

LIQUID SYSTEMS FOR RUBBER PRODUCTS INCLUDING TYRES

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ABSTRACT

Certain urethane systems have been found to be suitable for application in products usually made of black reinforced rubber with cord reinforcement. The products referred to are generally designed to operate under conditions which include dynamic load. Therefore, they must be able to sustain repeated flexing over a range of temperatures without growth or permanent deformation. Specific urethane systems suitable for such applications are found to be urea-urethanes, having a minimum of biuret structure. Surprisingly, these urea-urethanes are largely devoid of covalent crosslinks, and depend largely on hard segment or domain reinforcement for their unusual properties.

The fabrication of rubber products directly from liquid rubbers of low molecular weight has the advantage that the energy expended in processing and compounding rubbers of high molecular weight is eliminated. Furthermore, capital costs of heavy duty processing equipment such as Banbury mixers, mills, extruders and calenders may be avoided.

The urethane liquid systems originally discovered by Otto Bayer have found only limited application in the years subsequent to that discovery—in part because of some inherently inferior properties such as lack of water resistance—in part because attempts were made to substitute the urethane for conventional rubber in conventional rubber products, processed, compounded and reinforced with black and fabric just as conventional rubber items always have been. Urethanes didn't fit conventional rubber products any more than—as in the story of Cinderella—the glass slipper fitted the ugly stepsister. To make urethanes 'fit', you need a Cinderella process and a Cinderella product and you need to hang out a sign saying, 'No Ugly Stepsisters Need Apply'.

Specifically, the self-reinforcing nature of urethanes was largely ignored in early applications of these novel rubbers. Attempts to use black and fabric reinforcement resulted in performance inferior both to those of conventional rubber products and to unreinforced urethanes. Furthermore, it was assumed that the covalent crosslinks necessary to conventional rubber vulcanizates were also necessary to serviceable urethane rubber products. As a result, it became general practice to combine isocyanate-terminated prepolymers with water, difunctional alcohols or amines in proportions which left an

excess of isocyanate groups to form biuret or allophanate crosslinks. Muller¹ stated in 1957 that, 'In the previously-described procedure the quantitative ratios have been selected in such a way that, after reaction of the isocyanate-groups containing polyester with the cross-linking agent, i.e. after the chain-lengthening reaction, free isocyanate groups for the cross-linking reaction were still left. In other words, a lower quantity of cross-linking agent was used than would have corresponded to the NCO groups left. This makes it possible that the chain-lengthening and cross-linking reactions proceed continuously without interruption. This fulfils the conditions which are necessary for liquid-stage processing, for example, by casting method.'

Athey² in 1959 said that large urethane molecules, 'must be crosslinked to develop elastic properties' and that in curing isocyanate-terminated polymers with diamines slightly less than equivalent amounts of diamine should be added to obtain the best crosslinked vulcanizates. What has not been recognized before the work in the Firestone Laboratories is that urethanes made from isocyanate-terminated prepolymers by reaction with diamines, in equivalent or *slightly greater* than equivalent NH_2/NCO ratio, are stable, resilient rubbers *with low creep characteristics!* This, plus the high modulus characteristics of urethanes, suggest that their use in high performance rubber products without black or fabric reinforcement is not only possible but has outstanding possibilities. Material costs of such products may exceed those of conventional composites, but the reduced capital, labour and energy usage will often outweigh increased material costs.

We are unaware of any previous studies of the polyureaurethanes on creep or modulus at lower strains (up to 20 per cent elongation) and the effect of formulation variables on these properties. In our work we have used MOCA as curative for a prepolymer prepared from polytetramethylene ether glycols (PTMEG) and tolylene di-isocyanate (TDI). Some of the prepolymers were obtained commercially and some were prepared in the laboratory in order to obtain the rather wide variations in NCO content needed for the study.

The stress-strain curves shown in *Figure 1* illustrate the very high modulus at the lower strains obtained from MOCA-cured PTMEG prepolymers compared to a commercial tread rubber. The very large areas under the stress-strain curves even at 212 °F (100 °C) should be noted particularly. Also, it should be noted that the moduli at lower strains (e.g. at five per cent elongation) are essentially identical at 73 °F and 212 °F (22 and 100 °C).

The properties over a temperature range are shown in the plot of $\log(\text{stress})$ at high strains versus the reciprocal of the absolute temperature (T^{-1}) for the temperature range of 73–300 °F (22–148 °C) shown in *Figure 2*. The non-linearity of these graphs is apparent with a small change in slope appearing between 220 and 250 °F (104 and 120 °C). No transition has been observed by differential thermal analysis (DTA) or differential scanning calorimetry (DSC) to explain this change in slope. However, the appearance of the change in slope should not obscure the fact that the tensile strength at 300 °F is nearly 1 500 p.s.i. with a 550 per cent elongation.

Of even greater significance are the data obtained over a temperature range for stress at low strains. In *Figure 3* it can be seen that at strains up to 20 per cent there is an almost negligible effect of temperature up to 250 °F (120 °C) or perhaps even to 300 °F (148 °C). These data suggest that a urethane

LIQUID SYSTEMS FOR RUBBER PRODUCTS INCLUDING TYRES

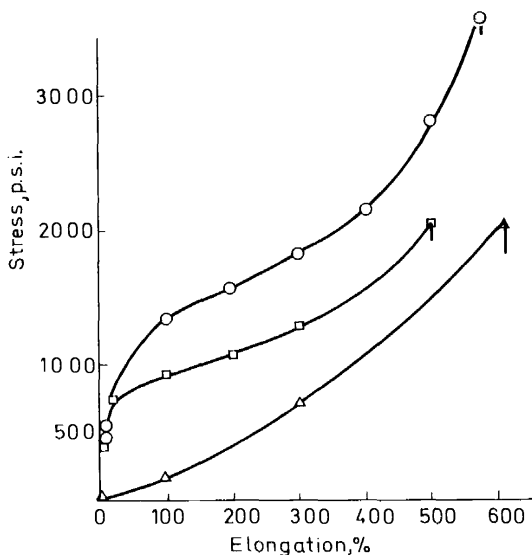


Figure 1. Polyurea-urethanes versus conventional tread rubber. Formulation: PTMEG prepolymer (6.4% NCO), 20 DOP, MOCA (NH₂/NCO 1.025). ○ Polyurea-urethane tested 73°F; □ polyurea-urethane tested 212°F; △ Conventional tread rubber at 73°F.

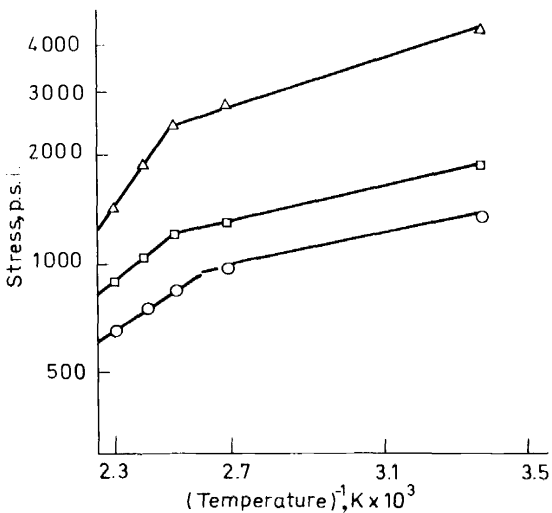


Figure 2. Stress at high strains versus T^{-1} . Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, MOCA (NH₂/NCO 1.025). ○ 100% elongation, □ 300% elongation, △ break.

product could be designed which would maintain its integrity and resist significant growth over a wide range of service temperature.

The level of low-strain modulus is also important for any urethane product designed to flex dynamically under load. The literature indicates that modulus is decreased as the NCO content of the prepolymer is decreased. Since both the spacing between urea segments and their concentration are simultaneously changed by a change in prepolymer NCO content, it became desirable to attempt to isolate these variables in order to determine the effect of each. Both the addition of plasticizers and of free TDI to already formed prepolymers were used to control the NCO content of the total mixture.

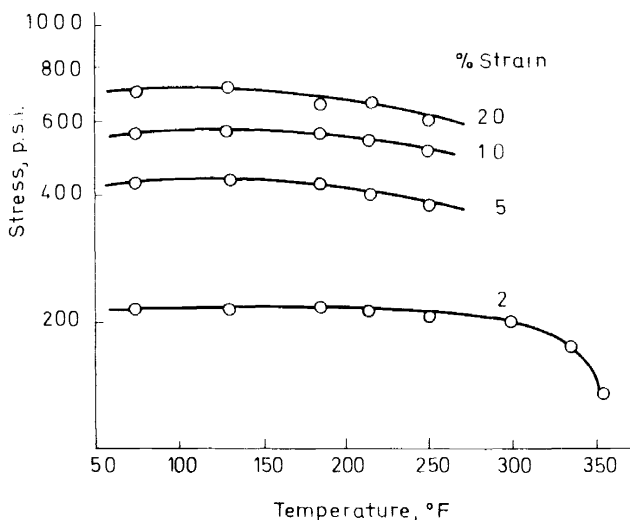


Figure 3. Stress at low strains versus temperature. Formulations: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, MOCA (NH_2/NCO 1.025).

The solid line in Figure 4 shows the change in five per cent modulus (stress at five per cent elongation) with NCO content in systems containing only prepolymer and MOCA. The circles represent formulations containing dioctyl phthalate plasticizer (DOP) in which the percent NCO is calculated on the total weight of plasticizer and prepolymer. The squares are for those formulations which contain both added TDI and plasticizer. It is obvious that the level of modulus is determined almost completely by the total percentage of NCO.

Table 1 illustrates that even large amounts of plasticizer have little effect on modulus and tear strength provided the NCO content is kept constant. Ultimate tensile strength at room temperature is reduced at the very high levels of plasticizer but even this effect nearly disappears at 212°F (100°C). It should be pointed out that formulations with over 40 parts per hundred of DOP result in oily surfaces that make such compositions unusable.

The stress-strain curves in Figure 5 show the results of different ways of formulating to 5.3 per cent NCO. At the lower levels of TDI the curves are

LIQUID SYSTEMS FOR RUBBER PRODUCTS INCLUDING TYRES

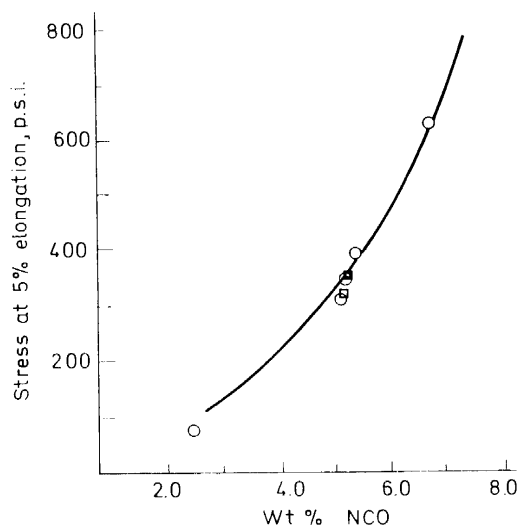


Figure 4. Stress at 5% elongation versus NCO content MOCA cured NH_2/NCO 1.025.
 -- Unplasticized, \circ plasticized, \square plasticized + free TDI.

virtually the same but at the highest level a considerable drop in modulus is noted. It is believed that this drop is actually the result of increasing the spacing between urea segments although it could be the result of heterogeneity resulting from the very rapid reaction of MOCA with free TDI. However, we conclude that the primary factor governing the physical properties of MOCA-cured PTMEG prepolymers is the total NCO content which of course governs the concentration of polyurea in the final formulation.

Without question the most important variable in formulating polyurea-urethanes is that of the ratio of amine to isocyanate (NH_2/NCO). Figures

Table 1. Plasticizers in MOCA-cured polyurethane

| % NCO of prepolymer ^a | 5.81 | 5.31 | 4.77 | 3.46 |
|----------------------------------|------|------|------|------|
| Pt DOP/100 prepolymer | 66 | 52 | 36.5 | 0 |
| Final % NCO | 3.50 | 3.50 | 3.50 | 3.46 |
| at 73° F (22° C) | | | | |
| 300% Modulus | 850 | 800 | 825 | 825 |
| Tensile | 2440 | 2520 | 3865 | 3690 |
| Elongation | 635 | 710 | 650 | 610 |
| Crescent tear | 222 | 216 | 242 | 219 |
| at 212° F (100° C) | | | | |
| 300% Modulus | 640 | 665 | 690 | 730 |
| Tensile | 1425 | 1740 | 1790 | 1340 |
| Elongation | 600 | 850 | 670 | 510 |
| Crescent tear | 114 | 137 | 143 | 129 |

^a All prepolymers prepared from reaction of PTMEG with toluene-2,4-di-isocyanate.

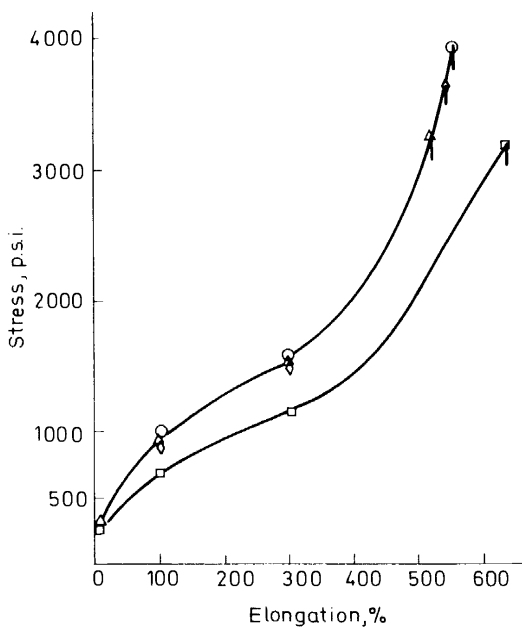


Figure 5. Stress versus elongation at constant NCO content of 5.3% MOCA cured NH_2/NCO 1.025. \circ 20 DOP + 0 TDI, \triangle 40 DOP + 2.5 TDI, \diamond 40 DOP + 7.6 TDI, \square 40 DOP + 9.0 TDI.

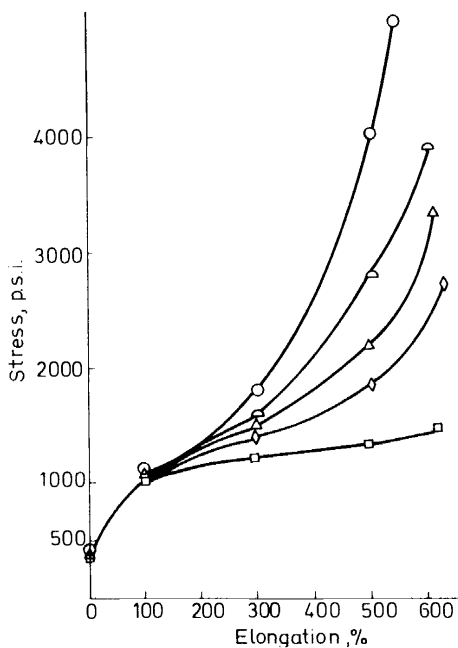


Figure 6. Stress versus strain at varying stoichiometry. Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, variable MOCA. \circ NH_2/NCO 0.95, \circ NH_2/NCO 1.00, \triangle NH_2/NCO 1.025, \diamond NH_2/NCO 1.05, \square NH_2/NCO 1.10.

6-12 illustrate its effect on many of the properties we consider critical. All data were obtained on a PTMEG prepolymer containing 6.4 per cent NCO, plasticized with 20 parts of DOP and cured with MOCA.

Figure 6 shows the stress-strain curves at 73 °F (22 °C) as the NH_2/NCO ratio is varied from 0.95 to 1.10. The principle feature of this series is that the curves are virtually superimposable up to 100 per cent elongation, but spread out considerably at the higher strains. Perhaps the most significant conclusion to be made from these data is that at strains likely to be encountered in dynamic service, stress is unaffected by NH_2/NCO ratio.

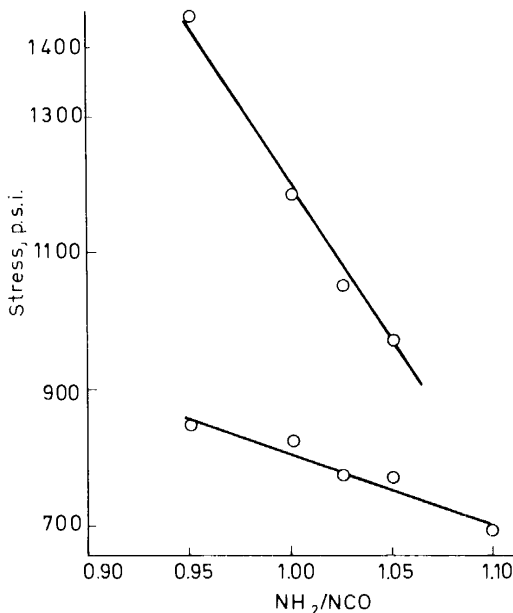


Figure 7. Modulus versus stoichiometry at 212 °F. Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, variable MOCA. Above: 300% elongation; below: 100% elongation.

The same general effect is observed as the test temperature is increased to 212 °F (100 °C) as shown on Figure 7. The 100 per cent modulus decreases only slightly while the 300 per cent modulus drops significantly as the ratio is increased. These effects have been recorded previously in the literature and are not surprising in view of the decreased crosslinking and molecular weight expected as the NH_2/NCO ratio increases.

The effect of NH_2/NCO ratio on tear resistance is shown on Figure 8. It can be seen that at 73 °F (22 °C) a small increase is observed as the ratio increases but at 212 °F (100 °C) a definite maximum is observed between ratios of about 0.98 and 1.08.

Similar maxima between about 0.98 and 1.08 are found with the two different tests for flex fatigue shown on Figure 9. Even though the conditions for the two tests are substantially different, the maxima occur at nearly the same ratios. The effect of NH_2/NCO ratio is very pronounced especially in

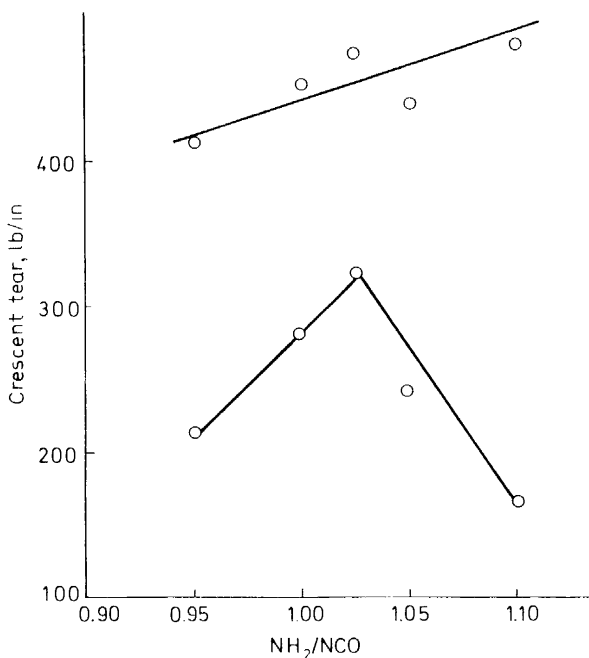


Figure 8. Crescent tear versus stoichiometry. Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, variable MOCA. Above: 73 °F; below: 212 °F.

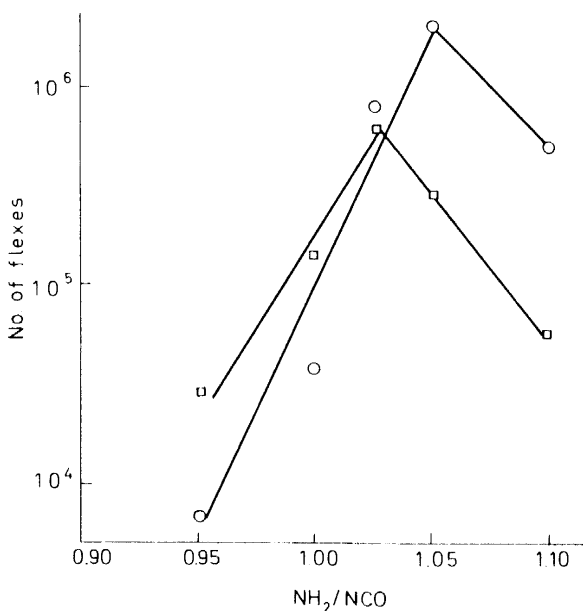


Figure 9. Flex life versus stoichiometry. Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, variable MOCA. ○ de Mattia 176 °F, □ Texus 73 °F.

the DeMattia test where there is a difference in flex life of 2.5 orders of magnitude between the NH_2/NCO ratios of about 0.98 and 1.08.

The most surprising results of the NH_2/NCO ratio are shown in stress-relaxation studies. We are indebted to Dr A. Y. C. Lou of our laboratories for this study which will be presented in detail in a later publication.

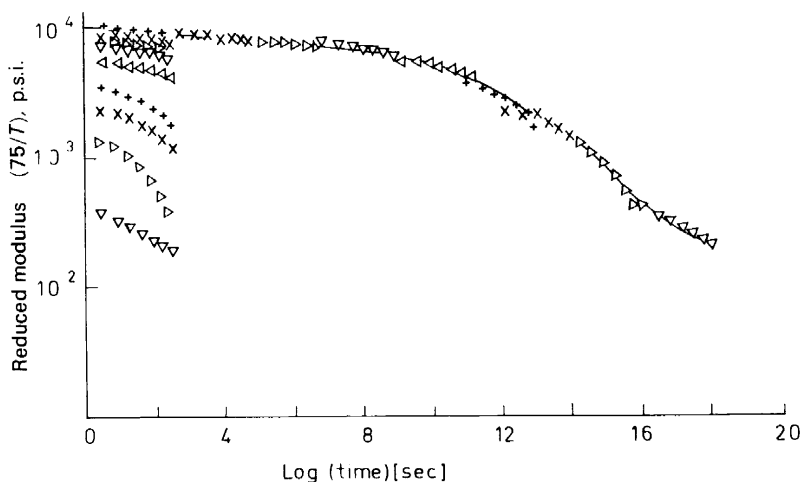


Figure 10. Typical master relaxation modulus curve. Temperatures ($T^{\circ}\text{F}$): +75, \times 185, \triangleright 250, \square 300, \triangleleft 335, \times 370, \triangleright 390, ∇ 400.

The decay of stress with time for relatively short times over a wide range of temperatures was measured. By applying time-temperature superposition principles a master curve of relaxation modulus versus time was obtained. One of these is shown on Figure 10. It is apparent from examination of this curve that after a relaxation modulus of 5000 p.s.i. is reached the decay becomes very rapid. Curves at other stoichiometries showed similar behaviour. Accordingly, the time to reach a modulus of 5000 p.s.i. is plotted against the NH_2/NCO ratio in Figure 11. Again a very sharp optimization is noted at ratios between 1.00 and 1.05. The time for such decay is 539 years at the peak. These results are directly contrary to what one would expect from previously published compression set data. For urethane products designed to serve under dynamic load over a range of temperatures and to resist service growth or long-term creep under these conditions, a NH_2/NCO ratio of about 0.98 to 1.08 is optimum rather than a lower ratio.

One other interesting and perhaps significant effect of stoichiometry variation is that of crosslink density. We have measured apparent crosslink density by swelling measurements in two different solvents. The results are shown on Figure 12. The data from tetrahydrofuran (THF) which is known to be a good destroyer of hydrogen bonds show the expected decrease in apparent crosslink density as the NH_2/NCO ratio increases. Although we suspect that even this solvent does not destroy the domain structure of the polymer completely, the values probably approximate the actual chemical crosslinks in the system. The upper curve shows the results when similar

measurements are made with chloroform (CHCl_3), which should have very little effect on the polyurea domains and should give the apparent crosslink density arising from a combination of chemical and domain type crosslinks. These results suggest that improvement in the structure and efficiency of the domains is more critical to properties required for dynamic serviceability under load than is chemical crosslinking. In fact, chemical crosslinking can be detrimental for urethane rubbers formulated to replace conventional rubbers reinforced with fabric and black in products designed for dynamic service under load.

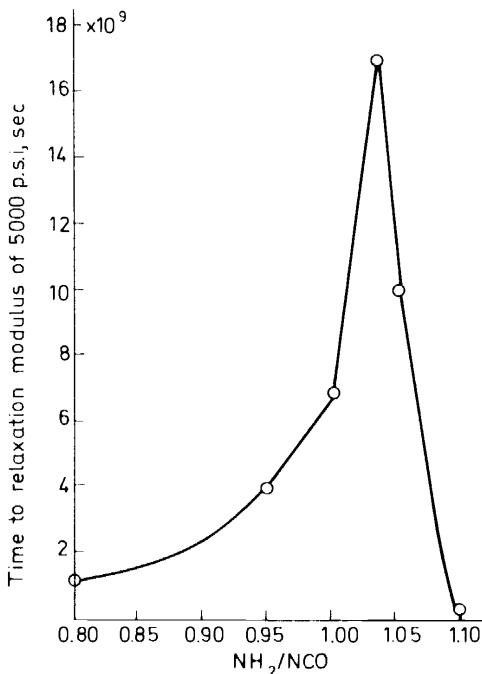


Figure 11. Relaxation time versus stoichiometry. Formulation: 100 PTMEG prepolymer (6.4% NCO), 20 DOP, variable MOCA.

The urea-urethanes discussed in this paper so far are suitable for applications requiring high modulus at low strains, resistance to creep and dynamic strain over a wide range of temperatures. For such applications, conventional rubbers, as has been said, require not only black but fabric reinforcement. However, high performance urea-urethanes are not serviceable under conditions where high temperatures and wear result from severe abrasive action, and black reinforcement of urea-urethanes in no way improves performance under this condition.

Of interest is the fact that various functionally terminated liquid polymers based on butadiene have become available, and that at least one of these is

LIQUID SYSTEMS FOR RUBBER PRODUCTS INCLUDING TYRES

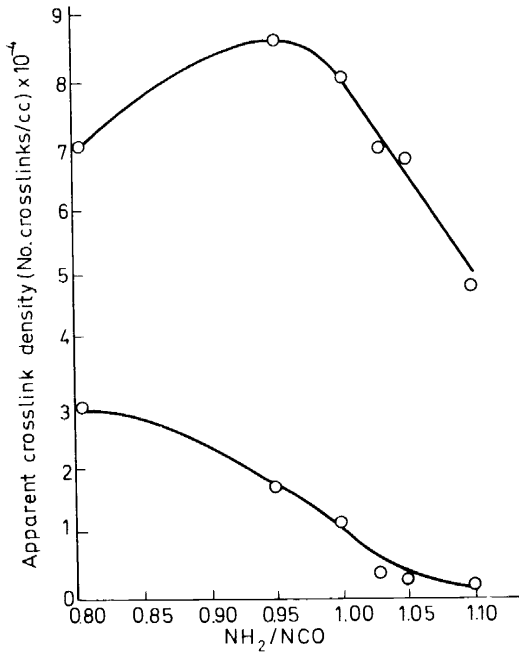


Figure 12. Apparent crosslink density versus stoichiometry. Above: CHCl₃; below: THF.

definitely reinforceable with carbon black as shown by data in Table 2, and therefore has some potential for applications in many, if not all, of the areas where conventional rubber is used, including those where severe abrasive action is experienced. At the same time these materials may be processed (e.g. injection moulded) before or concomitantly with chain extension to a high molecular weight and cross-linking to a three-dimensional, stable network.

Table 2. Liquid butadiene polymers

| Polymer feature | Liquid ^a gum | Liquid ^b black | Conventional tread stock |
|----------------------|----------------------------|------------------------------|-----------------------------|
| 73 °F (22 °C) | | | |
| 300% Modulus, p.s.i. | | 1225 | 1150 |
| Tensile, p.s.i. | 160 | 2225 | 2900 |
| Elongation, % | 230 | 495 | 560 |
| 212 °F (100 °C) | | | |
| Tensile, p.s.i. | 70 | 1100 | 1180 |
| Elongation, % | 80 | 310 | 385 |
| Ring tear, lb/in | 0 | 224 | 312 |

^a 100 Arco CS-15 (0.62 meq OH/g), 0.02 DBTL, 5.95 TDI.

^b 100 Arco CS-15 (0.62 meq OH/g), 0.05 DBTL, 5.95 TDI, 50 dry ISAF black, 15 Shell Durex 916 oil, 1.0 Ethyl 702 Antioxidant.

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