Physical Characteristics of Plasticized Epoxy System in the Post-Yield Stage

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Synopsis

Thermo-rheological analysis was conducted on epoxy–Versamid specimens drawn from different portions of beams subjected to a yield test. M_c values, characterizing the cross-link density and determined by a special method, show insignificant variation for unstressed (virgin), pre-yield, and post-yield zones of the material. It was concluded that the yielding process in the plasticized epoxy system consists mainly in disruption of physical bonds.

Introduction

Previous works[1,2] dealt with the mechanical behavior of a plasticized epoxy–Versamide system at room temperature at high stress levels. The stress–strain relationship at constant strain rate, as well as creep under constant high stress, reveal similar pronounced delayed-yield characteristics under tensile, compressive, and' flexural modes of loading (Figs. 1 and 2).

A similar mode of behavior was observed in other glassy amorphous or semicrystalline polymers.[3-5] Photoelastic examination of epoxy specimens revealed a clear residual pattern of slide lines oriented along the maximum shear stresses (Fig. 3). Deformation bands of the same orientation were also found for polystyrene,[6] nylon,[7] and Teflon[8] at the cold-drawing stage. It was suggested that this sliding effect is attributable to a diffusional mechanism activated at high mechanical energy levels, and thus can be formulated according to Eyring's theory for non-Newtonian viscous flow.[9] Experiments at low stress levels[2,10] indicate that such an epoxy system is characterized by anelastic behavior and thus rule out free Maxwellian viscous elements in the mechanism at these levels. It is reasonable to assume that the change from linear anelastic behavior to non-Newtonian viscous flow is mainly due to temporary disruption of internal links.

The object of the present work was to gain an insight into the structural properties of the tested epoxy system, before and after yielding. Rubbery

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zones of highly crosslinked polymers such as epoxides,[11] unsaturated polesters,[12] and acrylates[13] were recently studied, and the application of methods previously used for typical elastomers to highly crosslinked polymers was reported.[14]

In the present work, a method described by Cluff et al.[15] was used for determining the approximate crosslink density (characterized by the
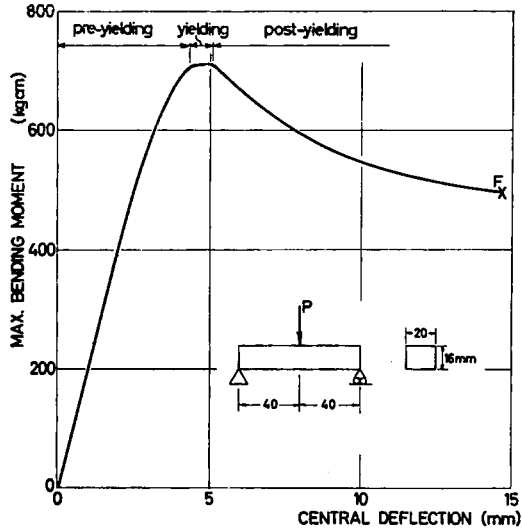

Fig. 1. Load–deformation curve for plasticized epoxy system in flexure at constant strain rate.
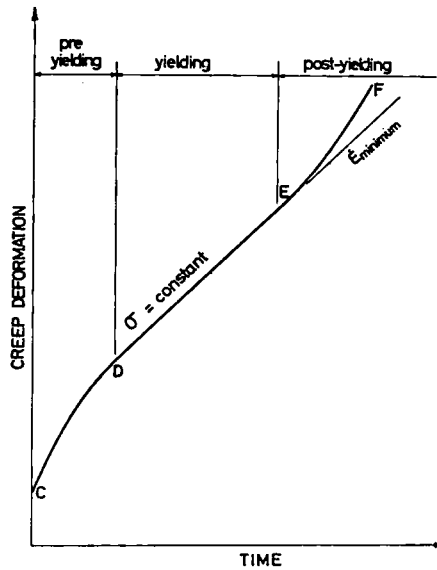

Fig. 2. Typical creep curve for plasticized epoxy system at constant high stress level.

average molecular weight of the network chain between two adjoining crosslinks, M_c), and examining the influence of the previous yielding process on the M_c of the tested epoxy system. This analysis was expected
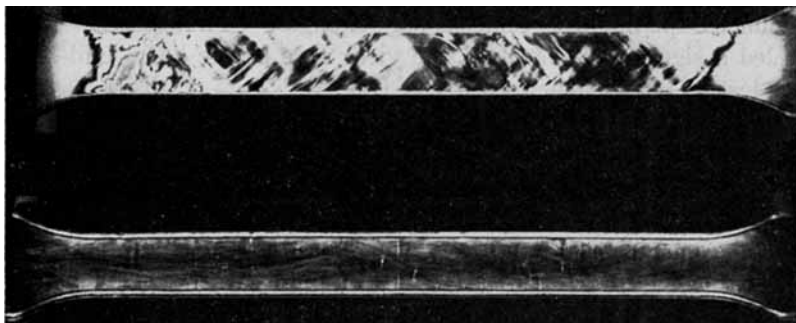

Fig. 3. Photoelastic residual pattern in tensile specimen: (a) yielded; (b) virgin.

to shed more light on the nature of the disruption process (temporary or permanent, only secondary physical bonds involved, or also scission of primary crosslinks).

Experimental

The epoxy system consisted of 1:1 Versamid 140 to Shell Epon 815 (by weight). The two ingredients were mixed at room temperature (23°C.) and underwent cold-setting overnight in the same environment. After demolding, the specimens were stored at 23°C. for testing at the age of 14 days.
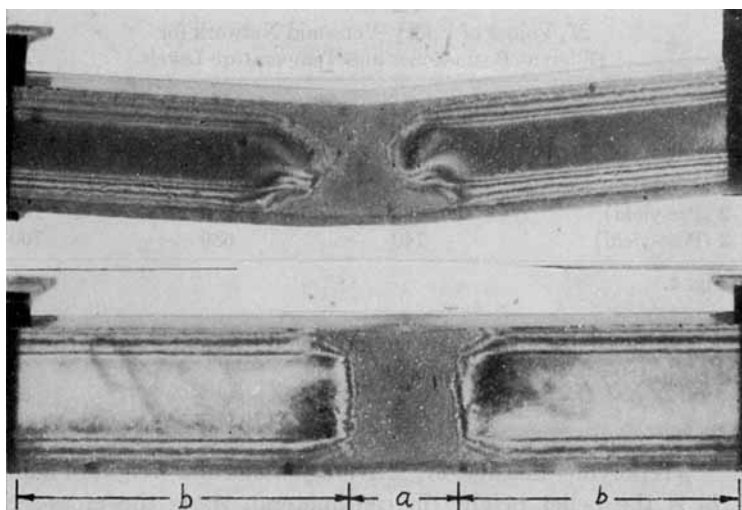

Fig. 4. Photoelastic pattern of flexural specimen; in (a) the post-yield zone and (b) the pre-yield zone: (top) front view; (bottom) bottom view.

The 16 × 16 × 100 mm. beams (for flexure) and 7 × 12 × 120 mm. specimens (for tension) were loaded to yield at constant strain rate, according to the procedure described previously.[1]

In the flexural tests, the post-yield behavior was characterized by pronounced permanent dimensional changes.* Photoelastic analysis revealed a significant change in the yield zone at the beam mid-section, which lost its birefringence sensitivity (Fig. 4).

Loss of birefringence was also observed at the necking sections of the tensile specimens. This behavior permitted convenient distinction between the yield section of the material (which undergoes plastic flow), and other parts which recover their original shape and structure by the prevailing anelastic mechanism. About 4 months after the test, pellets (10 mm. diameter, 4 mm. height) cut from different portions of the specimens, together with control pellets of "virgin" material, were subjected to swelling in dioxane at 35°C. (average swelling ratio 175%), for about 3 weeks (to equilibrium) and subsequently to compression at different temperature levels in a thermostatic bath (±0.1°C.), with deformations measured by means of a dial gauge (5 × 10^{-3} mm.) simultaneously with load variation.

Results and Discussion

Shear modulus verses temperature plots indicate almost identical behavior of the material in the yield zone (Fig. 5a) and the virgin material (Fig. 5b). Specific volume versus temperature plots (Fig. 6) indicate a well-defined glass transition point at about 35°C. in both cases, which also exhibit a pseudo rubbery plateau.

TABLE I
M_c Values of Epoxy–Versamid Network for
Different Beam-Zones and Temperature Levels

Zone[a]	M_c		
	70°C.	80°C.	90°C.
1 (Virgin)	780	760	760
2 (Pre-yield)	660	680	700
3 (Post-yield)	740	680	700

[a] See Fig. 4.

The M_c values listed in Table I were derived from eq. (1) for the rubbery pleteau region[14]:

$$\rho/M_c = (h_0 s/3A_0 RT) V_e^{-1/3} \qquad (1)$$

where: ρ is polymer density, M_c is average molecular weight of a network chain, h_0 is the pellet height (in centimeters), A_0 is the cross-sectional

* Curing at elevated temperature (100°C./1 hr.) almost restored the original shape, provided no cracking had occurred during yielding.

area (in square centimeters), S is the slope of load versus deformation curve in the rubbery plateau region (in kilograms per centimeter), R is the universal gas constant, T is the absolute temperature, and V_e is the volume percentage of effective chains in polymer (above 0.99 in the present case).
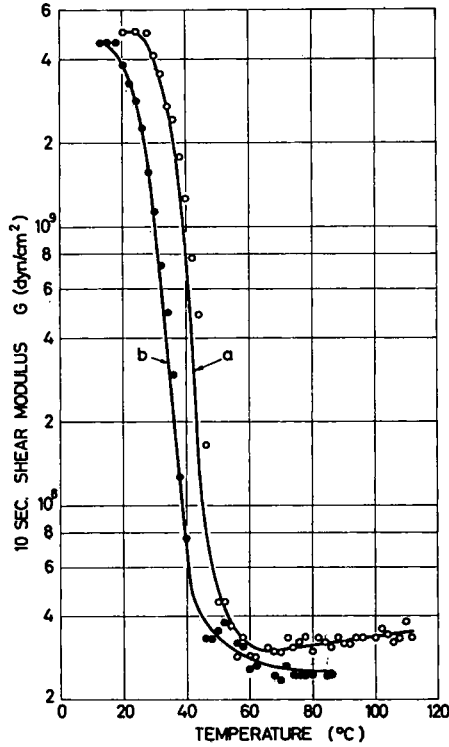

Fig. 5. Typical modulus vs. temperature relationship for plasticized epoxy system: (a) post-yield zone; (b) virgin material.
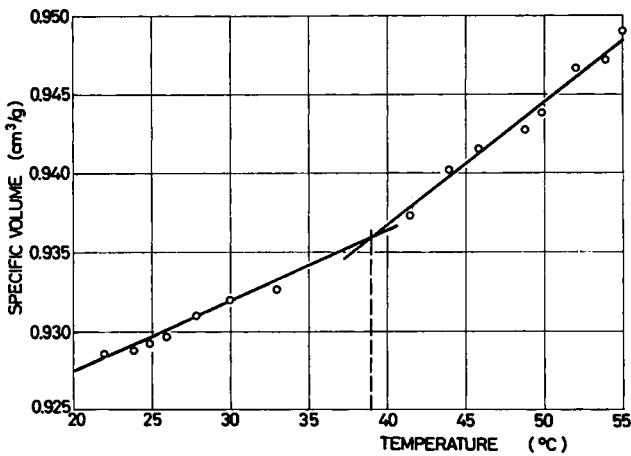

Fig. 6. Specific volume vs. temperature relationship for evaluating the glass temperature.

Discussion

The results described above for the epoxy–Versamid system are comparable to those obtained for other highly crosslinked polymers.[11–14] The M_c values obtained are in fair agreement with those of pure epoxy specimens under similar conditions. The temperature levels are well within the pseudo-rubbery pleateau region. The action of the dioxane consists apparently in disrupting the hydrogen bonds[15] in the amide groups due to the Versamid. This disruption and re-forming of the hydrogen bonds is believed to be the main mechanism governing the yield process.

The system apparently possesses a wide spectrum of physical bond strengths (similar to those observed in jelly[16] and unsaturated polyesters[17]), and, with most weak links disrupted by the dioxane, no further M_c growth is obtainable by temperature increase. Rupture of the physical bonds under load enables the system to undergo an entropy decrease, and unloading is expected to induce a tendency to entropy gain. This effect increases with temperature through increased diffusion rates, so that full deformational recovery can be expected at high temperature levels, in a relatively short time.

The main conclusion from Table I is that the yield process has no significant influence on M_c values and thus is not expected to be involved in the disruption of chemical primary bonds.

Conclusions

M_c values determined at different temperature levels for virgin, pre-yield, and post-yield zones of an epoxy–Versamid system indicate insignificant variations of the crosslink density. The yield process thus consists mainly in disruption of secondary—probably hydrogen—bonds, within the amide groups introduced by the Versamid plasticizer.

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Résumé

L'analyse thermo-rhéologique a été appliquée à des échantillons étirés d'époxy--vers-amide soumis à un test de rendement. Des valeurs M_c, caractérisant la densité de pon-tage et déterminées par une méthode spéciale, indiquent une variation insignifiante pour le matériau non-étiré (vierge) avant le point de rendement et après ce même point. On en conclut que les processus appliqués dans le système époxy plastifié consistent prin-cipalement dans la rupture des liens physiques.

Zusammenfassung

Eine thermo-rheologische Analyse wurde an Epoxy--Versamid-Proben, durchgeführt, die aus verschiedenen Teilen eines einem Zugversuch unterworfenen Stabes entnommen worden waren. Für die Vernetzungsdichte charakteristische und nach einer Spezial-methode bestimmte M_c-Werte zeigen für die unbeanspruchten (jungfräulichen) Zonen, die Vorfliess- und Nachfliesszonen des Materials nur geringfügige Änderungen. Man kommt zu dem Schluss, dass der Fliessprozess im weichgemachten Epoxysystem haupt-sachlich in der Sprengung physikalischer Bindungen besteht.