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Author(s): M Razmara, H Saidpour and S Arunchalam

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DMA Investigation on Polyurethane (PUR)

M. Razmara, S.H. Saidpour and S. Arunchalam

Abstract— To employ a new material in pipeline application was a subject of research in pipeline technology centre of University of East London. Since the classic mechanical test methods, such as the instrumented penetration and mechanical flexural tests are time consuming and cost intensive, the goal here was to investigate the extent of dynamic mechanical analysis (DMA) to provide correlations with these methods and is thus suitable for quicker and less expensive test for the stated area of application. In this study with help of Dynamic Mechanical Analyser (DMA), the new material was approved to be flexible Polyurethane (PUR).

Keywords—Polyurethane (PUR), Dynamic Mechanical Analysis (DMA), Dual Cantilever Bending (DCB).

I. INTRODUCTION

Some of the polymer materials, which can be used in pipeline applications are: Polyethylene, Poly Vinyl Chloride, and Poly Propylene. Polyurethane (PUR) is already used as an insulation material in pipeline application and it is recently interested to be used as a pipe itself.

The effective application of trenchless technique and producing a new pipe into the host pipe has encouraged the development of new material and methods of installation, including PUR by spray lining. Polyurethanes are high molecular weight polymers based on the polyaddition of polyfunctional hydroxyl-group containing compounds and polyisocyanates. Urethane resin system or Polyurethanes form a broad group of polymeric materials that contain urethane chemical groups and are associated with isocyanate chemistry [1], [5].

The reaction of three key ingredients produces flexible polyurethane foam: a polyol, a

diisocyanate, and water. The term “polyurethane” applies to a general class of polymers in which molecular chain segments are bound together with urethane linkages (-R-NH(C=O) NH-R-) [1], [13], [14]. Rigid polyurethane foams perform well in most areas of low-temperature insulations. Products in density ranging from approximately 30 to 200 kg m⁻³ withstand temperatures down to -196 °C.

Typical applications are: refrigerated vehicles, road and rail tankers, and vessels for refrigerated cargo, pipelines, liquid gas tanks for LPG and LNG and cryogenic wind tunnels [1], [3].

Rigid and flexible type of PUR already is been used in pipeline insulation application for liquid ethylene (-105 °C) and Liquid Natural Gas (-164 °C). Therefore, this study intends to investigate the thermo mechanical properties of PUR and to compare the results with rigid and flexible PUR in the literature.

A. DMA data of PUR

DMA is a widely used technique to examine the viscoelastic features of flexible PUR foams. In Fig.1-b storage modulus and tan δ are plotted as a function of temperature. The sample displays a T_g at about -50 °C, typical of flexible PUR foams this is followed by a rubbery plateau region up to 180 °C. The degradation begins after 200 °C, which is not shown here [1], [12].

Huh and Cooper (1971) have reported that PUR may exhibit two separate glass transition in the hard-and-soft-segment domains, respectively. In addition, crystallization may occur in one or both phases. Depending on the chemical composition, length, ratio of the components, method of preparation, and subsequent processing steps (prehistory), there may be considerable interphase mixing between the molecules of the two segments.

The rubbery soft-segment domains impart elastomeric properties. The more rigid hard-segment domains held together by intermolecular secondary (hydrogen) bonding and possibly by crystallization restrict viscous flow and act as physical cross-links for the rubbery soft-segment matrix. The lower temperature transition at -70 °C

M. Razmara is with the School of Computing and Technology University of East London, London, UK. (phone: +44-208-2055325; e-mail: m.razmara@uel.ac.uk).

S.H. Saidpour is with the School of Computing and Technology University of East London, London, UK. (e-mail: s.h.saidpour@uel.ac.uk).

S. Arunchalam is with the School of Computing and Technology University of East London, London, UK. (e-mail: arun@uel.ac.uk).

is associated with a change from stiff to rubbery character and the higher temperature transition is believed that the transition at about 130 °C is due to the break down of hydrogen bonded interactions of Van der Waal's forces between the rigid and flexible segments of PUR. Between these two transition regions, the modulus is much less affected by temperature and is sometimes referred to as a 'plateau' modulus [1], [4], [7].

Uhlig (1998) has been provided a graph of short term laboratory tests on standard PUR specimens, to obtain (Fig.1) reproducible characteristics on the one hand for research and development and on the other hand for application engineering and quality control [1], [8].

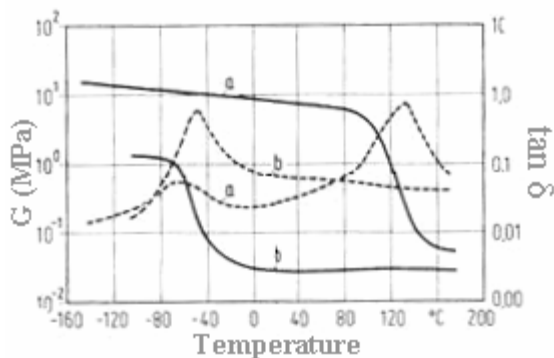


Figure 1. DMA spectra of G' and $\tan \delta$ of PUR
a. rigid PUR foam and b. flexible PUR foam

The temperature dependence of mechanical properties of rigid foams can be assessed based on results from the oscillating twist test (Fig.1a). The level of the shear modulus is virtually constant within the range -40 to +80 °C; this is characteristic of the wide temperature range in which rigid polyurethane foams can be used.

The difference between the modulus in a frozen condition and that at room temperature also gives an indication of changes in the impact strength. Above -60 °C, up to the softening range, the impact test will not show any appreciable change, while below -60 °C it will gradually decline [1], [9].

II. EXPERIMENTAL

A. Material and equipment used

Different samples of poly urethane (PUR) were cut from the pipes and prepared according to the standard [1], [9].

In this study, Netzsch Dynamic Mechanical Analyzer (DMA 242C) in, Dual cantilever bending (DCB) and penetration mode is used to measure the viscoelastic behaviour of PUR.

B. Procedure used

The exact values for each sample dimensions were entered into the computer for each calculation of storage, loss modulus and loss factor. The temperature range studied was -150 to 200 °C depends on their T_m , the heating rate was 2 - 3 °C/min, the frequency was 1 Hz, and the operations were carried out in the DCB and penetration mode. The storage modulus and the mechanical damping of the plastic are measured as a function of the temperature in the DMA test. After the sample has been fixed and cooled by liquid nitrogen, for about half an hour to minus 150 °C at about 2 K/min, a computerized, fully automatic system measured and recorded the storage and loss modulus and damping curves. The PUR sample was also tested in penetration mode. The cylinder shape sample with 6 mm diameter and thickness of 2.5 mm.

The following adjustments have been applied:

- *Dual cantilever bend (DCB):*

L, Support Span for all tests is 2 x 16 mm, Frequency: 1 Hz; Samples dimensions: 55 mm x 12 mm x 2.5 mm ; Max Dynamic Force: 4 - 5 N, Proportional Factor: 0, Amplitude: 30 - 40 μ m

- *Penetration mode:*

3 mm push rod diameter, Frequency: 1 Hz; Samples dimensions: 7.07 mm² cross section x 2.5 mm depth; Max Dynamic Force: 4 - 6 N; Proportional Factor: 1.2 - 1.3, Amplitude: 30 - 45 μ m

III. RESULTS AND DISCUSSION

The viscoelastic behaviour of one of the PUR samples, which are tested in DCB mode, is shown in Fig.2. The E' inflection at -39°C correlates with the peak in the loss modulus curve, E'' at same temperature and with the peak in loss factor, $\tan \delta$ at -2°C which is attributed as α relaxation or T_g followed by a rubbery plateau region.

The second peak in E'' at -132 °C correlates with β transition, which is due to initial mobility of molecular side chain segment and may assume as impact strength of PUR at room temperature. By increasing freedom of movement in side chain, the strength of transition increases [1], [8].

The very small peak in β transition states the poor impact resistance of PUR. It is suggested that additional information such as actual impact test data above and below the relaxation to be used to verify the influence of β transition in impact resistant behaviour [1], [4].

The third peak in $\tan \delta$ curve at 72°C appears to be an artefact, possibly due to water evaporation from the porous PUR which may built up during the tightening of DCB sample holder due to sample contraction at sub zero temperature.

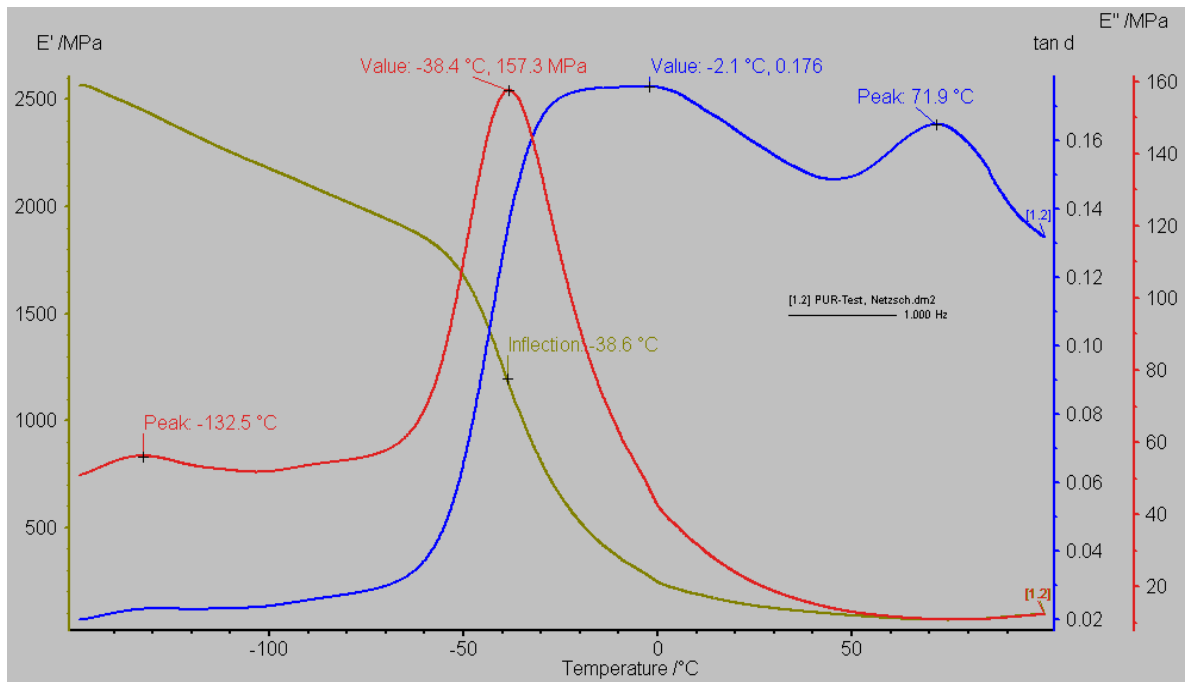


Figure 2. DMA test results for PUR performed in DCB mode

By comparing the gained results from PUR samples and the result obtained from literature and Fig.1b it is confirmed that the PUR subjected to pipe line application is flexible Polyurethane foam.

To ensure that the peak is a relic through using of DCB grip and it is not a property of PUR; another test was run in penetration mode (Fig. 3).

As it was expected, the third $\tan \delta$ peak in DCB mode is disappeared in penetration mode test. The β relaxation peak which is visible in E'' curve in DCB mode at -132.5°C (Fig. 2) has disappeared in penetration mode possibly due to be deficient in water. Thus β transition has slightly appeared in inflection point at -31°C of E' shoulder (Fig. 3).

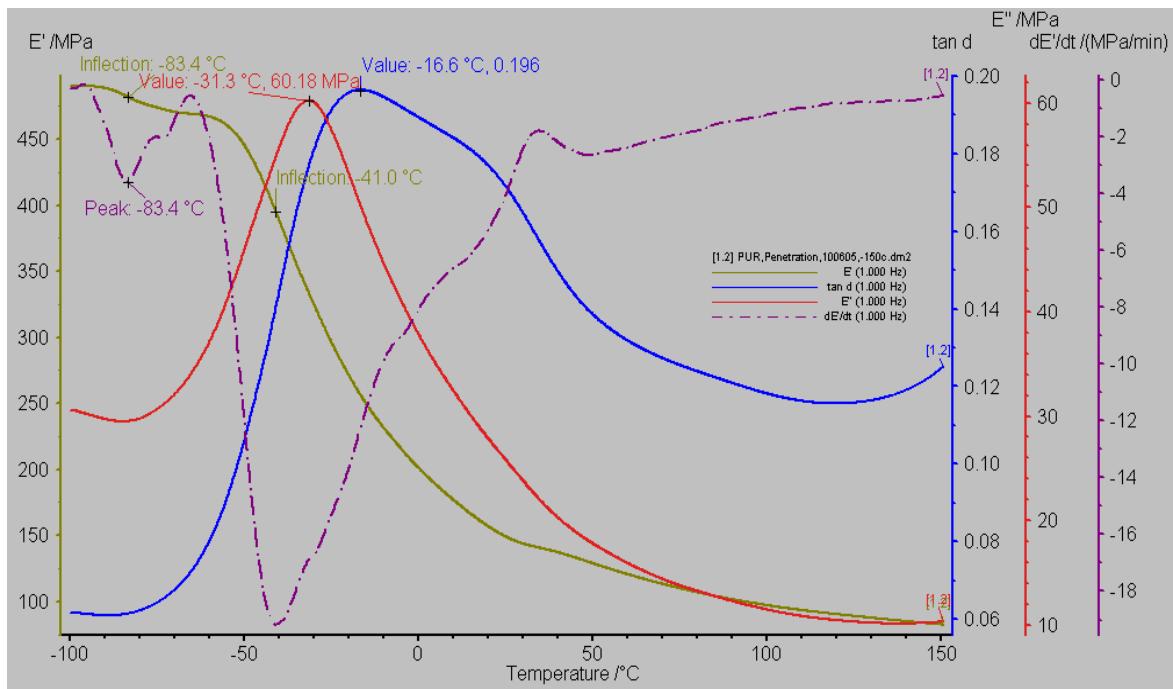


Figure 2. DMA test results for PUR performed in penetration mode

To confirm that this is a secondary transition of the material, the first derivation of E' or dE'/dT was obtained helping to determine the T_{β} at -83°C [10].

An important effect of water is to increase the strength of β relaxation. It is evident that the diluents is effective plasticizer in removing constraints on the amorphous segments thus increasing mobility due to increasing free volume (reduction in T_{β}) and making more confirmation available to reorientation (increasing in β intensity) [4]. Fig. 2 verifies this idea by signifying the more intense β relaxation peak in E'' than Fig. 3.

The T_g in Fig. 3 has shifted to lower temperature in compare with the same material tested in DCB at about -17°C in $\tan \delta$ peak, -31°C in E'' curve which is corresponding with inflection point at -41°C in E' .

IV. CONCLUSION

- The subjected PUR is recognized as flexible PUR foam.
- The broad $\tan \delta$ peak at T_g corresponds with enough time to stress relaxation of PUR.
- An important effect of water is to increase the strength of β relaxation. Pipe liner materials should balance E' and E'' to optimize the properties needed to form the required toughness and relieve stress.

- A very high amount of E'' in PUR shows that Pipe deflection (out of roundness) will exceed the allowance limit for the pipe material [2].

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