Toughness of model polymeric networks in the glassy state: effect of crosslink density

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Relationships between the microscopic structure (chemical composition and topology) and the macroscopic properties, especially the toughness, of well defined polymeric networks below T_g, were investigated. Model networks were prepared from a triisocyanate, i.e. tris(4-isocyanatophenyl)-thiophosphate (Desmodur RFE) and well defined polymeric diols, namely poly(propylene glycol)s (PPGs) of various molecular weights (425, 725, 1000, 2000, and 4000). The experimental equilibrium rubber moduli of the various Desmodur–PPG networks are in good agreement with those calculated by means of the theory of branching processes. These networks are therefore considered to behave as model polymeric networks. Toughness was measured as a function of the crosslink density at temperatures well below the T_g. The model networks are surprisingly tough. A linear dependence of the critical stress intensity factor, K_{Ic}, on the strand density is observed. The size of the plastic zone is related to the maximum extensibility of the network chain. Other properties of the glassy state (e.g. glass modulus and yield stress) have only a very slight dependence on the crosslink density.

(Keywords: model networks; crosslink density; toughness)

INTRODUCTION

Thermosets are rigid and brittle, with the latter property limiting the application of these materials. The most common way of toughening thermosets is the addition of either rigid or rubbery fillers, or fibres. Apart from this, the intrinsic toughness of the matrix material can also be changed. One of the parameters that is believed to influence the intrinsic matrix toughness is the crosslink density. Increasing the intrinsic matrix toughness can be desirable, for example, Pearson and Yee[1] claim that the tougher the matrix material, then the more effectively it can be toughened by the addition of a second (rubbery) phase.

The ultimate mechanical properties of thermoset matrices are formed in the final stage of conversion[2]. It is thought that the presence of network defects can have a detrimental effect on certain mechanical properties. However, the concentration of these network defects is low and it is therefore difficult to unravel the exact relationships between the network structure and mechanical behaviour. Many research groups have tried to study the influence of crosslink density on mechanical properties by changing the stoichiometry and thus the crosslink density of the system[3–10]. However, in this way one not only changes the crosslink density, but also the amount of dangling ends, the concentration of residual functional groups and other network defects. In our opinion, the change in concentration, and probably also the actual presence, of these defects obscures the influence of the crosslink density on the mechanical behaviour. Others[1,11–13] have studied model networks prepared by the stoichiometric endlinking of well defined bifunctional monodisperse (pre)polymers with crosslinkers. The crosslink density of these networks can be tailored by varying the molecular weight of the prepolymer. If full conversion is reached, this method should give networks which do not contain significant amounts of dangling ends and residual reactive groups. Furthermore, the chains between elastic active crosslink points are of equal length. One might presume that the mechanical properties of these networks are good, since no short chains are present which can fail at relatively low extension ratios. Surprisingly, above T_g the mechanical properties of well defined homodisperse networks are poor, when compared to bimodal networks[14,15]. The effect of the molecular-weight distribution between crosslink points on the mechanical properties in the glassy state has not been studied up until now.

LeMay and Kelley[11] have studied the mechanical properties, below their T_gs, of a series of diglycidyl ether of bisphenol A (DGEBA) resins, ranging in molecular weight from 380 to 2600 $\mathrm{g\,mol^{-1}}$, endlinked with diaminodiphenylsulfone (DDS). They found that the yield stress, σ_y, and Young's modulus, E, in the glassy state are not very dependent on the crosslink density. However, they claim to have found a proportionality of the strain energy release rate, G_{Ic}, to the square root of the molecular weight between crosslink points, $M_c^{0.5}$. Levita[12] and Pearson and Yee[1] have studied the same systems, and have found linear relationships between G_{Ic} and M_c (Pearson and Yee), or between the critical stress intensity factor, K_{Ic}, and M_c (Levita). A major drawback of this system, however, is the decreased functionality of, especially, the high-molecular-weight DGEBA resins (DGEBA-2600, $f = 1.4$). Thus, these thermosets cannot be defect free, and in addition, the concentration of defects varies with the crosslink density.

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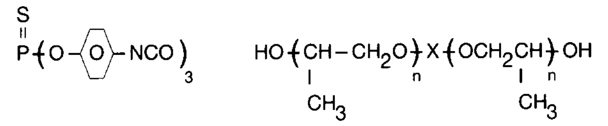


$$\mathrm{HO}\{\underset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2O}\}_n\mathrm{X}\{\mathrm{OCH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\}_n\mathrm{OH}$$

Desmodur RFE PPG

Scheme 1

Fischer has studied the mechanical properties, including G_{Ic}, of a different type of epoxy thermoset[13]. In this work, he observed a linear relationship between the half-crack opening displacement, which is equal to $G_{Ic}/2\sigma_y$, and the molecular mass between the crosslinks.

We have prepared model networks from a triisocyanate, tris(4-isocyanatophenyl)-thiophosphate (Desmodur RFE), and well defined polymeric diols, such as various poly(propylene glycol)s (PPGs) (*Scheme 1*). The polydispersity of the PPGs is low ($M_w/M_n < 1.1$), with only the polydispersity of PPG(4000) amounting to a value as high as 1.3. The crosslink density of the network is altered by varying the molecular weight of the PPG ($M_{n,PPG} = 425$, 725, 1000, 2000, and 4000). The Desmodur–PPG system has also been studied by Andrady and coworkers[16,17] and by MacKnight and coworkers[18,19]. In these studies, only the mechanical properties above T_g were measured, and the discussion of any relationships between the crosslink density and the mechanical properties was limited.

In the present work, the relationships between the mechanical properties below T_g and the network structure are explored. Equilibrium rubber moduli were measured and compared with moduli calculated by means of the theory of branching processes, in order to investigate the 'perfectness' of the network. Furthermore, the glass modulus and the yield stress were determined as a function of the molecular weight of the PPG. The toughness of the networks, expressed as the critical stress intensity factor, K_{Ic}, was measured in the glassy state as a function of the crosslink density, the temperature and the testing speed.

EXPERIMENTAL

Poly(propylene glycol)s with nominal molecular weights of 425 ($M_w/M_n = 1.08$), 725 ($M_w/M_n = 1.05$), 1000 ($M_w/M_n = 1.05$), 2000 ($M_w/M_n = 1.03$), and 4000 ($M_w/M_n = 1.3$) were obtained from Aldrich, and were dried by azeotropic distillation with benzene (water content less than 0.15 mol per 100 mol of hydroxyl groups). Desmodur RFE, which was kindly supplied by Bayer, was recrystallized at low temperatures from dry, alcohol-free dichloromethane. The purity was higher than 99.5% NCO (titration with dibutylamine). The purity was also analysed by h.p.l.c. A single peak was found for dibutylamine derivatives of Desmodur (column, HP-18 nucleosil (12 cm); eluent, 75% acetonitrile/25% phosphate buffer (0.05 M, pH = 3, 50 mg triethylamine)). All chemicals were stored under nitrogen.

Stoichiometric amounts of Desmodur and PPG were mixed at 80–90°C under nitrogen. The slurry was stirred until a clear solution was obtained and then poured into a gel bath. The network was cured for ~80 h at 80–90°C under nitrogen, until no more NCO resonances (2271 $\mathrm{cm^{-1}}$) could be observed by Fourier transform infra-red (*FT*i.r.) spectroscopy.

Solfractions were determined by two successive extractions for periods of one week using dichloromethane, at room temperature; the amount of extractable material was measured.

Rubber moduli were determined by dynamic mechanical analysis (d.m.a.) using a RDA-2 dynamic mechanical spectrometer in torsion mode (typical strip dimensions = $20 \times 40 \times 2\ \mathrm{mm^3}$). Equilibrium moduli were extrapolated from the experimental moduli measured at different frequencies.

Small-angle X-ray scattering (SAXS) measurements were performed with a Kratky camera equipped with a Braun position detector. The sample–detector distance was 490 mm and the generator power was 2 kW (40 kV, 50 mA). The recorded intensities were corrected for both absorption and scattering of air.

Test bars for K_{Ic} measurements were prepared from 4 mm thick sheets. Specimen dimensions were approximately $\sim 4 \times 8 \times 36\ \mathrm{mm^3}$. Samples were prenotched with a single-point fly cutter (notch tip radius of 0.1 mm) and notched by either tapping (glassy samples) or sliding (rubbery samples) a razor blade into this prenotch.

The quasi-static K_{Ic} measurements were performed in single edge notched bend (SENB) geometry, according to the protocol for K_{Ic}/G_{Ic} testing prepared by ESIS[20]. The tests were performed on a Zwick 1474 tensile tester, at a testing speed of $10\ \mathrm{mm\ min^{-1}}$. Testing was carried out at various temperatures below T_g, with the samples in contact with air. Impact K_{Ic} measurements were performed, according to the draft protocol of ESIS, on a Zwick rel servohydraulic machine. The testing speed was $1\ \mathrm{m\ s^{-1}}$, at a testing temperature which was 40°C below T_g.

Tensile bars according to ISO R527 type 1 halved were made from 2 mm thick sheets. The yield stress, σ_y, was measured at a strain rate of $10\ \mathrm{mm\ min^{-1}}$ at various temperatures below T_g. The glass moduli were determined at various temperatures below T_g using a laboratory-built torsion pendulum apparatus, operating at 0.2153 Hz.

RESULTS AND DISCUSSION

Structure of the Desmodur–PPG networks

In order to prove that the structure of the network is as one would expect it to be, on the basis of its stoichiometry and chemistry, the structure is examined here (i) by *FT*i.r. spectroscopy, (ii) by comparing experimental and calculated properties, particularly the equilibrium rubber modulus (G_r), and (iii) by using SAXS and optical microscopy.

No NCO resonances were observed in the *FT*i.r. spectra of the cured networks, and therefore, the conversion is judged to be more than 98%. *Table 1* lists the equilibrium rubber modulus (G_r), the experimental solfraction (w_s), and the density (ρ) of the various networks, with respect to the molecular weight of the PPG. The solfractions are small and independent of the crosslink density.

According to the rubber elasticity theory, G_r must be inversely proportional to M_c or proportional to the strand density:

$$G_r = \frac{A\rho RT}{M_c} = A\nu kT \tag{1}$$

Table 1 Equilibrium rubber moduli (G_r), solfraction (w_s), and density (ρ) of the Desmodur–PPG networks as a function of the molecular weight of PPG

M_n (PPG) (g mol^{-1})	n^a	$G_r^{\,b}$ (MPa)	$w_s^{\,c}$ (%)	ρ (kg m^{-3})
425	7	3.9	0.082	1198
725	12	2.65	0.45	1142
1000	17	1.98	0.53	1111
2000	34	1.24	0.99	1058
4000	69	0.41	0.62	1034

[a] Calculated from the hydroxy number and g.p.c. data
[b] $T = 323$ K, with the exception of PPG(425), where $T = 353$ K; error = 5%
[c] Using $CHCl_2$ as solvent

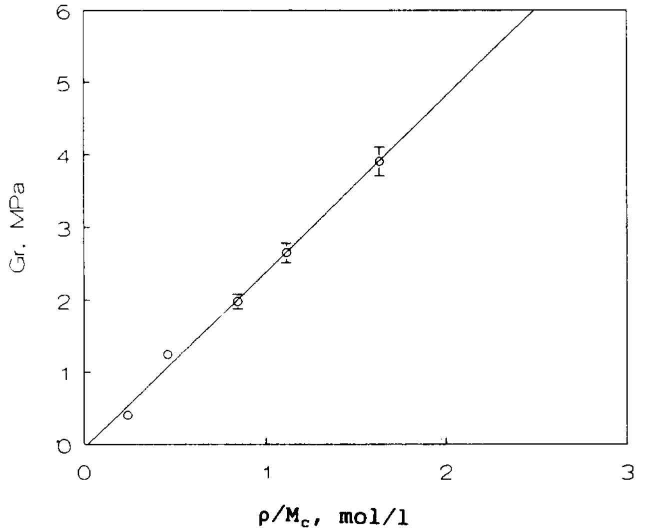


Figure 1 Equilibrium modulus, G_r, as a function of ρ/M_c for the Desmodur–PPG networks

in which A is the front factor, ρ is the density, R is the molar gas constant, T is the temperature, k is the Boltzmann constant, and ν is the strand density. The experimental values of G_r are plotted *versus* ρ/M_c^{theor} in *Figure 1*, where $M_c^{\text{theor}} = M_{\text{PPG}} + 2/3 M_{\text{Desmodur}}$. In order to calculate M_c^{theor} the assumption is made that full conversion is reached. Furthermore, it is assumed that no physical crosslinks are present. The experimental G_r values do indeed depend linearly on ρ/M_c^{theor}. Therefore, the experimental findings are in accord with the rubber elasticity theory. According to Treloar[21] the rubber elasticity theory holds when the number of equivalent random links is larger than 25, or when the equilibrium rubber modulus is below 1 MPa. The equivalent random linkage of PPG is ~10 monomeric units. It must therefore be concluded that one should not use the rubber elasticity theory to estimate the crosslink density of these Desmodur–PPG model networks. However, excellent agreement between the theoretical (theory of branching processes) and experimental rubber moduli is found (see below). Therefore, we assume that the deviation from Gaussian chain statistics results in only a small change in G_r.

The conversion of the various networks can be calculated from the sol fraction, using the theory of branching processes, if the kinetics of the curing reaction are known[22,23]. The reaction of the Desmodur triisocyanate material and alcohols can be described by a second-order reaction model. The course of the reaction of Desmodur with various poly(ether) alcohol species in dilute solutions can be described by assuming a negative substitution effect[24]. This effect is the result of a unique combination of reactants, solvent, and reaction conditions. We assume that this kinetic model is also an appropriate description for the network formation reaction of Desmodur and the various PPGs in bulk.

The experimental conversions (α), determined from the sol fractions, are listed in *Table 2* as a function of the molecular weight of PPG; α ranges from 0.97 to 0.99. These conversions are in accord with conversions determined by using *FT*i.r. spectroscopy. Various features of the (supra)molecular structure of the networks were calculated at the different experimental conversions. *Table 3* lists the theoretical M_c at full conversion (M_c^{theor}), the theoretical M_c at the experimental conversion α ($M_c^{\text{theor}}(\alpha)$), and the theoretical strand density at the experimental conversion ($\nu^{\text{theor}}(\alpha)$). As expected, the theoretical crosslink density at the experimental conversions is smaller than the crosslink density at full conversion. The experimental strand densities (ν^{exp}) were calculated from the G_r values by using equation (1), with $A = 1$ (see *Table 3*). The affine limit of the rubber elasticity theory is used because the crosslinker is large and relatively immobile when compared to the PPG chains[25]. Only small differences between the experimental and calculated strand densities are observed (see *Figure 2*). Therefore, the structure of the Desmodur–PPG networks

Table 2 Conversion (α) and calculated fractions, A_0–A_3, of the Desmodur–PPG networks as a function of the molecular weight of PPG

M_n (PPG) (g mol^{-1})	α	A_0	A_1	A_2	A_3
425	0.99	0	0	0.030	0.97
725	0.98	0	0	0.060	0.94
1000	0.98	0	0	0.060	0.94
2000	0.97	0	0.001	0.089	0.91
4000	0.98	0	0	0.060	0.94

Table 3 M_c^{theor}, $M_c^{\text{theor}}(\alpha)$, M_c^{exp}, $\nu^{\text{theor}}(\alpha)$, and ν^{exp} of the Desmodur–PPG networks as a function of the molecular weight of PPG

M_n (PPG) (g mol^{-1})	M_c^{theor} (g mol^{-1})	$M_c^{\text{theor}}(\alpha)$ (g mol^{-1})	M_c^{exp} (g mol^{-1})	$\nu^{\text{theor}}(\alpha)$ (10^{25} m^{-3})	ν^{exp} (10^{25} m^{-3})
425	734	834	902 ± 45	86.5	84.5 ± 4.2
725	1024	1174	1157 ± 58	58.6	59.5 ± 3.0
1000	1314	1486	1507 ± 75	45.0	44.4 ± 2.2
2000	2300	2807	2291 ± 115	22.7	27.8 ± 1.4
4000	4330	4891	6773 ± 330	12.7	9.2 ± 0.4

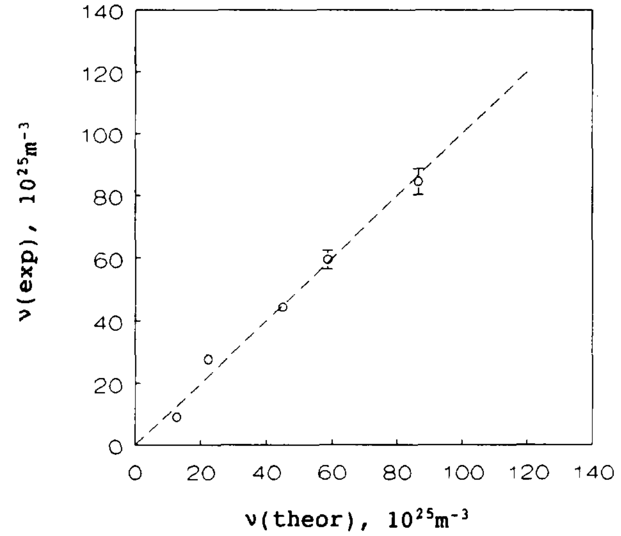
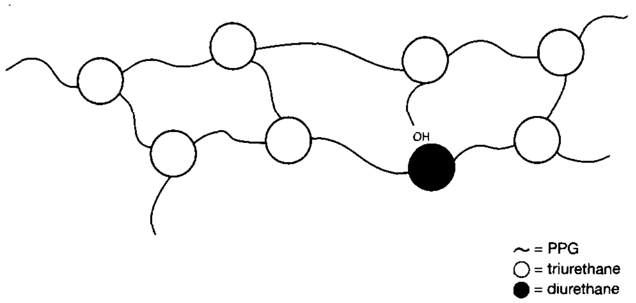


Figure 2 ν(theor) vs. ν(exp) for the Desmodur–PPG networks



Scheme 2 Schematic representation of the Desmodur–PPG network structure

appears to be an ideal one, with no additional physical crosslinks being present.

Computer simulations based on the theory of branching processes can be used to depict the structure of the network. The amounts of Desmodur (A_0) and mono-, di- and triurethane (A_1, A_2, and A_3, respectively), are calculated and listed in *Table 2.* No unreacted Desmodur is present, with the amount of monourethane, A_1, being negligible. The fraction of diurethane species, A_2, is small (=0.03–0.09), and therefore, there will be an equally low fraction of triurethane species with one connected PPG chain dangling. It seems unlikely that any significant numbers of the diurethane species will be connected to each other, considering the relatively small amount present. Thus, only a few of the triurethane crosslink points will be separated by one diurethane chain extension point, while virtually none will be separated by more than one extension point. A schematic representation of the network structure is depicted in *Scheme 2.*

Heterogeneities may have a large influence on certain mechanical properties, in particular the toughness, of thermosets. Therefore, the morphology of the Desmodur–PPG networks was examined. The networks are transparent. Optical microscopy studies were performed on 10 μm microtomed samples of Desmodur–PPG(425) and Desmodur–PPG(4000), but no structural features were observed. Furthermore, SAXS was used to study possible heterogeneities of the networks. The P=S fragment in Desmodur has a high (electron) density ($\rho = 1.7 \times 10^3$ kg m^{-3}) compared to PPG ($\rho = 1.0 \times 10^3$ kg m^{-3}) which results in a high scattering power of Desmodur in comparison to that of the PPG. SAXS investigations were carried out on Desmodur–PPG(425), –PPG(2000), and –PPG(4000), and it was found that the scattering intensities were very low for these materials. A clear maximum is observed for Desmodur–PPG(2000) and –PPG(4000) (*Figure 3*). However, the interpretation of these scattering curves is not straightforward. A theoretical framework for the calculations is not available since in these systems point scattering (by the P=S group) occurs, rather than scattering by blocks. However, it can be deduced that agglomeration of Desmodur is unlikely, given the low scattering intensities. The SAXS results indicate that hard segments, caused by hydrogen bonding between the urethane units (which can be present in linear polyurethanes) are, in fact, absent in these Desmodur–PPG networks. This is probably due to geometrical constraints. Furthermore, the temperature dependence of the equilibrium rubber moduli excludes the presence of additional physical crosslinks arising from hydrogen bonding of the urethane units[26].

We can therefore summarize the major points concerning the structure of these networks as follows:

(a) the Desmodur–PPG networks are the best defined polymeric networks known so far;
(b) the isocyanate–alcohol reaction is nearly complete, so there are only a few dangling chains;
(c) the topological structure is ideal;
(d) this system is therefore perfectly suited for studying relationships between the structure of a polymeric network and its mechanical properties.

Mechanical properties of the glassy state

Table 4 lists the glass transition temperatures, and the glass moduli (G_g) at a temperature of T_g–50°C, determined from d.m.a. studies of the various Desmodur–PPG networks. The T_g values decrease with an increasing weight fraction of PPG (i.e. a decreasing crosslink density). The interdependence of T_g and the crosslink density is discussed in a separate paper[27]. G_g does not appear to be very dependent on the crosslink density. In fact, since the glass modulus of the network is determined by van der Waals intermolecular forces (and packing density)[28], G_g is not expected to depend on the crosslink density.

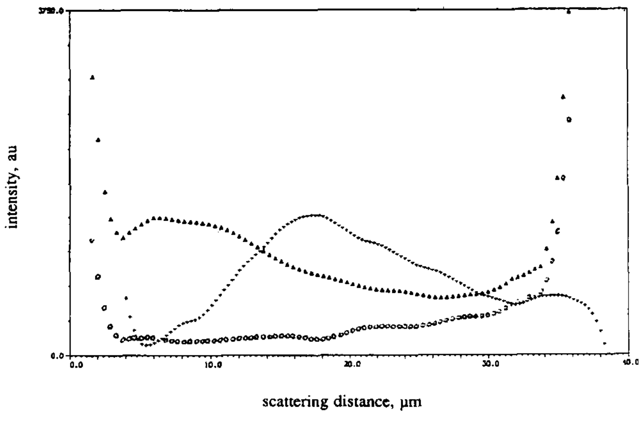


Figure 3 Deconvoluted SAXS scattering curves: (○) Desmodur–PPG(425); (△) Desmodur–PPG(2000); (+) Desmodur–PPG(4000)

Table 4 Glass transition temperature (T_g) and glass modulus (G_g) of the Desmodur–PPG networks as a function of the molecular weight of PPG, determined by d.m.a. (0.2153 Hz)

M_n (PPG) (g mol^{-1})	T_g (°C)	G_g (GPa)[a]
425	36	1.1
725	−3	1.1
1000	−27	1.1
2000	−53	1.3
4000	−62	1.2

[a] Glass modulus determined at T_g–50°C

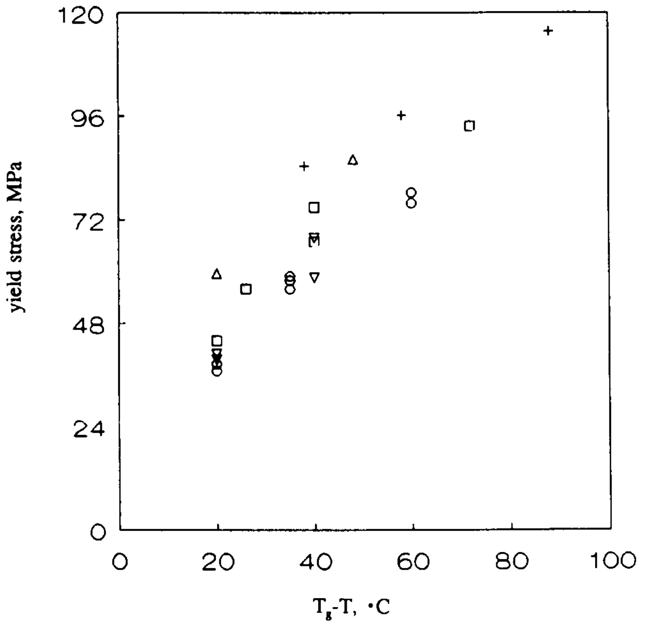


Figure 4 Yield stress, σ_y, as a function of the difference between the testing temperature T and T_g for the Desmodur–PPG networks with different poly(propylene glycol)s: (○) PPG(425); (▽) PPG(725); (□) PPG(1000); (△) PPG(2000); (+) PPG(4000)

The yield stress σ_y was plotted as a function of the difference between the testing temperature and T_g (see *Figure 4*). The samples show either necking, thus causing a drop in the stress, or a pronounced non-linearity in the stress–strain curve, prior to sample failure.

LeMay and Kelley[11] have shown that the yield stress of epoxy–amine model networks is independent of the crosslink density and depends only on the difference between the temperature of testing and T_g. In contrast, we find for our samples that the higher the crosslink density, then the lower is its yield stress at a certain temperature distance from T_g. For example at $T_g - T = 40$°C the yield stress for Desmodur–PPG(425) is expected to be ~60 MPa, whereas the yield stress for Desmodur–PPG(4000) is ~85 MPa. The curves in *Figure 4* lie significantly higher for the samples that have higher crosslink densities.

Table 5 lists the K_{Ic} values measured at various temperatures and at two different testing rates. Some of the values are not valid according to the protocol used as a result of too much plasticity, even though the tests were carried out at temperatures far below the T_g; these values are marked with an asterisk. In the case of the Desmodur–PPG(1000) network, the test becomes valid when the temperature is lowered. In all cases, the value of K_{Ic} rises with decreasing temperature, although the dependence of K_{Ic} on temperature for these samples is, in general, not very strong. The K_{Ic} value of the Desmodur–PPG(425) network was also measured at one temperature in double torsion geometry and an identical value for K_{Ic} was found in this case.

The validity of the high-rate tests could not be investigated, since the yield stress of the Desmodur–PPG networks is not known at these high strain rates. Investigation of the failure type and the force–deflection curve, however, leads us to assume that the tests are valid. The K_{Ic} values, for both the low- and high-strain-rate tests, are surprisingly high for neat thermosets. The values for both the low and the high strain rates are inversely

Table 5 Values of K_{Ic} as a function of testing speed and temperature for various Desmodur–PPG networks

M_n (PPG) (g mol^{-1})	K_{Ic} (MPa m$^{0.5}$)		T_{test} (°C)	T_g–T_{test} (°C)
	1 mm min^{-1}	1 m s^{-1}		
425	1.96±0.07		0	35
	2.04±0.14		−55	55
	2.16±0.10		−85	85
		1.90±0.05	−5	40
725	2.82±0.08		−70	67
	3.20±0.01		−100	97
		2.12±0.08	−43	40
1000	2.96±0.12[a]		−62	34
	3.41±0.08		−80	52
		2.87±0.36	−68	40
2000	4.33±0.18[a]		−105	53
		3.30±0.41	−92	40
4000	4.94[a,b]		−150	88
		3.57±0.45	−102	40

[a] Not valid according to ESIS protocol

[b] Only one sample bar tested

proportional to the strand density (*Figure 5*), with the dependence being very strong when compared to other thermosets. Furthermore, K_{Ic} decreases upon increasing the testing rate.

A possible reason for the very high K_{Ic} values could lie either in the fact that we have been able to synthesize ideal networks, or result from the chemical compositions of these networks. As has been pointed out in the Introduction, the presence of network defects can have a deteriorative effect on the mechanical properties of a network. We have shown that in the Desmodur–PPG networks few imperfections and residual functional groups are present. Furthermore, the chain length distribution between the crosslink points in these networks is narrow. One might assume that all chains can be extended to roughly an equal length and unwanted premature chain failure might be delayed, leading to a higher fracture toughness. Apart from these topological considerations, also, of course, the combination of a urethane and a polyether could be the origin of the high toughness of these materials. If this is the case, the apparent strong dependence of K_{Ic} on the crosslink density could, in fact, be caused by the dependence of K_{Ic} on the chemical composition of the network.

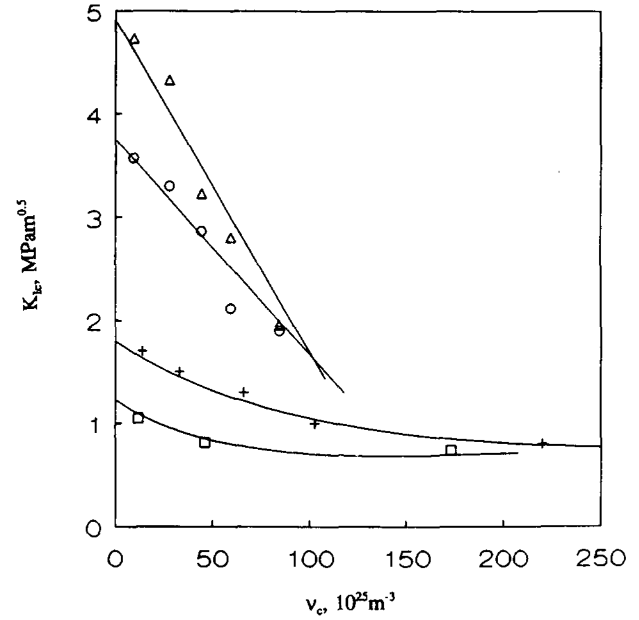


Figure 5 K_{Ic} as a function of strand density for the Desmodur–PPG networks and other thermosets: (△) Desmodur–PPG quasi-static; (○) Desmodur–PPG impact; (□) epoxies, data from ref. 1; (+) epoxies, data from ref. 13

In *Figure 6* K_{Ic} is plotted as a function of the yield stress at two different temperature distances from T_g. Interpolated values are used and a linear dependence between either K_{Ic} or σ_y and the temperature is assumed. A linear dependence between K_{Ic} and σ_y is found at a constant $T_g - T$. Lowering the temperature or the crosslink density increases K_{Ic} as well as the yield stress. The yield stress is strongly dependent on $T_g - T$, but only slightly dependent on K_{Ic}. The temperature dependence of K_{Ic}, however, increases with decreasing crosslink density. The finding that K_{Ic} and σ_y both increase in this way, is in accordance with the behaviour of thermoplastics such as PMMA[29], but not with some of the available literature data on thermosets. However, in the case of the latter, only the temperature dependence of the yield stress has been investigated, whereas K_{Ic} has been generally measured at a constant temperature[1,3].

Fischer[13] has proposed a dependence between the size of the deformation zone and the molar mass of the network strands, but K_{Ic} and the yield stress were both measured at constant temperatures. In *Figure 7* the size of the plastic zone[29], $r_p = (2\pi)^{-1}(K_{Ic}/\sigma_y)^2$, for the Desmodur–PPG networks at different values of $T_g - T$, are plotted as a function of the strand density. The zone size increases (i) with increasing temperature (as expected) and (ii) with decreasing crosslink density. Actually, a linear dependence of r_p and the strand density ($1/M_c$) can be deduced. There appears to be a relationship between the size of the plastic zone of the Desmodur–PPG networks and the maximum extensibility, r_{max}/r_0, of poly(ethylene glycol) (PEG) chains having the same degree of polymerization as the PPG chains (see

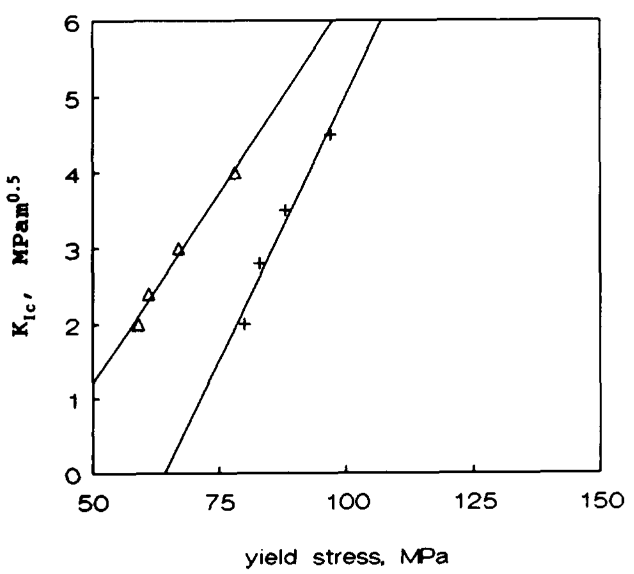


Figure 6 K_{Ic} as a function of the yield stress for the Desmodur–PPG networks at different temperatures: (△) $T_g - T = 40$; (+) $T_g - T = 60$

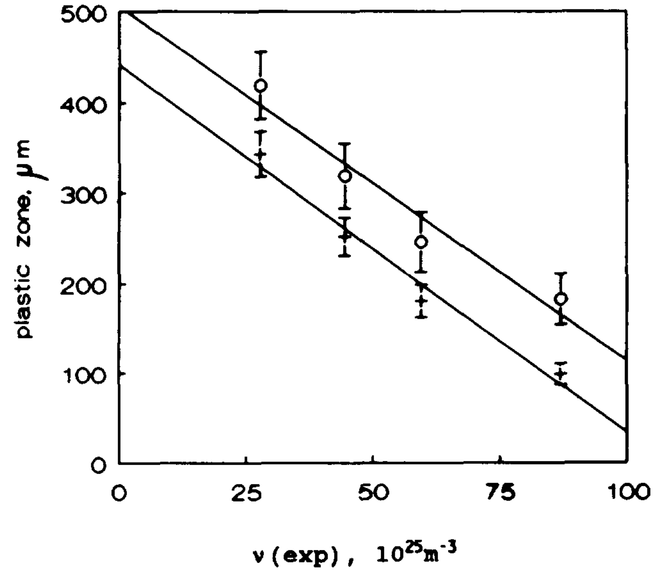


Figure 7 Plastic zone size vs. the strand density for the Desmodur–PPG networks at different temperatures: (○) $T_g - T = 40$; (+) $T_g - T = 60$

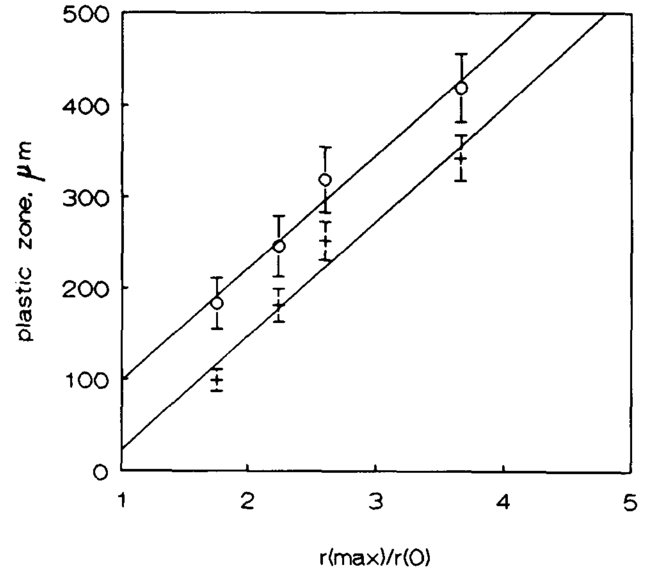


Figure 8 Plastic zone size of Desmodur–PPG networks vs. the maximum extensibility of PEG chains (r_{max}/r_0) at different temperatures: (○) $T_g-T=40$; (+) $T_g-T=60$

Figure 8). Values for the maximum end-to-end distance, r_{max}, were obtained from fully extended minimum energy configurations, while r_0 was calculated using the Rotational Isomer State (RIS) model[30], applying the statistical weights of Abe *et al.*[31].

Our results indicate that the yield stress, as well as the plastic zone size, increases with decreasing crosslink density. For the Desmodur–PPG model networks the yield stress appears not to be the only factor to be considered when determining K_{Ic} at a certain T_g-T. Furthermore, the size of the plastic zone appears to be governed by the maximum extensibility of the network chain. The number of strands in the plastic zone has only a very slight dependence on the crosslink density.

CONCLUSIONS

We have prepared Desmodur–PPG networks with varying crosslink densities. These networks have very few imperfections, with the fraction of dangling ends lying between 0.03 and 0.09. The crosslink density is as expected, given the prepolymer, the crosslinker and the reaction mechanism. No heterogeneities in the structure could be found by either optical microscopy or by SAXS. The fracture toughness of the investigated resins is surprisingly high for a neat thermoset, when measured at both high and low strain rates. The toughness shows a linear relationship with the strand density. Together with a rise in K_{Ic} for lower crosslink densities, we also find a rise in the yield stress. This last observation is unexpected and we do not yet have a satisfactory explanation for it.

There are two possible explanations for the high K_{Ic} value and the fact that it rises with decreasing crosslink density. The first possibility is that our networks have an ideal topology, and are without any significant amounts of network defects that are thought to be ruinous to the ultimate properties. Therefore, in this case the measured ultimate properties represent the real undisturbed properties of the crosslinked network. Consequently, if this is the case, the crosslink density strongly determines the intrinsic toughness of thermoset systems. The other possible explanation is that the high toughness is caused by the specific chemical composition of the network systems, and this therefore changes when the composition is altered as we vary the network density. Further research will be carried out in order to elucidate these uncertainties.

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