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Material properties

Chain dynamics in foamed polysiloxane materials: Influence of the tin catalyst phase on material properties

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ABSTRACT

We report on our underpinning science activities investigating the through life performance properties of foamed polysiloxanes. These materials are manufactured through tin octanoate based condensation cure chemistry. The tin catalyst plays an important role, not only in determining crosslink density and microstructure, but also potentially influencing properties (compression set and load retention) important to through life performance. In this study, Mossbauer Spectroscopy and X-ray fluorescence has been used to assess the nature and distribution of the tin species and show evidence for highly localized catalyst regions, including a mobile tin phase. In addition, testing was carried out using a NMR MOUSE (Mobile Unit for Surface Exploration) together with a CPMG (Carr Purcell Meiboom Gill) spin echo sequence to probe chain dynamics through the measurement of spin-spin or transverse relaxation (T_2) responses. We have used model polysiloxanes to demonstrate that the NMR MOUSE capability is relatively sensitive to crosslink density. In general, the more resticted the environment around a given chain structure, the more rapidly it is likely to relax, and potential chain confinement effects of the tin phase may be assessed through the measurement of T_2 parameters. Our work shows that the tin catalyst has a binding action and affects the dynamics of the relatively more rigid environments (such as crosslinks) as well as the mobility of chain ends and mid chain components (long T_2). Load retention properties are reduced with increased tin catalyst loading, and this ties in with the influence of the tin particles on chain dynamics. The observations reported here support our initiative to develop predictive models representative of the through life performance of foamed polysiloxanes.

1. Introduction

Foamed polysiloxane materials have increased applications in a number of fields and ageing studies are required to develop predictive models relating to through life performance. After production and initial testing for zero time properties, materials can potentially show elevated compression set and load-retention properties that may exceed relatively tight product design specification limits. These issues can also follow through into service life, and strategies are required to be in place to alleviate concerns and help underwrite the availability and through life performance of these components.

Tin (II) compounds are frequently used in the manufacture of specialized foamed polysiloxanes. These compounds act to catalyse the condensation chemistry of dihydroxy terminated polydimethylsiloxane with alkoxysilanes [1,2]. The tin octanoate catalyst plays an important role in determining the final properties of the polymer material in terms of crosslink density and load retention. The underlying chemistry coincides with the conversion of 2-ethylhexanoate ligands to carboxylic acid

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and the accumulation of acidic species within the polymer matrix [3].

Unfortunately, residual catalyst present in the cured material is known to cause accelerated ageing of the material. The presence of acidic species, combined with the unreacted residual tin (II) compounds in the rubber, is of significant concern as these species can be catalytically active in polymer hydrolysis and network rearrangement processes [4].

Studies by Van Der Weij [5] investigating the underlying chemistry has shown that the main reactive tin species is an organotin hydroxide which is a hydrolysis product of the tin carboxylate ligands. The formation of the reactive tin hydroxide is dependent on finite levels of water within the gum, and carboxylic acid is produced as a byproduct during the hydrolysis reaction.

The acid is known to have a significant impact on the thermal stability and ageing properties of the polymer by accelerating protonation of the siloxane bond and reducing the energy barrier for hydrolysis of the polymer [6]. In particular, Stein et al. [7] has shown evidence for significant siloxane bond rearrangement processes (cleavage and recombination of siloxane linkages) that accelerate chemical stress relaxation effects and reduce the load retention properties of the material. Generally, many problems (but not all) associated with the manufacture of the pads is historically connected with the Tin (II) catalyst, and the catalyst has the potential to influence the important load bearing and ageing properties of the material [8].

In this study we have focused on investigating the potential influence of the catalyst phase on chain dynamics as this is directly important in determining compression set and load retention characteristics. Relaxation mechanisms in NMR are well characterised and proceed via one of two pathways – termed the T_1 and T_2 relaxation times. The T_1 relaxation is termed spin lattice or longitudinal relaxation and is based on the re-equilibration of the excited nuclear spins with their surroundings. The T_2 relaxation is termed spin-spin or transverse relaxation and is the process where energy is transferred between the spins in the sample by other spinning nuclei.

NMR relaxation data of stereochemically different nuclei will give useful information on the local environments of these nuclei. The more resticted the environment around a given group type, the more rapidly it will relax. The spin-spin or transverse relaxation time (T_2) is diagnostic of the rigidity of the material. A rubber with high crosslink density results in spins being held in close proximity to other spin active species, resulting in rapid T_2 relaxation times. More mobile materials generally exhibit longer T_2 regimes and this phenomenon can be used to assess the extent of crosslinking and potential age related changes in polymer systems.

2. Materials

The foamed polysiloxanes of interest were prepared by curing a silicone resin (supplied by Rhodia Silicones) containing a blend of ingredients: polysiloxane-diols, small amounts of hydrogen-methyl polysiloxane, tetraalkoxy silane and fumed silica filler. An organotin ingredient, stannous 2-ethylhexanoate, supplied as a 77% w/w solution in 2-ethyl hexanoic acid, was used as a cure initiator. Typically, 5 wt. of catalyst is mixed into the polysiloxane resin. The key functional groups within the formulation are recognised as RO-Si (from the tetrapropoxysilane); Si-OH (from the diphenylmethylsilanol, silanol terminated polydimethylsiloxane and the silica filler surface); and Si-H (from the polymethylhydrosiloxane).

After the initial cure, the material was post-cured in air at elevated temperatures to deactivate or remove reactive functional groups or species from the material and so alleviate potential residual cure effects. Prepared samples were analysed for total tin content by Neutron Activation Analysis (NAA). These measurements were conducted at the NAA facility of Imperial College at Silwood Park.

3. Tests

3.1. Chemical analysis

Mössbauer experiments were performed to assess the nature of the tin phase in the foamed materials. These studies were performed in transmission mode using a calcium stannate source, and spectra were deconvoluted using standard methods to separate contributions from Sn(II) and Sn(IV) peaks. Further details of the experimental process used have been reported in an earlier publication [4].

3.2. X-ray fluorescence (MXRF)

Confocal micro X-ray fluorescence (MXRF) studies were carried out to map the distribution of the tin species throughout the material. A Horiba XGT-5000 was used to image the S5370 foam in cross section. A fused silica polycapillary with a controlled spot size was used for high resolution elemental imaging. The partial vacuum system of the XGT allowed for determining the location of the Sn catalyst residue within the foam.

3.3. NMR MOUSE (Mobile Unit for Surface Exploration)

T_2 measurements were carried out using a Carr Purcell Meiboom Gill (CPMG) spin echo sequence on a Bruker 'NMR MOUSE'. A NMR MOUSE (Mobile Unit for Surface Exploration) and a CPMG spin echo sequence were used to assess T_2 as a function of tin content. The NMR MOUSE is a small permanent magnet operating in the region of 15 MHz proton frequency and equipped with a series of coils to allow T_2 measurement to be carried out at depths of up to 5 mm from the sample surface.

These experiments were carried out using the CPMG echo sequence and 1000 echoes with 5 second delays between scans to ensure no spin saturation was occurring, and varying the delays between 0.16 ms and 0.35 ms between echoes gave results consistent to within 1%. The measured relaxation curves for the tin catalysed rubbers show a binary exponential decay of a very short T_2 component (around 5-10 ms) and a longer T_2 component (around 50-70 ms); these are consistent with a crosslinked