Elastomeric behaviour of crosslinked poly(aryl ether ketone)s at elevated temperatures

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A new approach to thermally stable elastomers for use between temperatures of 180°C and 275°C has been developed. Wholly aromatic poly(aryl ether ketone)s of various molecular weights have been synthesized with maleimide end groups. These structures have glass transition temperatures (T_gs) in the 150°C range, and when thermally crosslinked, they exhibited elastomeric characteristics $\sim$30–50°C above their T_gs ($\sim$200°C). The moduli of the networks at 200°C were comparable to those of unreinforced poly(dimethylsiloxane) elastomers (1–2 MPa) and the elongations ranged from 200 to 300%. The poly(aryl ether ketone) elastomers showed exceptional thermal stability with little weight loss up to 490°C. The results from the chemorheology and stress relaxation measurements are discussed and compared to poly(dimethylsiloxane) networks.

(Keywords: poly(aryl ether ketone): thermal stability; elastomeric behaviour)

Advances in the automotive, petroleum, electrical, electrophotographic and other industries have required the use of elastomers which will operate continuously at elevated temperatures (⩾200°C) and in environments which include fuels, lubricants and chemicals. Although the material requirements for these applications vary, generally these elastomers must show exceptional thermal oxidative stability, solvent resistance and retention of mechanical properties over extended periods of time. The organosiloxane-based networks are the most widely used due to their availability, ease of processing (liquid injection moulding) and good thermal stability. However, these systems have an upper use temperature of $\sim$175°C. Alternatively, perfluoroalkyl-based elastomers such as Viton®, Kal-res® and Fluorel® have the required thermal stability and solvent resistance to operate continuously at temperatures up to 250°C in harsh environments. However, drawbacks to these systems include processability, vulcanization (network formation), expense, adhesion and filling which sharply limit their utility in many applications.

A new approach in the design of thermally stable elastomers has been investigated, in which thermally stable polymer chains were designed with low glass transition temperatures (T_gs, $\sim$150°C) and then crosslinked. In this way, elastomeric systems for use at temperatures of 150–350°C could be obtained to fulfil a goal long sought by polymer scientists. For our initial experiments we used poly(aryl ether ketone)s since they have T_gs between 145°C and 165°C, are amenable towards melt processing, show exceptional thermal stability and are easily prepared and functionalized. Bis(amino) aryl ether ketone oligomers were synthesized by a nucleophilic aromatic substitution polymerization according to a published procedure[1] (*Scheme 1*). Three oligomers were prepared with molecular weights ranging from $\sim$5000 to 10 000 g mol^{-1}, and the characteristics of these oligomers (**1a–c**) are shown in *Table 1*. These oligomers were subsequently reacted with maleic anhydride to give the reactive maleimide end groups (**2a–c**, *Scheme 2*). The oligomers were then crosslinked through a free radical, thermally induced reaction of the maleimide end groups to afford thermally stable networks (**3a–c**) with T_gs of $\sim$160°C (*Table 1*).

The modulus–temperature behaviour for networks **3a–c** is shown in *Figure 1*. The moduli at temperatures below 150°C are high and typical of an engineering thermoplastic. At the T_g the moduli drop two to three

Table 1 Characteristics of functionalized aryl ether ketone oligomers

Sample	$\langle M_N \rangle$ (g mol^{-1}) Theory	$\langle M_N \rangle$ (g mol^{-1}) Experimental	$[\eta]^{CHCl_3}_{25^\circ C}$ (dl g^{-1})	T_g (°C)
1a	5000	5000	0.33	151
1b	7500	7500	0.42	153
1c	10 000	10 000	0.59	159
3a				175
3b				–
3c				168

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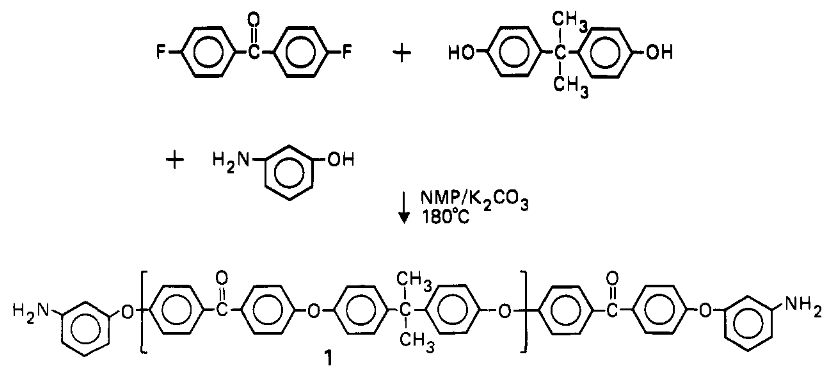
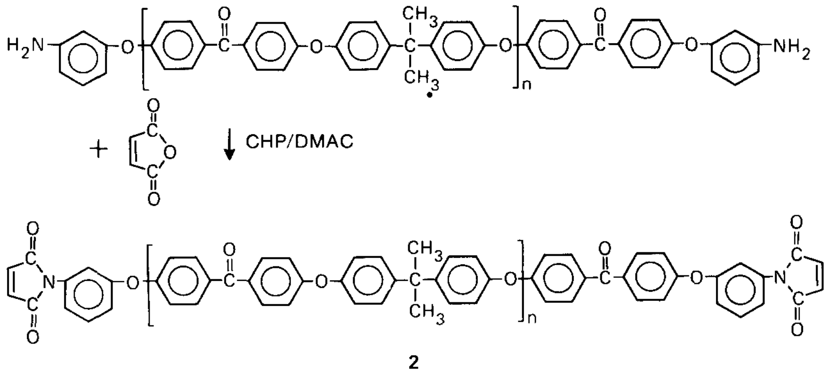


Scheme 1



Scheme 2

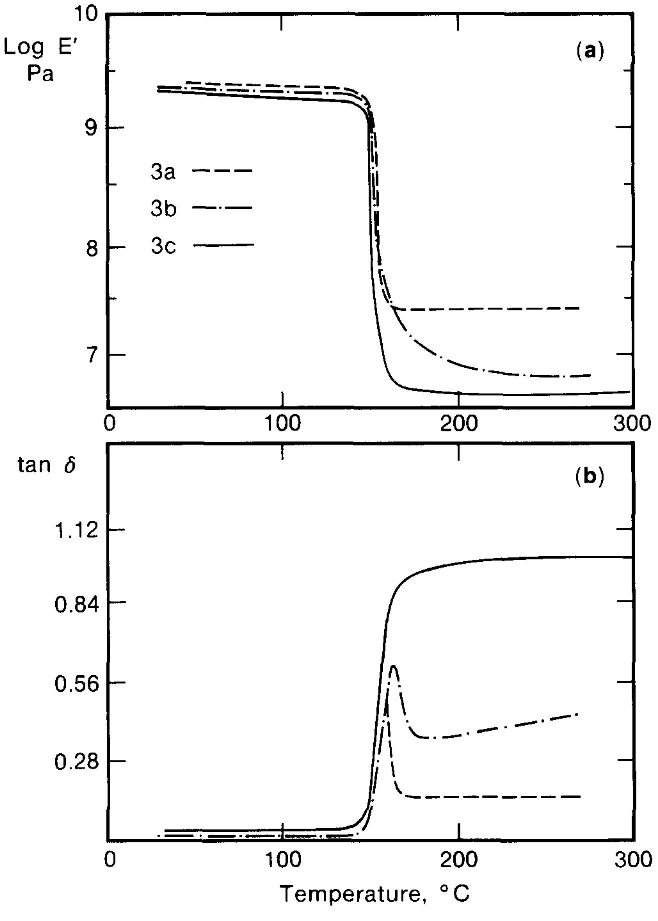


Figure 1 Dynamic mechanical behaviour of **3a** (– – –), **3b** (— ·) and **3c** (——): (a) log*E'* *versus* temperature; (b) tan δ *versus* temperature

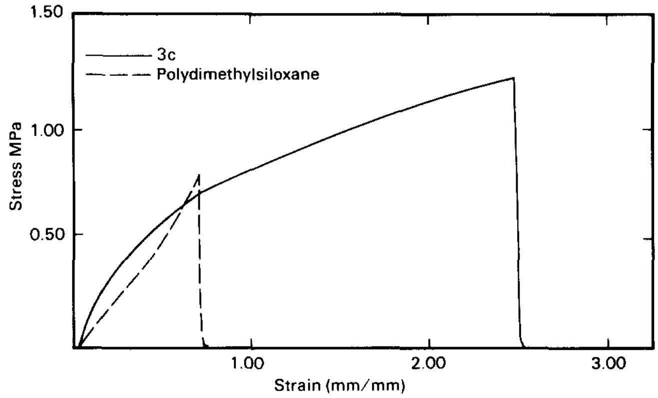


Figure 2 Stress–strain curves for **3c** (——) and PDMS (– – –)

orders of magnitude directly into the rubbery regime and level off to high temperatures. The modulus drop was more pronounced for the networks comprised of the higher molecular weight oligomers. This was not unexpected since these elastomers have a lower crosslink density. An extended leathery region was not observed for any of the networks investigated, indicative of a uniform crosslink density.

The elastomeric properties of the poly(aryl ether ketone)s at high temperatures were exceptional. *Figure 2* shows the stress–strain curves at 200°C of the poly(aryl ether ketone) network (**3c**) and a poly(dimethylsiloxane) (PDMS) network, respectively, for the purpose of comparison. Although the PDMS in *Figure 2* (Sylgard 182, Dow Corning) is a deliberately selected material of extra toughness, the network of poly(aryl ether ketone)

Table 2 Summary of mechanical properties

Sample	Modulus (MPa)	Stress at break (MPa)	Elongation to break (%)	Hysteresis[a]
3c	2.40	1.34	205	9–14 (20) 13–16 (100)
3c filled with 40 wt% ZnO	2.35	1.50	180	13 (20) 8–13 (40) 12–14 (150)
Sylgard 182 (PDMS)	1.01	0.49	60	14–18 (50)

[a]Applied strain values in parentheses

demonstrates a far more superior mechanical behaviour at the elevated temperature than that of the PDMS in terms of strength, toughness and modulus. The crosslinked poly(aryl ether ketone)s can be stretched up to 250% elongation, compared with 75% for PDMS, while the modulus decreases significantly from 1.82 to 0.27 MPa after passing the 'yielding regime' from 0.35 to 0.75 strain approximately (*Table 2*). In contrast to this, the PDMS undergoes a noticeable strain hardening at as early as 50% elongation, a characteristic not desirable for compliant engineering rubbers. The toughness, calculated from the area under the stress–strain curve, of the poly(aryl ether ketone) network is roughly seven times that of the tough PDMS. Since the T_g of **3c** is nearly 250°C higher than that of the siloxane elastomer, the chain mobility at 200°C is lower resulting in an increased relaxation rate, and the improved toughness probably resulted from an increase in the viscoelastic response or internal viscosity[2–5]. Evidence for this effect can be seen in the dynamic mechanical spectra where the tan δ of the samples above T_g is high, indicative of a tough elastomer.

Although the crosslinked poly(aryl ether ketone)s can be stretched to high elongations, the strains recover as the stress is released. Mechanical hysteresis was characterized by measuring the residual strains, ε_r, at zero stress in the materials when the applied deformation was released at the same crosshead velocity of 2.54 cm min^{-1}. The applied strain, ε_a, was selected at 20 and 100% elongation, just before and after the 'yielding regime'. It was found that the hysteresis, $\varepsilon_r/\varepsilon_a$, is practically constant before and after the 'yielding', and is comparable to, if not slightly less than, that of the PDMS (*Table 2*). The low hysteresis also suggests that the crosslinked poly(aryl ether ketone)s are amorphous even at high temperatures and large deformations as expected.

When a large portion of filler was incorporated into the poly(aryl ether ketone) networks, the exceptional mechanical behaviour was still retained. *Table 2* also shows the results of the stress–strain data of **3c** filled with 40 wt% ZnO particles. The filled material still possesses high elongation to break, low modulus and low hysteresis. A similar strain softening was also observed after the mild 'yielding' which seems to take place at a lower strain compared to that of the unfilled resins. Prior to final rupture, however, strain hardening was observed. The decrease in 'yield strain' and the final strain hardening probably are due to the strain amplification effect from the rigid ZnO fillers. All these data indicate that the poly(aryl ether ketone) networks behave as soft, compliant and tough elastomers at high temperatures.

Based on t.g.a. (*Figure 3*) the thermal stability of the aryl ether ketone networks was excellent compared to a PDMS network. In fact, the onset of weight loss occurred at temperatures in excess of 490°C. Isothermal ageing at 250 and 300°C showed weight losses of 0.01 and 0.20 wt% h^{-1}, respectively, clearly demonstrating the exceptional thermal stability.

In addition to t.g.a. experiments, the thermal stability of the poly(aryl ether ketone) networks was further analysed by chemorheology at 200°C. The chemorheology results for **3c** and the same PDMS control (Sylgard 182, Dow Corning) are shown in *Figures 4a* and *b*. The normalized load is plotted as a function of log(time) for both an intermittent (*Figure 4a*) and continuous (*Figure 4b*) stress relaxation using a constant 5% elongation. The continuous stress relaxation data

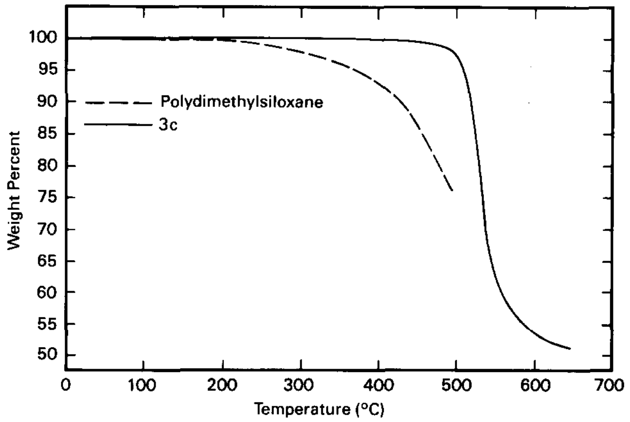


Figure 3 T.g.a. thermograms for **3c** (——) and PDMS (– – –)

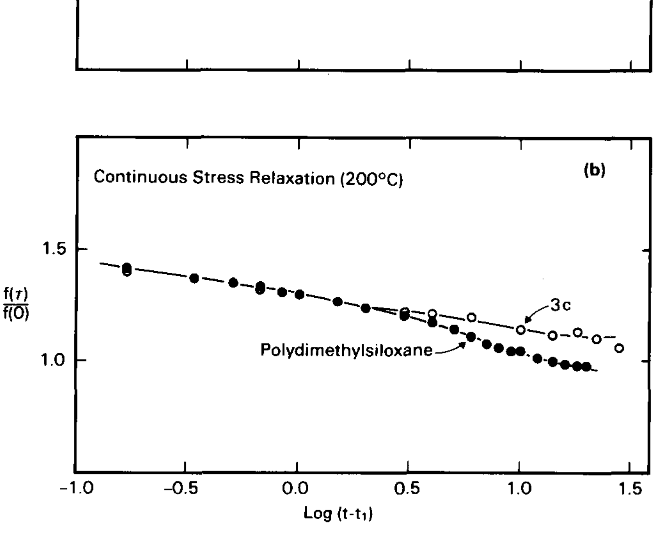


Figure 4 Chemorheology results for **3c** (○) and PDMS (●): (a) intermittent and (b) continuous stress relaxation at 200°C

give the chain scission as a function of time at high temperatures. A basic assumption employed in chemorheology, however, is that the chains in the sample are extremely mobile at the test temperatures such that they attain their equilibrium almost instantaneously. This assumption is certainly true for PDMS where the testing temperature is 320°C above the T_g. But, since the crosslinked poly(aryl ether ketone)s have T_gs around 160°C, being only 40°C above the T_gs, the validity of the above assumption is no longer sound. However, if we consider the stress drop measured in the continuous stress relaxation of the crosslinked poly(aryl ether ketone)s to be the sum of the contribution from the chemical changes in the network chain structure and that due to physical relaxation, the data become an upper bound for chain scission during the experiment. In *Figure 4a*, the stress relaxation measured for the poly(aryl ether ketone) network, the upper bound of the actual chain scission, is significantly smaller than that of the PDMS. This is consistent with the t.g.a. results which indicate good thermal stability of the new materials. On the other hand, the intermittent stress relaxation data should give the total network density of the polymer and the difference between the intermittent and continuous relaxation data is the contribution from crosslinking upon thermal degradation. However, because of the complicity arisen from the high T_g of the crosslinked poly(aryl ether ketone)s mentioned above, it is hard to carry out and interpret the data of the intermittent relaxation experiments. The actual stress lags behind the applied strain during each short pulse, leading to drifting of the stress and strain values at the released state. The drifting although small in quantity can affect greatly the subsequent data collection even if the drifting is corrected.

A new approach to thermally stable elastomers has been demonstrated using maleimide functional aryl ether ketone oligomers. These materials, when thermally crosslinked, exhibit elastomeric characteristics ~50°C above their T_gs (~200°C). The moduli and elongation to break of the new elastomers were comparable to an unfilled PDMS rubber, and the thermal stability, as measured by t.g.a. and chemorheology measurements, was considered exceptional.

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