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Physical & Thermal Properties of Model Polysiloxane Rubbers: Impact of Crosslink Density and Tin Concentration

M. Patel, P.R. Morrell and A.R. Skinner*

MLP group, AWE plc, Aldermaston, RG7 4PR, U.K.

Summary: The influence of the tin octanoate catalyst on the physical and thermal properties of RTV 5370 polysiloxane rubbers has been studied. To assess the likely influence of crosslinking on a number of physical and thermal properties in polysiloxanes, "model siloxane networks" (representing networks of well defined composition/structure) have been formulated by the hydrosilylation of polysiloxane diols of known average molecular weight with tetraethoxysilane curing agent. It was found that linear swell and the crystallisation melting transitions of these systems were both significantly affected by changes in crosslink density. A selection of RTV5370 foamed rubbers with different tin concentrations were prepared in a similar manner to assess the influence of the tin catalyst. For these materials it was found that the area of the crystalline melting transition decreased with increasing tin concentration, an effect indicative of increased crosslinking. Samples with double the standard amount of tin (10% wt catalyst) show a shift in the crystallisation transition to higher temperature with no further effect beyond this concentration. Furthermore, the storage modulus (E') of the rubbers at room temperature appears to be independent of the tin catalyst concentration. Through correlation with the data from the model siloxanes, these results suggests that increasing the catalyst concentration appears to induce additional crosslinking interactions that are stable at low temperatures but not stable at room temperature.

Introduction

In general, there are two main technologies used to produce cellular polysiloxane rubbers, each having certain advantages and disadvantages over the other. The first method is based on the use of low molecular weight silicone gum in which the cellular structure is produced by a simultaneous tin catalyst accelerated condensation polymerisation reaction and gas formation within the mould. Normally a dihydroxy terminated poly dimethylsiloxane containing a small amount of silica filler, together with a polyfunctional ($f>2$) crosslinking agent (e.g. tetrapropylsilicate) is used. A suitable quantity of organotin catalyst is added to initiate the reaction. Tin (II) and Tin (IV) catalysts (in particular dialkyltindicarboxylates or tindicarboxylates) are most frequently used to catalyse the condensation reaction of the dihydroxy terminated

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polydimethylsiloxane with the alkoxysilanes. For a polyfunctional crosslinking agent this will result in gelation[1]. Initiated by the tin catalyst, the reaction of terminal or side-chain silane hydrogens with the hydroxy groups on the polysiloxane chains will generate hydrogen gas as the blowing agent in these systems. The second method of producing polysiloxane foamed rubbers requires the use of relatively high molecular weight gum in which water soluble spherical particles are added (as pore formers) and then subsequently removed (by washing with water) after the rubber has been shaped and set in a mould.

In an assessment of the effects of stannous 2-ethylhexanoate catalyst on the polysiloxane diol in the absence of crosslinking agent, a possible chain extension reaction arising from the catalyst induced condensation of the silanols has been reported by X.W.He[2]. Based on these findings, it was concluded that excess residual catalyst will result in effectively longer polysiloxane diol chains and as a result, the molecular weight between crosslinks (M_c) formed from end-linking in the presence of crosslinking agent (e.g. tetraethoxysilane) will be significantly higher than expected. Similar studies by S.J. Clarson[3] showed that, at concentrations of 1 and 1.5 wt %, the stannous 2-ethylhexanoate promotes significant chain extension of the polysiloxane diol chains in the absence of the crosslinking agent at 20°C. For catalyst concentrations of $<0.1\%$ weight catalyst, however, no significant chain extension effects were observed in the polysiloxane gum. Chain extension effects were reported to be insignificant in the presence of the curing agent.

Research into the mechanism by which tin compounds catalyse the condensation reaction has shown the system to be complex with the actual catalyst being an organotin hydroxide which is a hydrolysis product of the tin octanoate[4]. The formation of the reactive tin hydroxide is dependent on finite levels of water within the gum. Carboxylic acid is also produced during the hydrolysis reaction which is consistent with the observation that the cure is retarded by the addition of carboxylic acid to this equilibrium reaction[5]. Subsequent reaction of the organotin hydroxide with the alkoxy silane is reported to generate silanolates (compounds containing Sn-O-Si linkages that are sensitive to silanols). The organotin hydroxide, being the true catalyst, is regenerated as the polymerisation proceeds.

The aim of the work reported here is to develop an improved understanding of the influence of the tin catalyst on the physical and thermal properties of the material. Of particular interest is whether there is a link between rubber crosslink density and the catalyst concentration. Due to the relatively complex nature of commercially available polysiloxane rubbers and the inherent disadvantages of the condensation polymerisation technique (e.g. operator dependence, batch to batch variation, difficulty controlling density, cell size, product modulus, etc.), "model siloxane networks" (representing networks of well defined composition/structure) have been formulated and characterised. These model compounds, of differing crosslink density, were prepared so that the influence of crosslinking on a number of physical and thermal properties including linear toluene swell, crystallisation and mechanical performance could be assessed. A method for the synthesis of model compounds utilising the end-linking of functionally terminated linear polydimethylsiloxane chains has been reported by R.C. Hedden[6] and was used to generate the systems studied in this work.

Experimental Procedures

Materials & synthesis of model polymers

The RTV5370 polysiloxane rubber samples of differing tin content were prepared by adding a known amount of XY-70 catalyst (stannous 2-ethylhexanoate) to 30g of RTV5370 gum (supplied by Rhone Poulenc and containing the curing agent tetrapropyl orthosilicate) and the mixture was vigorously stirred for approx. 15 seconds. 20g of this mixture was added to a 15cm diameter (2 mm deep) mould. The polymer was cured under ambient conditions for 20 minutes and then postcured at 70°C for 16 hours. A selection of RTV5370 polysiloxane rubbers with catalyst concentrations of 4.2, 5,5.8,6.7,10 and 15 wt % were prepared using this method.

The dihydroxy terminated polydimethylsiloxanes used in these investigations were purchased from Fluorochem Ltd. A total of six polymers were obtained having quoted M_n (polystyrene equivalent number average molecular weights) of 400-700, 1500-2000, 4200, 18000, 26000 and 58000 g/mol. Networks were prepared by a hydrosilylation end-linking reaction at room temperature. This involved stirring the dihydroxy terminated polydimethylsiloxanes with the stannous 2-ethylhexanoate catalyst (1 wt%) and the tetraethoxysilane (5 wt %) curing agent. The samples were left to cure overnight under ambient conditions. The soluble fractions of the networks were extracted in toluene to remove residual impurities and to extract out unattached chains.

Characterisation of the model siloxanes

Chemical Analysis

The dihydroxy terminated polydimethylsiloxane gums were analysed using ^{1}H, ^{13}C and ^{29}Si Nuclear Magnetic Resonance (solution NMR). For each polymer, the results confirmed the presence of two different proton environments, namely CH_3 and OH, and the ^{29}Si NMR showed the presence of two silicon environments, namely Si-OH (-11ppm) and O-Si-O (-22ppm). The ^{13}C NMR studies also showed the presence of the methyl groups.

Thermal Analysis

A TA Instruments 2910 Differential Scanning Calorimeter (DSC) was used to assess the thermal characteristics, including phase transitions, within the model polymers over the temperature range -140°C to 100°C.

Thermomechanical Analysis

A TA Instruments 2940 Thermomechanical Analyser (TMA) was used to monitor the linear swell response (with respect to thickness) of the model samples. Liquid toluene was injected into the chamber containing a sample of known thickness. The dimensional changes were monitored over time until equilibrium swell conditions were achieved.

Solvent Uptake Measurements

A known amount of rubber was placed in toluene for 48 hours and then re-weighed to determine the solvent uptake. The crosslink density (expressed as the G-factor) was calculated from the solvent uptake[7].

Characterisation of the RTV5370 polysiloxane rubber

Tin Content

The RTV5370 polysiloxane rubber samples were analysed for tin content by Neutron Activation Analysis (NAA). These measurements were conducted at the NAA facility of Imperial College at Silwood Park. On analysis, the RTV5370 polysiloxane rubbers prepared using 4.2, 5,5.8,6.7,10 and 15 wt % of tin octanoate catalyst, were found to have a tin concentration of 1.1, 1.4, 1.5, 1.9, 2.9 and 3.9 wt % respectively. The tin concentration was also re-determined after extraction in toluene to assess the amount of tin tightly bound to the network.

Soluble Fraction Measurements

Extractable matter measurements were made on the RTV5370 polysiloxane rubber samples. A known amount of rubber was placed in toluene and extracted for 48 hours (ambient conditions). After extraction, the samples were allowed to dry overnight before being re-weighed. The percentage solvent extractable matter was calculated from the change in sample weight.

Differential Scanning Calorimeter

A TA Instruments 2910 Differential Scanning Calorimeter (DSC) was used to assess the phase transitions within the RTV5370 polymers. Sample were heated at 10°C/min.

Thermomechanical Analysis

A TA Instruments 2940 Thermomechanical Analyser (TMA) was used to assess the load-bearing properties of the samples. Experiments were conducted to monitor the stress relaxation characteristics of the RTV5370 polysiloxane rubber samples at 25°C using a constant compressive strain of 10%.

Dynamic Mechanical Thermal Analysis (DMTA)

A polymer Labs DMTA was used to assess the dynamic mechanical properties of the RTV5370 polymers. These measurements were performed by the Department of Chemistry, Physics and Environmental Sciences at the University of Sussex.

Results and Discussion

Model polymers of defined structure

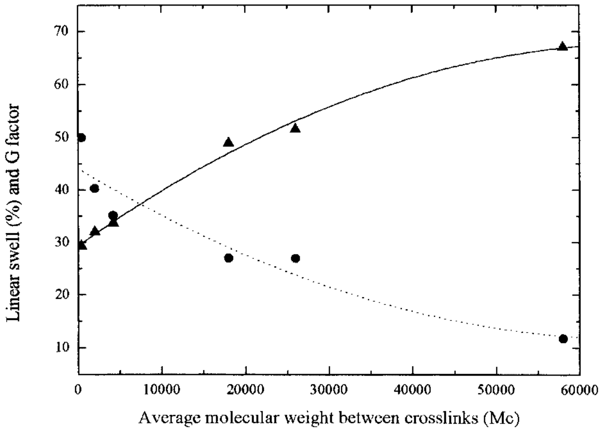

Figure 1: Linear swell (▲) and solvent uptake (G-factor, ●)

Figure 1 shows the variation in linear swell characteristics for toluene uptake with crosslink density. It is evident that the model polymers clearly show differences in network crosslink density with the most highly crosslinked material (Mc, 400 g/mol) showing the lowest linear swell (30% increase in sample thickness) and the highest G-factor value (50%). G-factors are determined from the solvent uptake and are representative of the crosslink density of the rubber as described by Flory[8].

These results demonstrate that the hydrosilylation end-linking method of capping precursor chains of different molecular weights was successful in preparing structures that vary in network crosslink density and which do not suffer significantly from network imperfections (such as unattached chains).

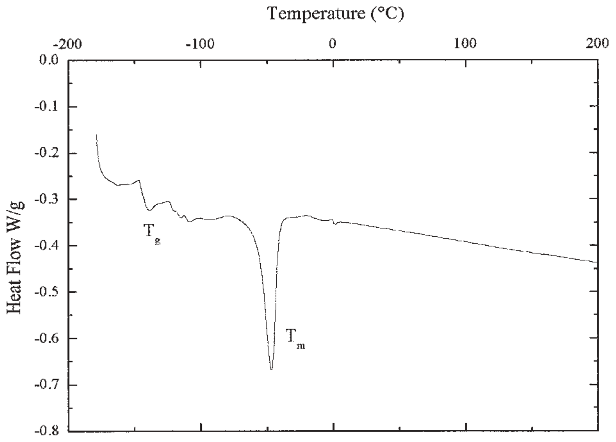

Figure 2: Typical DSC trace of model siloxane (Mc: 26,000 g/mol)

In order to assess the impact of crosslink density on thermal characteristics (in particular thermal transitions) the model polymers were tested using Differential Scanning Calorimeter (DSC). Figure 2 shows a typical DSC trace of a model polymer. The main thermal transitions are a glass transition temperature (T_g) at –120°C and a melting transition (T_m) centred at –45°C. The DSC trace does not give a clear indication of a heat of crystallisation (T_c) presumably because the rate of crystallisation and the cooling rate is such that the crystallites form during the cooling setup of the cycle (and are therefore not recorded by the DSC) with little crystallisation on heating.

Our studies indicate that the network crosslink density can significantly influence the crystallisation characteristics of the polymer, see Figure 3. Interestingly, within experimental error, no significant changes in Tg were observed as the crosslink density was varied.

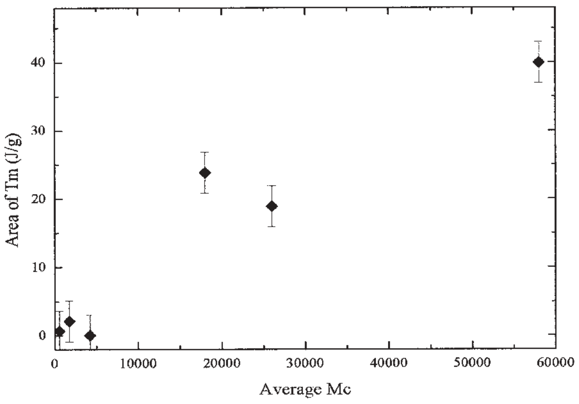

Figure 3: Impact of crosslink density on crystallinity

Crystallisation is a phenomenon strongly dependent on the ability of polymer chains to align/move into required positions and it is presumably more difficult for a polymer with a high crosslink to carryout this process. This effect could be considered similar to the impact of bulky side groups (e.g. phenyl rings) which will also reduce the ability of a polymer to crystallise.

RTV5370 polysiloxane rubber samples of different tin content

To assess the extent of incorporation of the catalyst into the polymer network, toluene extractable matter measurements were made on the RTV5370 polysiloxane rubber samples and the extracted samples re-analysed for tin using NAA. Samples with catalyst concentrations of 5.8 wt% (representing a Tin concentration of 1.5%) and above showed larger toluene soluble fractions (see Figure 4) and a reduction in tin content (see Table 1), suggesting that some unreacted catalyst is being leeched out by the extraction process.

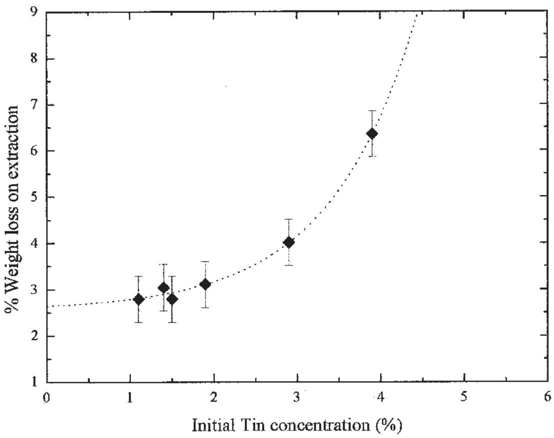

Figure 4: Solvent extractable matter

The % weight loss on extraction correlates with the weight loss expected from the decease in % tin (arising from loss of residual unreacted catalyst) if organic species associated with the catalyst are also taken into account. The presence of additional catalyst does not appear to be causing significant changes to the amount of non-network siloxane species present within the rubber. For those samples containing 10% and 15% XY70 catalyst, a significant amount of tin still remains after solvent extraction suggesting it is tightly bound to the network.

Catalyst Concentration (%)	**4.2**	**5.0**	**5.8**	**6.7**	**10.0**	**15.0**
% Tin*	1.1	1.4	1.5	1.9	2.9	3.9
% Tin after toluene extraction**	1.2	1.4	1.5	1.8	2.4	3.0
change	-0.1	0.0	0.0	0.1	0.5	0.9

Table 1: Tin content (from NAA) of toluene extracted samples (* ± 0.05%, ** ± 0.07%)

Figure 5 shows a typical DSC trace of a RTV5370 polymer. Whilst the overall features are similar to those found for the model polymer (see Figure 2) in this case, the crystallisation melting transition is significantly lower in intensity and there is a large heat of crystallisation (centred at –85°C). The reduced size of the melting peak is presumably because RTV5370 polysiloxane is formulated by the manufacturers to contain phenyl groups to help enhance high temperature stability and reduce crystallinity at low temperatures. The large heat of crystallisation (T_c) may be explained by the rate of crystallisation and the cooling rate being such that the crystallites predominately develop during the heating stage of the cycle with little crystallisation on cooling i.e. rapid cooling 'quenches' the material which maintains its amorphous character even at low temperatures.

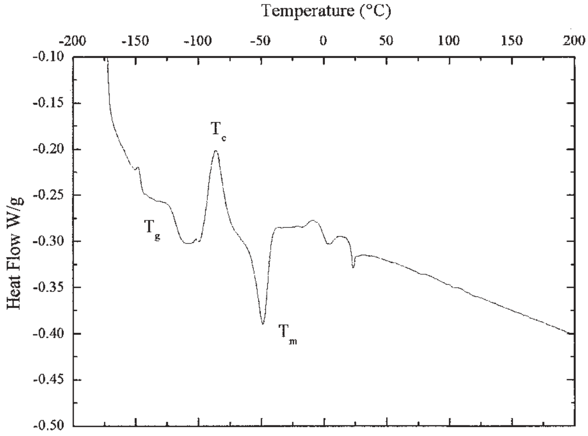

Figure 5: Typical DSC Trace of virgin RTV5370 rubber

Figure 6 shows that increasing the catalyst concentration is clearly detrimental to the crystallisation properties with samples having higher catalyst levels showing a very small or no melting (T_m) transition.

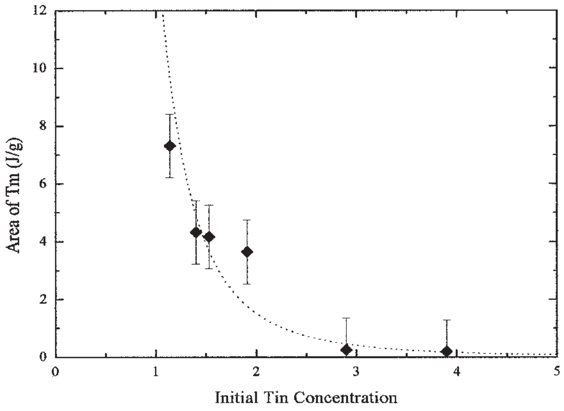

Figure 6: Impact of tin concentration on crystallinity

Evidently, the additional catalyst is reducing the ability of the polymer chains to align sufficiently for crystallisation and comparison with the results for the model siloxanes, suggests this is due to increased crosslinking of the polymer.

To examine whether changes in crosslink density are taking place with increasing catalyst content, the mechanical behaviour of the RTV5370 rubbers was assessed by DMTA. The tan δ plots (see Figure 7), show that increasing the catalyst concentration leads to a material that requires more energy to align the chains for crystallisation (indicative of increased crosslinking) as reflected in a small but measurable shift of the main tan δ peak from –95 to –80°C as the catalyst concentration is increased to 10 wt %. Above this the effect is negligible. The area under the main tan δ peaks also differ indicating differences in the degree of crystallinity. In the corresponding modulus plots (see Figure 8) the RTV5370 rubbers show an increase in E' above Tg followed by a falling modulus. The increase in E' is representative of crystallisation of the rubber, followed by melting. Samples with high tin concentration, in particular the material containing 10 wt % catalyst, show a shift to higher temperature with no further effect beyond this concentration and this observation is consistent with the tan δ data.

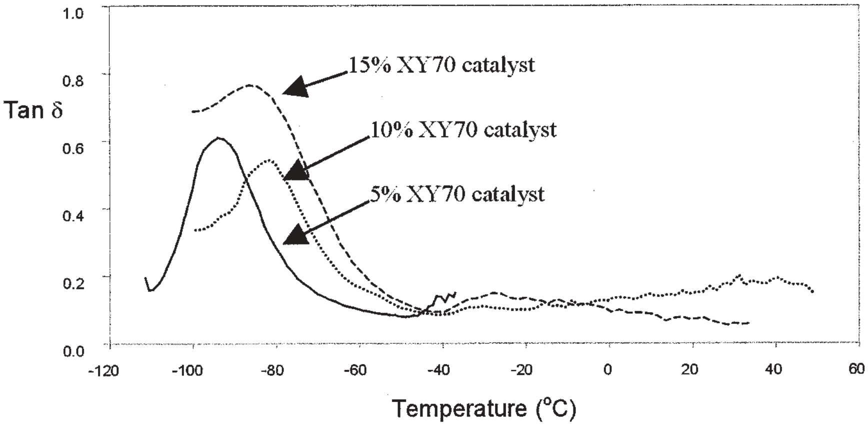

Figure 7: DMTA plot of tan delta (damping)

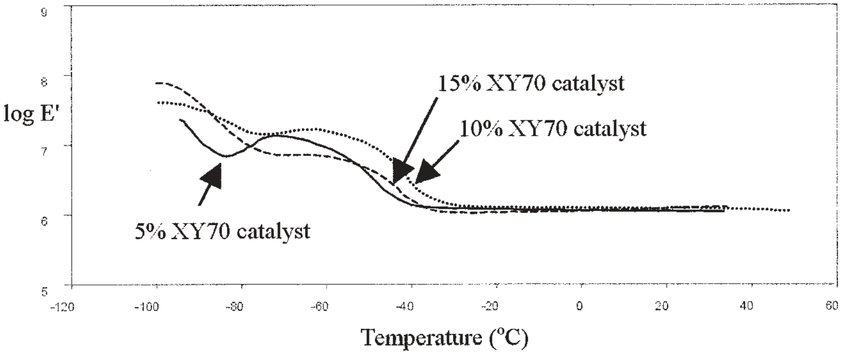

Figure 8: DMTA plot of storage modulus

Comparison of DMTA and DSC results

The DMTA and the DSC results agree in that the main effect of the tin catalyst appears to be to influence the low temperature crystallisation properties of the rubber, presumably by increasing crosslink density. The DMTA data suggests that for samples having double the standard amount of tin, the crystallisation behaviour shifts to higher temperatures (indicating greater energy is required to induce crystallinity as a result of increased crosslinking) and for tin concentrations above this no further change is indicated. The DSC results show that higher catalyst concentrations result in very small or no melting (T_m) transitions. This effect possibly arises from increased crosslinking in the polymer and the reduction in the ability of the polymer chains to align sufficiently for crystallisation.

A possible source of increased crosslinking resulting from increasing the tin concentration is the formation of tin(IV) oxide (SnO_2) from hydrolysis of the catalyst. Such species, having active surface groups (e.g. OH), might increase the effective crosslink density of the polymer[9] by forming hydrogen bonding like interactions. Figure 9 shows an overall increase in the rate of stress relaxation (suggesting a more mobile structure) for those samples having a higher tin concentration. This suggests that any possible increased crosslinking from the tin is weak/unstable in terms of load bearing/retention characteristics at room temperature. Catalyst hydrolysis effects will also generate increased quantities of carboxylic acid within the polymer. Such acidic species will accelerate siloxane exchange reactions and also lead to an increased rate of stress relaxation[10] as the tin concentration is increased.

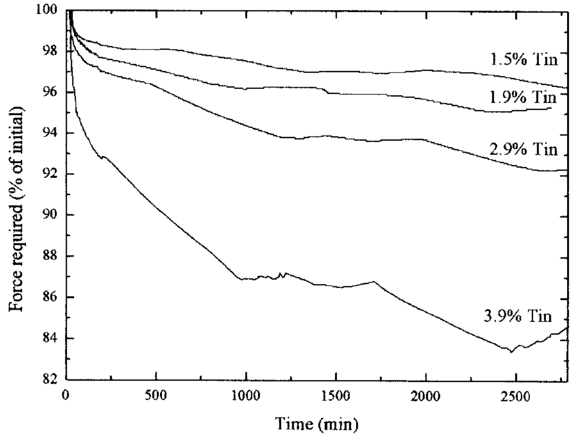

Figure 9: Stress relaxation properties (10% strain and 25°C)

Conclusions

The model siloxanes of different crosslink density have proved a useful tool in developing our understanding of the link between structure and physical/thermal properties. Linear swell, as well as the crystallisation melting transition, was both found to be influenced by changes in crosslink density.

Studies on the effect of tin catalyst concentration in RTV5370 polysiloxane rubbers has shown that the area of the crystalline melting transition, as measured by DSC, decreased with increasing tin concentration. DMTA studies have shown that increasing the catalyst concentration leads to a shift of the tan δ and storage modulus (E') peaks to higher temperatures. It is also found that the storage modulus of the rubbers at room temperature appears to be independent of the tin catalyst concentration. Through correlation with model siloxanes, these results suggests that increasing catalyst concentrations appears to induce additional crosslinking interactions that are stable at low temperatures but not stable at room temperature. The stability of these bonding interactions also appears to be low when placed under load for long periods of time, as evidenced by poorer stress relaxation properties as the tin concentration is increased. A possible source of increased crosslinking, through hydrogen bonding, is the formation of stannic oxide particles from hydrolysis of the catalyst.

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References

[1] J.WEN, J.E. MARK, J.J. FITZGERALD, Macromoleculer reports, A31, 1994, p429.
[2] X.W.HE, J.M.WIDMAIER, J.E. HERZ AND G.C. MEYER, Eur. Polym. J., 24, p1145, 1988.
[3] S.J. CLARSON, ZAIMING WANG AND J.E. MARK, Eur. Polym.J. vol. 26, No. 6, p621, 1990.
[4] F.W. VAN DER WEIJ, Makromol. Chem., 181 (12), 1980, p2541
[5] J.TOYNBEE, Polymer, 35, No. 2, 1994, p438.0
[6] R.C. HEDDEN, H. SAXENA, AND C.COHEN, Macromolecules, 2000, 33, p8676
[7] ZHANJIE TAN, RAIMUND JAEGER, G. JULIUS VANCSO, Polymer, 35, No 15, 1994, p3230
[8] P.J. FLORY, "Principles of Polymer Chemistry", Cornell University Press,
[9] P.G. HARRISON, "The Chemistry of Tin", Blackie, 1989.
[10] M.ZELDIN, J. Polym. Sci. 1983, 21, p1361.