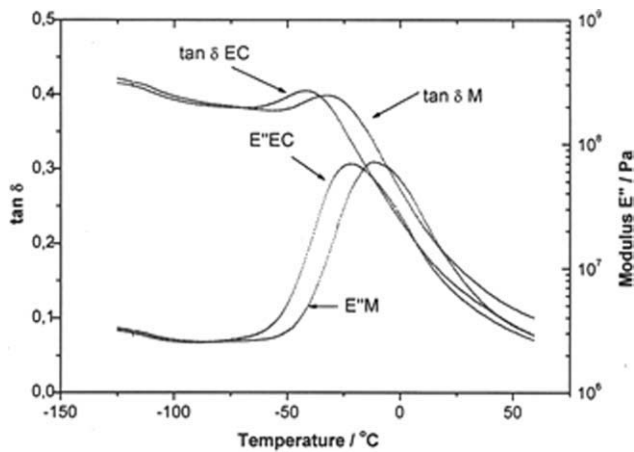


Figure 6 Curves of $\tan \delta$ and loss modulus (E'') for elastomers EC and M as a function of temperature. Heating rate: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and oscillation width: 0.80 mm.

larger capacity of damping at low temperatures, which is desirable for use as a mortar.

In general, EC and M curves, present profiles that are very similar between them, except for the displacement in the points of glass transitions. It can be observed in Figure 6 that the EC elastomer has the advantage of presenting lower glass transition temperature when compared with M.

As the dynamic behavior of the elastomers, shown by the E' and E'' moduli and $\tan \delta$ curves, do not present accentuated differences, can be concluded that ETHACURE[®] 300 can substitute MOCA[®] in those applications that demand dynamic properties of the polyurethane elastomers. ETHACURE[®] 300 still presents some advantages when compared with the MOCA[®], such as, it is not a cancer agent and it is in the liquid state at room temperature. That makes easier the preparations and the use in lower temperatures.

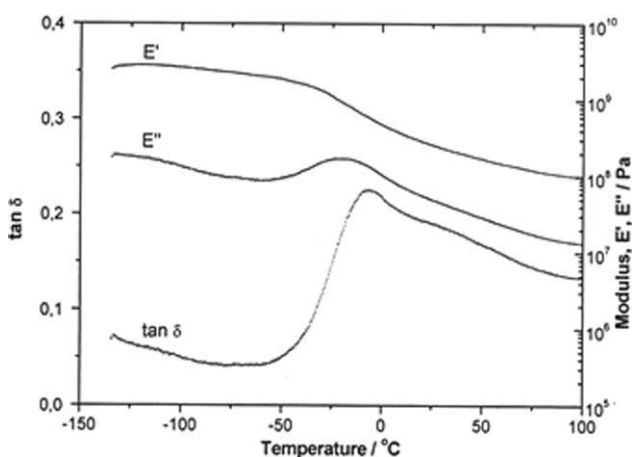


Figure 7 Curves of storage modulus (E'), loss modulus (E'') and $\tan \delta$ for mortar AEPTMEG/E300. Heating rate: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and oscillation width: 0.80 mm.

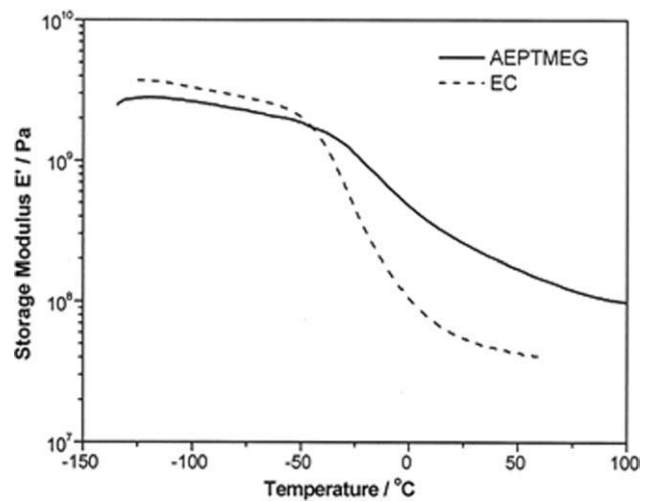


Figure 8 Curves of the storage modulus E' as a function of temperature for the systems EC and AEPTMEG/E300. Heating ratio: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and oscillation width 0.80 mm.

Viscoelastic behavior of the elastomeric mortar

DMTA of the PTMEG/TDI/ETHACURE[®] 300 (AEPTMEG/E300) elastomeric mortar was accomplished to average its dynamic mechanical behavior. Figure 7 shows the profile of variations of medium values for storage modulus (E'), loss Modulus (E''), and $\tan \delta$ as a function of the temperature.

The profiles of the curves, Figure 7, for elastomeric mortars, in spite of the loads, are similar to the curves of the elastomers previously analyzed, with the accentuated fall of the storage modulus (E') for temperatures above the glass transition. The decay of the tangent is smaller than for the previous elastomers, although the values of the $\tan \delta$ are also low. The T_g (obtained from the E'' peak) in this case is -21°C .

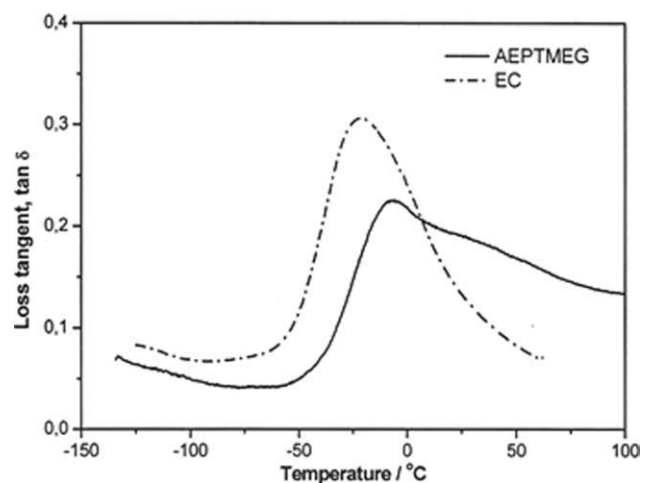


Figure 9 Curves of $\tan \delta$ versus temperature for the systems EC and AEPTMEG/E300. Heating ratio: $3^\circ\text{C}/\text{min}$, frequency: 1 Hz, and oscillation width: 0.80 mm.

Figure 8 compares the E' curves versus the temperature for the EC elastomer and the AEPTMEG/E300 mortar. It can be observed that above -40°C , E' values for the mortar becomes higher than the obtained to the elastomer, indicating a higher modulus of elasticity for the elastomeric mortar. Particularly, between 0 and 50°C , approximately, the temperature range in which the mortar will work, an adequate reinforcement is provided by the fillers, and it is just the need for the practical use. The lower E' value for the mortars in the region below T_g is generated by the higher content of the fillers, which turns the material fragile in these conditions, besides suggesting that the interaction between the polymer and the fillers is weak.

In Figure 9, the profiles of curves of $\tan \delta$ as a function of the temperature for AEPTMEG/E300 mortar and elastomer EC are showed. It can be observed that the mortar presents $\tan \delta$ values lower than the elastomer until the glass transition temperature (-50 to 0°C) and, after this region, it presents a higher $\tan \delta$ values, indicating that the mortar present a better capacity of damping than the elastomer without fillers. However, $\tan \delta$ values are still low, indicating that mortar has a good capacity to recover the strain after removing the applied force. So, the mortar can suffer thermal or mechanical stresses without presenting a permanent strain.

In Figure 9, it is also possible to observe that the behavior below T_g can be explained by the lower polymer content in mortar, in the sense that it is responsible for the storage modulus (E'). Above T_g , however, the friction of the fillers amongst themselves and with the polymer resin can contribute significantly for the energy dissipation, increasing the $\tan \delta$ values.^{18,19}

CONCLUSION

The elastomer processed by ETHACURE[®] 300 presents dynamic mechanical properties very similar to the one observed to this material processed by MOCA[®]. But the former has two important advantages: it is in liquid state at room temperature and it is not a cancer cause agent. Thus ETHACURE[®] 300 can be considered as a cure agent capable to replace MOCA[®].

The presented results show that the elastomeric mortar developed from PTMEG/TDI/ETHACURE[®] 300 can be applied as elastomeric lips of joints for structures in concrete, mainly because it presents lower $\tan \delta$ values, indicating a good capacity of recovery of the strain after retreating the applied force. This mortar can suffer thermal or mechanical stresses without presenting permanent strain, the one which gives to the mortar the necessary flexibility to accompany the efforts of vibrations. The fact of presenting low glass transition temperature (-21°C) is another advantage, because this property qualifies the elastomeric mortar to be used in works at environmental conditions with low temperatures maintaining elastomeric characteristics.

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