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Siloxane-Urea Segmented Copolymers

2. Investigation of Mechanical Behavior

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SUMMARY

The mechanical behavior of new siloxane-urea segmented copolymers, based on amino terminated poly(dimethylsiloxane) oligomers of about 1000 to 4000 <Mn> and 4,4'-diphenylmethane diisocyanate (MDI), has been investigated. These segmented block copolymers appear to form microphase texture and display mechanical behavior which is in some ways comparable to filled silicone elastomer systems as well as segmented polyurethanes. Preliminary studies of the effect of hard segment content on mechanical properties are also reported. As expected, the stress-strain behavior reflects composition changes.

INTRODUCTION

Silicone elastomers have received wide-spread attention since their first appearance on the market in the mid 1940's. A number of review articles have appeared in the literature (LEWIS 1962, HUNTER 1964,POLMANTEER 1970, BOBEAR 1973,WARRICK et al. 1979) dealing with the technology of silicone elastomers and new developments. The most common or widely used silicone elastomer is principally based on polydimethylsiloxane (PDMS). Such special interest in silicone elastomers emerges because of a combination of properties which are unique in the array of synthetic polymers. These inherent properties of silicone elastomers include - extreme weather and thermal stability due to a strong Si-O bond (POLMANTEER 1981), high flexibility at low temperatures due to low intermolecular forces (POLMANTEER and HUNTER 1959), good release properties, incompatibility with most organic compounds, excellent electrical properties, high surface tension, high permeability to gases, hydrophobicity (LEWIS 1962) and good biocompatibility (NOLL 1968, BRALEY 1973). However, because of its poor mechanical properties, many of its initial potential applications have suffered in terms of performance.

Above its glass transition temperature, PDMS behaves as a viscous liquid unless it is of extremely high molecular weight and/or crosslinked (WARRICK et al. 1955). One of the earlier techniques used to modify the relatively weak crosslinked network of silicone rubber included reinforcement by small particle active filler such as silica (CEKADA 1967, POCKNELL et

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al. 1969,EIRICH 1972). Reinforcement is important to silicones because the unfilled methyl gumstocks are too weak to be of much use (0.35 MPa tensile strength at ambient conditions). Nevertheless, the silicone elastomers have been of considerable theoretical interest because of their close approximation to an ideal model for experimental elastomer investigations (MARK and ANDREDY 1981, ERMAN and FLORY 1978).

A silicone elastomer network is weak because flaws or microcracks encounter little resistance to growth due to the high mobility of the chains at room temperature. In order to achieve high strength, it is imperative that a structual modification be introduced, which can impede the growth of these microcracks. Particulate fillers or plastic domains are effective mechanisms for imparting toughness (SMITH 1974). The unique characteristic properties of silicone elastomers have been studied in many block copolymers. The combination of flexible siloxane block segments such as PDMS with rigid blocks of either high temperature melting crystalline structures or high temperature softening glasses provide copolymers with 'built-in' reinforcement. These block copolymers are of special interest because tailor-made qualities may be incorporated in the macromolecules through a judicious choice of substituents and synthesis procedures (NOSHAY and McGRATH 1977). Utilizing the unique properties of silicone, block copolymers containing PDMS as the soft segment and various thermoplastics such as polystyrene (SAAM 1971), poly(α-methylstyrene) (MORTON 1974), bisphenol - A polycarbonate (VAUGHN 1969), polysulphone (NOSHAY et al. 1971) have been synthesised and studied. These block copolymers range from thermoplastics to thermoplastic elastomers depending on their composition and/or size of segments. Hence, they can be, in favorable cases, fabricated either from the melt or from solution (MATZNER et al. 1977). However,in general, melt processibility can be limited by the excessively high viscosities exhibited by two phase melts (MATZNER and McGRATH 1973).

MATERIALS

The novel siloxane - urea segmented copolymers synthesized by YILGOR et al. (1982) were utilized in this work. Four different oligomers of amino terminated polydimethylsiloxane (PSX), with the molecular weights <Mn> of 1140, 1770, 2420, and 3670 were reacted with MDI to provide urea linkages as has been described (YILGOR et al. 1982). The stoichiometric ratio of [-NCO] to [$-NH_2$] for all samples was 1.0. The segmented copolymer obtained with the 1140 molecular weight PSX and MDI is referred to as PSX-1140-MDI-82, where 82 represents the weight % of siloxane blocks. Similar nomenclature is employed for other samples.

EXPERIMENTAL

Films of the siloxane-urea copolymers were prepared by compression molding the dried material at 170°C and 10,000 psi. After removal from the press, all samples were immediately quenched to room temperature and placed under vacuum until further testing.

Dog-bone specimens were cut from the film for the mechanical testing of the segmented copolymer. Mechanical measurements included stress-strain, stress relaxation, tensile hysteresis, and permanent set behavior. These tests were performed on an Instron Model 1122. All stress-strain and hysteresis measurements were carried out at a strain rate of 200% min $^{-1}$ based on the initial sample length. Stress relaxation experiments were performed by stretching the sample to different elongations at an initial elongation rate of 10,000 % min^{-1}.

Tensile hysteresis experiments were performed by deforming and unloading the dog-bone specimen to increasing strain levels for each successive cycle. The end of each cycle was concluded when the Instron read zero stress. Strain levels ranged from 25 % to 900 %. The percent hysteresis for a given cycle was calculated by the ratio of area bounded by the loading and unloading curve to the area under the loading curve. The area was calculated using a digital planimeter.

Permanent set measurements were carried out in a similar manner. The sample length was measured after each cycle. Each cycle was concluded when the sample showed zero stress. The kinetics of further recovery were also studied over a twenty four hour period at the room temperature of 25°C for the purpose of contrasting this behavior with the instantaneous values.

All experiments were carried out on well-aged (eg. 7 days old) samples.

RESULTS AND DISCUSSION

The engineering stress-strain curves for samples with different PSX molecular weight and hence variable urea segment content are shown in Figure 1. All the curves are shown up to the fracture stress of the sample. The curve for PSX-1140-MDI-82 shows the presence of a yield point, possibly because of non-uniform deformation which is sometimes seen in thermoplastic elastomeric block segmented copolymers. The ultimate elongation varies from 600 % to 900 % depending on the molecular weight of PSX. For the purpose of comparison, curves are also included for two filled as well as an unfilled system of silicone elastomer, reported earlier in the literature (POLMANTEER and LENTZ 1975, LEVIN et al. 1974). The moduli are also reported in Figure 1. On comparing the values of the initial modulus, it is found that they are directly related to hard segment content, as expected.

The tensile strength of 12.00 MPa was obtained for PSX-1140-MDI-82 with an ultimate elongation of 600 %. A value of 13.00 MPa has been reported by POLMANTEER and LENTZ (1975) for a silicone system filled with about 40 % of Me_3SiO_4treated silica particles after 4 hours of heat treatment.

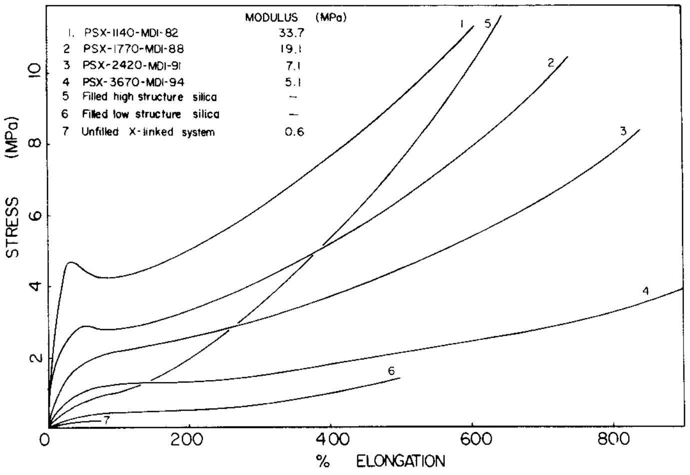

Figure 1. Stress vs. percent elongation behavior for siloxane-urea segmented copolymers as a function of molecular weight at 25°C. Curves 5 and 6 from POLMANTEER and LENTZ (1975) and curve 7 from LEVIN et al. (1974)

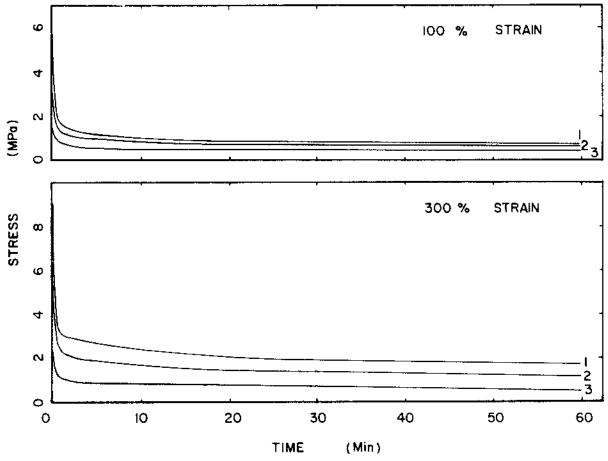

Figure 2. Stress relaxation behavior for (1) PSX-1140-MDI-82 (2) PSX-1170-MDI-88 and (3) PSX-3670-MDI-94 for 100 and 300 % elongations at ambient conditions

The ultimate elongation for this filled system was 645 % (values reported by BOONSTRA et al. (1975) for the same system are considerably lower). For an unfilled but crosslinked system, a value of about 0.30 MPa has been reported with a maximum elongation of 75 % (LEVIN et al. 1974). Considering that PDMS with a molecular weight between 1000 and 4000 is a viscous liquid at room temperature, the segmented block copolymer structure has dramatically changed the properties and behavior of PDMS. Not only are the good elastomeric properties obtained, these segmented systems compare very well with the filled elastomer systems and, importantly are easily thermally processed.

The stress relaxation curves (shown in Figure 2) illustrate that for this copolymer the stress decays rapidly to a near equlibrium value. For all samples this near equilibrium character was reached within two hours, dropping to about 25% of the initial value. This confirms the fact that we are dealing with a psuedo crosslinked system, for the material would have continued flowing rapidly (relaxing) after stretching if this had not been so.

In Figure 3,the hysteresis behavior is shown as a function of elongation. With an increase in the molecular weight of PSX, the % hysteresis decreases. It is worthwhile to notice that for PSX-3670-MDI-94 we have only 6 % hard segment by weight. Inspite of this, the segmented siloxane-urea copolymers show only 53 % hysteresis at 100 % elongation. This compares with some conventional polyether-MDI-BD based polyurethanes, containing 35 % hard segments, which show 30 % hysteresis at 100 % elongation and 40 % at 500 % elongation (ABOUZAHR 1981). Figure 4 illustrates the instantaneous permanent set behavior as a function of elongation. Although the instantaneous permanent set is quite large (especially for PSX-1140-MDI-82), the kinetic behavior shows dramatic differences for longer time intervals between cycles. For example, the permanent set for 100 % elongation had an instantaneous value of 60 %. This value dropped to 13 % after 10 minutes and 6 % after 24 hours. For relatively moderate molecular weight systems (the intrinsic viscosities for these materials lie between 0.2 and 0.8 (YILGOR et al. 1982)), the segmented siloxane-urea copolymers show remarkable recovery.

The results of dynamic mechanical behavior have not been presented here but the experiments run on a TMA device (YILGOR et al. 1982) and dynamic mechanical viscoelastometer (Rheovibron) for these materials clearly show the two phase nature of this system. An indication of partial segment mixing was also seen from the Rheovibron results as the Tg of -110°C for PSX-3670-MDI-94 increases to -99°C for PSX-1140-MDI-82. The transition in E' from glassy to the rubbery region was more gradual for the 1140 molecular weight material when compared to the 3670 molecular weight sample. This may suggest a degree of mixing between the two phases for low molecular weight material, although further work is necessary to confirm or disprove this speculation. The increase in Tg may also be partially due to the restriction of the soft segment ends

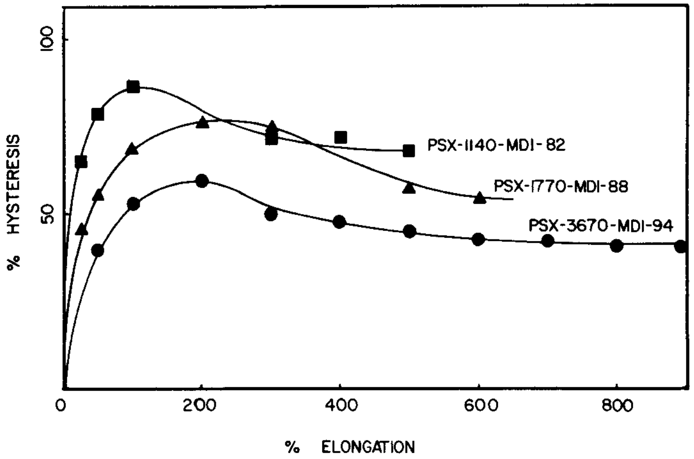

Figure 3. Percent hysteresis vs. percent elongation behavior for siloxane-urea segmented copolymer system

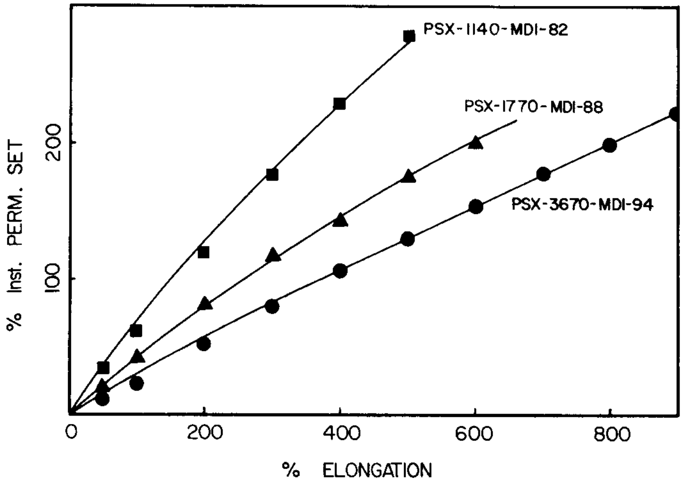

Figure 4. Percent 'Instantaneous' permanent set at different elongations for siloxane-urea segmented copolymer system

caused by the MDI linking.

CONCLUSIONS

The ultimate tensile properties of the different molecular weight samples in Figure 1 have been considered. The samples show no abrupt increase in stress at high elongations. The tensile strength decreases when the molecular weight of polydimethylsiloxane oligomer is increased. This is expected since any increase in molecular weight decreases the hard segment content and hence the hard domains are likely to be smaller and certainly fewer in number. The data presented demonstrates that the properties depend on the molecular weight of the PSX segment and that high strength necessitates a dispersed phase or microphase texture.

The stress-at-break does increase rapidly with the concentration of hard segments. This increase can be attributed primarily to a broadening of the relaxation spectrum, which gives an increased capability for energy dissipation (SMITH 1974). However, the ultimate elongation decreases with an increase in hard segment content, since the siloxane segments become smaller.

A two phase domain formation is supported by results from TMA (YILGOR et al. 1982) and dynamic mechanical results. These MDI hard segment domains thus act as physical crosslinks in the rubbery phase and prevent it from flowing. The hard segment domains also clearly serve as reinforcing filler materials.

The segmented siloxane-urea copolymers show interesting recovery behavior. Even for a small amount of hard segments, they display hysteresis behavior which is comparable to other segmented copolymer systems of higher hard segment content.

Regarding future studies, the effect of chain extenders is being studied. The structure-property relationships for siloxane-urea segmented copolymers prepared from dimethyl diphenylsiloxane oligomer are also being investigated and will be reported in due time.

ACKNOWLEDGMENTS

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