Measurement of Environmental Stress Cracking of Polymers using DMTA

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ABSTRACT

Environmental Stress Cracking (ESC) has been found to be responsible for about 30% of the failures of engineering plastics in service. This type of failure may be induced by the design, packaging, or exposure to secondary fluids such as lubricants or cleaning agents. Recent developments by some equipment manufacturers allow testing of polymeric materials in contact with fluids over wide temperature ranges. The aim of the paper is to determine the practical use of Dynamic Mechanical Thermal Analysis (DMTA) fitted with a fluid bath accessory for the study of ESC on the physical properties of polymeric materials in contact with aggressive fluids. The study presented in this paper was performed on Paltuf Polycarbonate immersed in Acetone and Dimethyl Sulfoxide (DMSO). Acetone is shown to cause a severe loss of material properties within a short period of exposure and that fluid interaction causes cracking in the presence of a stress raiser. Dimethyl Sulfoxide is shown to cause cracking of the material within seconds of contact with a stressed sample. Although this study is in its initial stages, the results indicate that DMTA could provide a powerful tool with which to understand the effects of ESC.

INTRODUCTION

Despite being studied over the last 50 years, ESC still accounts for the majority of polymer product failures [1]. Chemical resistance data for commonly used plastics is available from most polymer manufacturers; however, this data in itself does not indicate the polymers suitability for use in a particular chemical environment under stress. Environmental Stress Cracking (ESC) of polymer materials is comparable to the stress corrosion failures found in metals [2]. Plastics exhibit ESC through exposure to an aggressive chemical environment under the influence of stress. The cause of the stress may be a consequence of processing resulting in residual stress, or externally applied stress. Control of critical variables in the moulding process along with proper design can minimise the effects of residual stress [3]. ESC prediction by Hansen Solubility Parameters (HSP) is well known, this method is based mainly on the affinity of a polymer for a particular chemical agent. The solubility-parameter approach is only moderately useful for correlating stress-cracking behaviour with the ability of a liquid to swell a plastic [3]. In the real world, single chemical compositions are rare and fluids can be prepared in any number of chemical combinations. A thermodynamic approach using the Hildebrand solubility parameter (δ) has been carried out [4], it was found to hold to the thermodynamic correlations for a single chemical environment but not to be so in chemical mixtures. Stress applied externally can result from a number of sources including assembly processes, transportation, storage, or be part of the intended end-use of the device. Stress-crack resistance can be determined by a standard testing procedure whose results can be related to the stress / strain levels observed in end-use conditions. It is generally accepted that ε_c (critical strain at which cracking or crazing occurs) is an excellent guide to ESC behaviour [3]. A number of ASTM and ISO tests have been developed to evaluate ESC based on ε_c [Table 1]. These tests differ primarily in how the stress is applied. The optimal test method for an application should be based on the failure criteria established by the designers. Other testing methods exist including Moiré Fringe Extension, and Rising Strain Rate. In these tests the material is tested in air and in the fluid of interest. The onset of cracking or crazing is taken as the difference in strain when compared to air and is often referred to as the departure strain. However, the departure strain should not be taken as the time to crack initiation. Research has shown DMTA capable of testing the effects of fluids on polymers [5 – 6]. In this work, it is proposed to determine if a DMTA machine fitted with a fluid bath accessory is capable of detecting the effects of fluid contact under stress in polymeric materials.

Test Standard	Description
ASTM D 1693	Environmental Stress Cracking of Ethylene Plastics
ISO 4600	Resistance to ESC, Ball/Pin Impression Method
ISO 4599	Resistance to ESC, Bent Strip Method
ISO 6252	Resistance to ESC, Constant Tensile Stress Method

Table 1 ESC Test Standards

Experimental

Dynamic Mechanical Thermal Analysis (DMTA) is a thermal analysis method, for conducting viscoelastic measurements on polymeric materials. The method imparts an oscillatory load to a polymer material and measures the phase difference (δ) between the elastic and viscous components. The method is sensitive to the effects of temperature and strain on the transition phases of these materials [Figure 1]. DMA has been used to show the effects of navel fuels [5], and methanol [6] on the glass transition temperature (T_g) of polymers and elastomers. In these studies, the polymer was subject to pre-immersion in the fluid until equilibrium conditions had been achieved. The influence of pre-immersion time on the effects of ESC has a significant bearing on the durability and service performance of products. In these cases the application of stress and fluid contact did not coincide. Pre-immersion of the polymer in an aggressive fluid can reduce the severity of ESC; therefore the time delay between contact with the fluid and the applied stress should be minimal [7]. The effects of pre-immersion times on strain rate have been studied [8] using Lexan Polycarbonate in contact with ethanol, in this study a pre-immersion time of 300 hours equated in a shift to a higher strain rate. Work using a fluid bath and a humidity chamber has been carried out [9 - 11]. All polymer samples used in the experiment were cut from extruded sheet, in order to prevent crack initiation from other sources the edges were smoothed using 600 and 1200 grade wet and dry paper, the fluids used were analytical grade materials [Table 2]. The DMTA machine used was a Triton Technologies Tritec 2000A fitted with the company's fluid bath accessory and Churchill chiller / heater unit, which allowed testing at room temperature. All samples were run under the following conditions frequency 1Hz, load 9N, displacement 0.05 mm. The samples were placed in the single cantilever fixtures of the DMTA machine, and clamped to a torque of 25 cNm. The chiller / heater unit was allowed to stabilise the fluid at 22^0C for one hour prior to experimentation. Many chemicals attack polycarbonate; a particularly severe chemical for the majority of amorphous polymers is Acetone, if left in contact with the fluid these types of polymers will dissolve. A dip test indicated that PC could withstand the effects of Acetone for a number of hours before decomposition occurred. In contrast, Acrylonitrile Butadiene Styrene (ABS) began to dissolve almost immediately upon contact. A second sample of Polycarbonate was prepared as above and subject to immersion in Dimethyl Sulfoxide (DMSO). It has been reported that polycarbonate under strain, cracks on contact with this fluid [3]. In order to capture this phenomenon with DMTA the material was run in air for four minutes and the bath was raised into position. The reason for this delay is to the allow time for the temperature probe to stabilize, the time to do this is on average 30 seconds. Under normal DMA use temperature / time scans the machines main use, this delay has little effect.

Material	Supplier
Paltuf Polycarbonate (PC)	Palram
Fluid	Supplier
Acetone	Fisher Scientific UK Ltd
Dimethyl Sulfoxide	Fisher Scientific UK Ltd

Table 2 Materials and fluids

Polycarbonate (PC) is a typical amorphous polymer that shows clear ESC behaviour. The material used in this paper was Paltuf Polycarbonate sheet used in various industries in such applications as protective shields for factory machinery protective helmet visors and stadium roofing. The material is a standard grade PC, showing good impact resistance and weatherability. Acetone is a familiar product to most consumers and can be found in nail polish remover however, it may be present in a number of other consumer items including cleaning agents, lacquers and adhesives. Dimethyl Sulfoxide is an intermediate chemical product used in the production of paint strippers, semiconductor cleaners and pharmaceuticals.

Results

Dip testing of the Polycarbonate in Acetone was carried out overnight, on removal the polymer was found to be tacky to the touch, and there was no evidence of discolouration. The sample was removed from the DMTA machine after 3 hours immersion and inspected. The sample was found to have discoloured, swelled and cracking was evident around the edges [Figure 2]. The storage modulus (E') [Figure 3] shows the effect of the Acetone, the exponential nature of E' indicates that the fluid attacks the material rapidly, and that the severity of the attack declines with time. Other data from this graph should not be ignored, tan delta (δ) which is the ratio of the elastic (E') and viscous (E'') components of the material gives an indication of the

plasticizing effect of the fluid with respect to time. It could be seen [Figure 2] that cracking had taken place. From E' [Figure 3] it was difficult to determine if the DMA had detected any of the cracking which had occurred [Figure 2]. The software for the machine is capable of recording data at every second of the isothermal period, one of the applications of the DMA technique is in predicting material properties over decades of time. Due to the compactness of the data the first order derivative (dE'/dt) was taken. This approach effectively amplifies the data highlighting any peaks. The resulting graph [Figure 4], shows the effect of this technique on E' nine peaks were highlighted indicating that transition effects occurred, the time interval between the peaks are presented in Table 3. The data for the DMSO fluid is presented in [Figure 5]; the resulting graph indicates that the material underwent a transition 30 seconds after immersion [point A Figure 5] upon removal from the machine the specimen was inspected for damage. Gentle pressure indicated that the specimen had cracked. Immersion in DSMO also caused discolouration of the material similar to that of Acetone without the accompanying swelling. The transition event caused a substantial fall in E' of the material making this easy to see. Taking the derivative (dE'/dt) revealed that the initiation of the event occurred 24 seconds [point A Figure 6] before the peak of the event [point B Figure 6].

Peak Period (min)	Difference (min)
29.7	41.5
71.2	26.5
97.7	24.1
121.8	8.3
130.1	19.1
149.2	9.1
158.3	6.3
164.6	7.7
172.3	8.7

Table 3 Period of peaks

Discussion

Much of the polymer testing for ESC is carried out using ε_c, ISO, or ASTM standards, these tests are cheap, quick and relatively easy to perform their main disadvantage is the lack of information gained. In today's high performance low failure environment, more sophisticated techniques that are required. Polymer materials are time, temperature and environment dependent, a change in one of these will have effects on material properties. In normal use, DMAI is sensitive to the detection of transition behaviour in polymer materials. However, it is not without its problems. Clamping of the material sample is known to affect the results, as does temperature lag between the temperature probe and the sample. Recently the National Physics Laboratory (NPL) in the United Kingdom has issued a guide [12] for the use of DMA and other thermal analysis techniques with composites and adhesives. In general, the maximum sample thickness of a thermoplastic is 4mm and for composites 2mm; using a low heating rate of 3^0K/Min allows the sample to reach an even temperature. Cracking [Figure 2], indicates that swelling of the material in Acetone causes the material to fracture in the presence of a stress raiser. The effect seen in Figure 5 has little to do with swelling. The time taken for the transition to occur allows little time for this phenomenon to develop. In this case clamping effects must be taken into account. The aim of future research is to investigate the use of DMTA equipment with a fluid bath accessory in observing polymer degradation in an aggressive fluid environment.

Conclusions

The discussion above outlines a technique for the detection of ESC using DMTA equipment with a fluid bath accessory. The sensitivity of the technique allows the detection of transitions in the material. Initial data discussed above indicates that the method could provide a powerful tool for the understanding and prediction of ESC behaviour in polymeric materials. This work is in its early stages and at the time of writing research is still ongoing to determine the relationship between the data obtained and the effects shown in the graphs and the physical evidence. Use of this technique, for the assessment of ESC may provide engineers, designers and manufactures with a better understanding of a phenomenon that has dogged the industry for over fifty years.

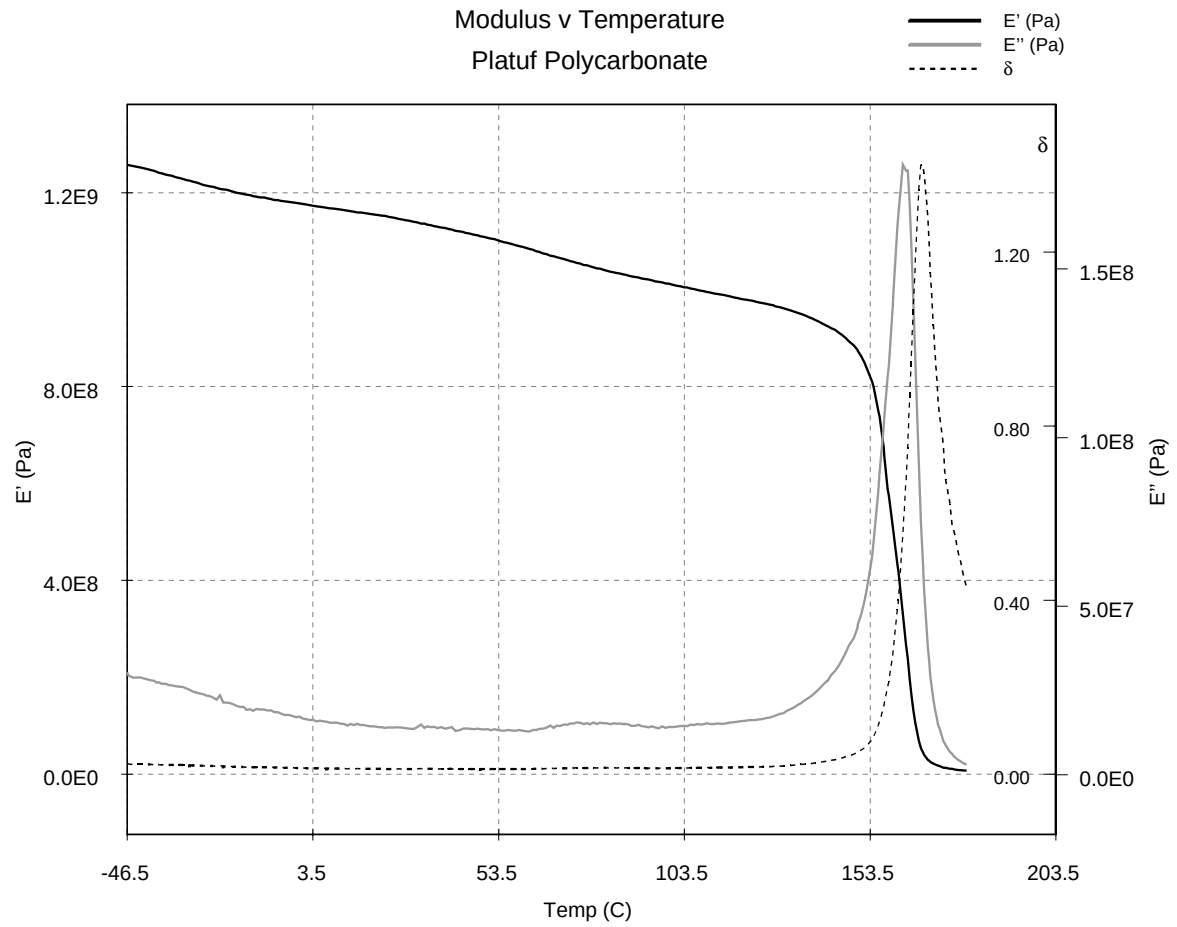

Figure 1. Typical DMTA temperature scan of Paltuf PC

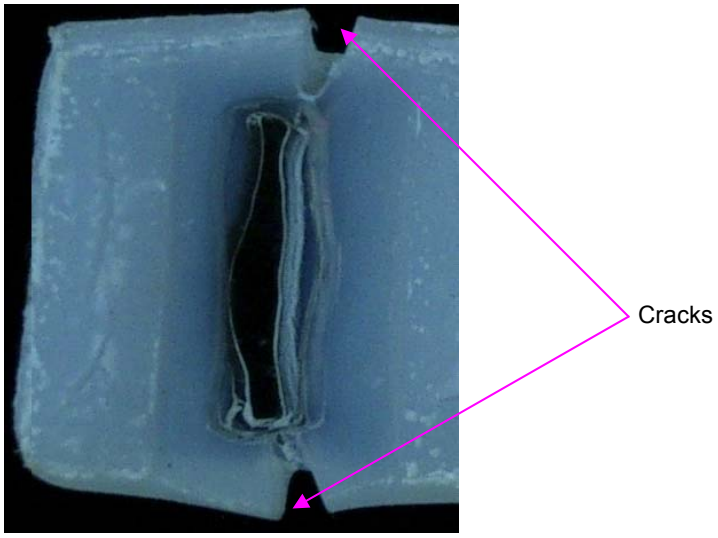

Figure 2 Paltuf PC after 3 Hours Acetone Contact

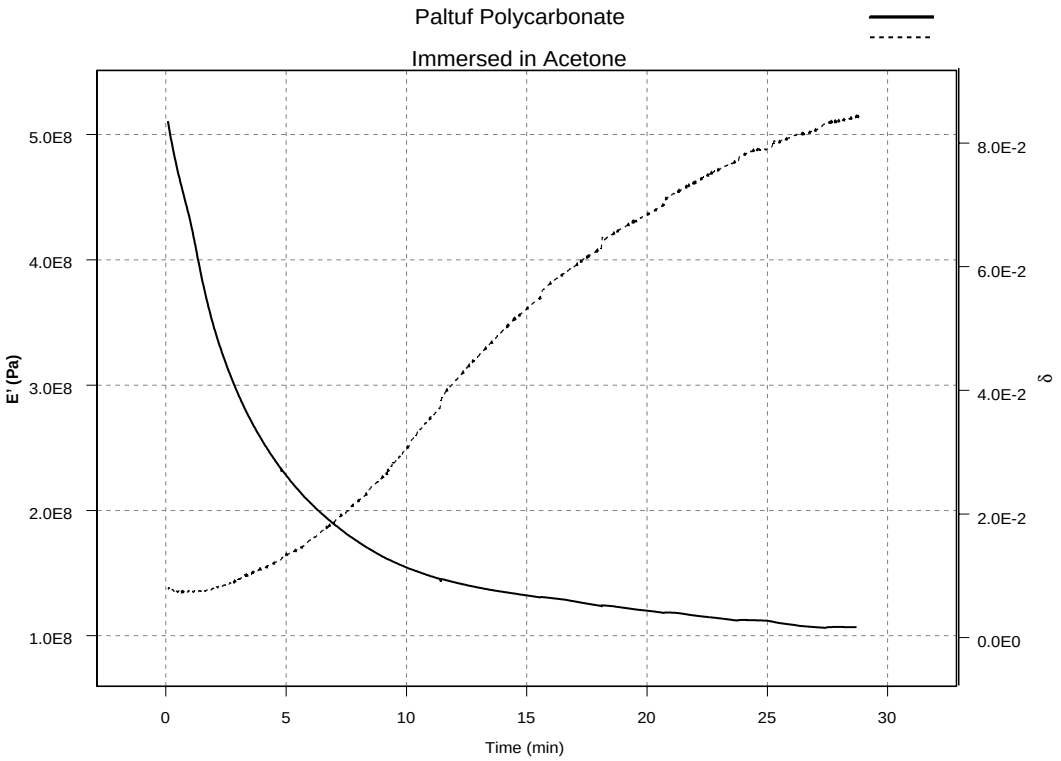

Figure 3 Paltuf PC before taking the derivative (dE'/dt)

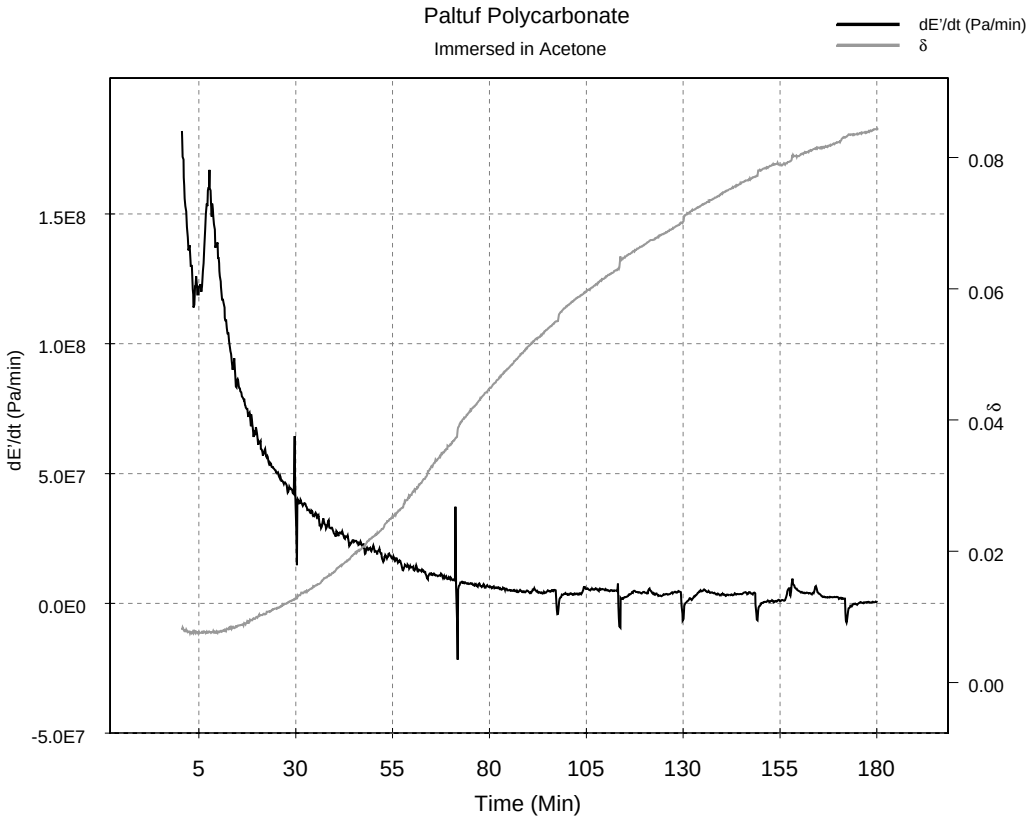

Figure 4 DMTA data showing peaks and loss of modulus E' with respect to time

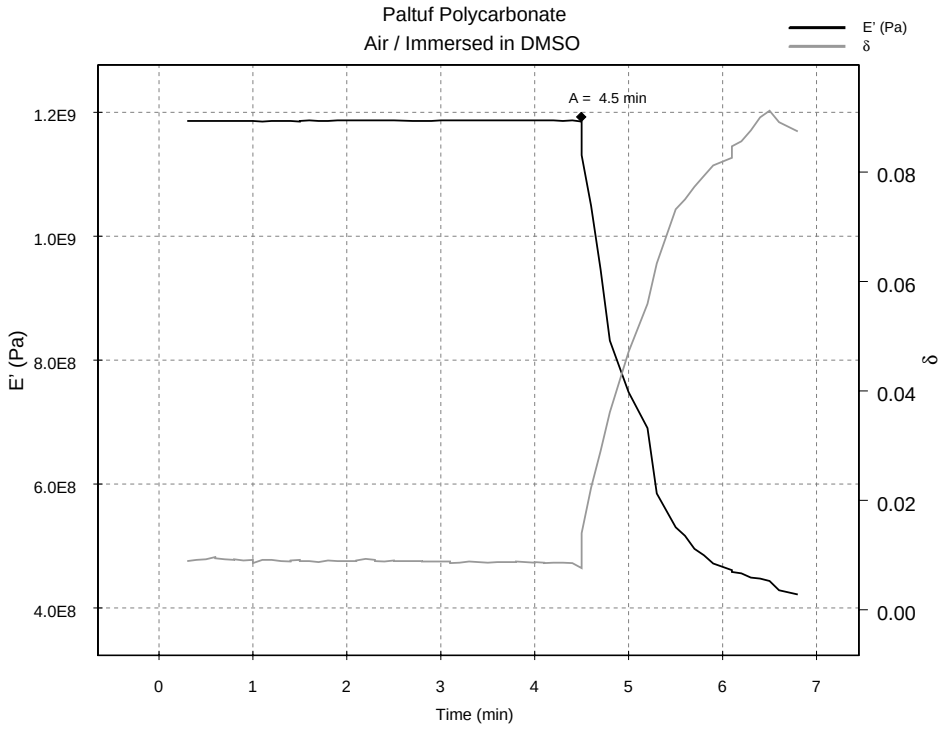

Figure 5 Paltuf Air / DSO DMA data

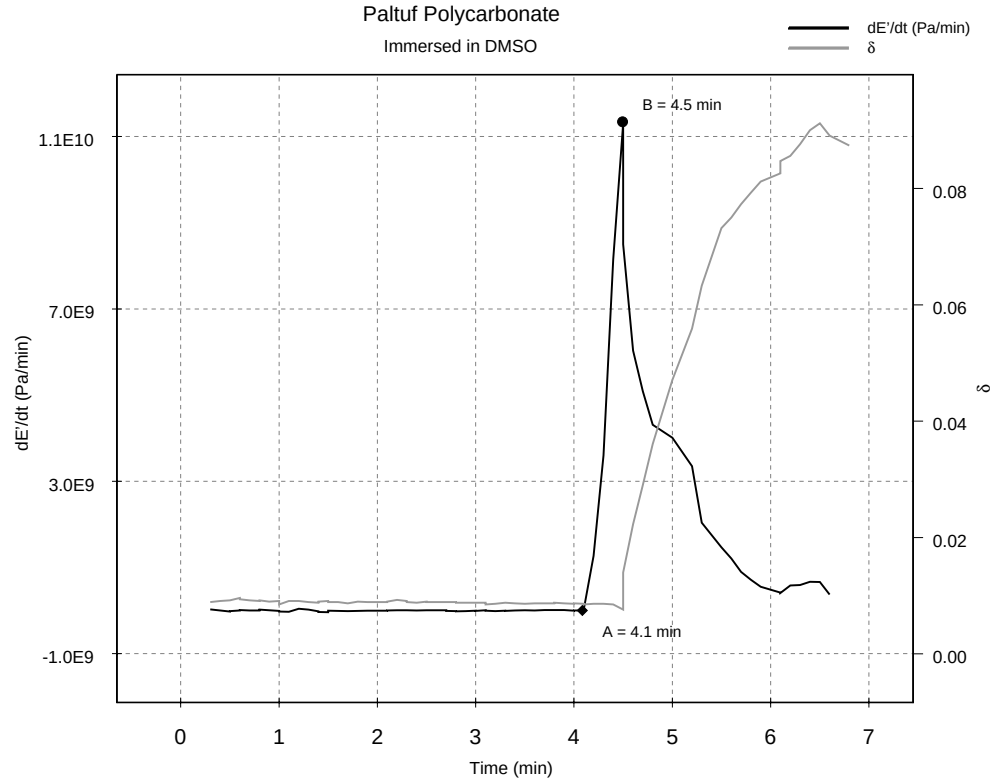

Figure 6 DMTA data showing peaks and loss of modulus E' with respect to time

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