Packing Density of the Amine-Crosslinked Stoichiometric Epoxy Networks

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Synopsis

The packing densities (Van der Waals volume/molar volume) were determined at 293 K for various epoxide–amine stoichiometric networks. They are noticeably higher than those of linear polymers except strongly hydrogen bonded ones [polyamides, poly(vinyl alcohol)]. By extrapolation of the dilatometric data, it was found that the packing densities at the frontiers of the glassy state (0 K and T_g) of the epoxy networks are comparable to those of linear polymers having the same theoretical hydrogen bond density (polyamides). However, for a given packing density at 0 K, the packing density at T_g is higher for a network than for the corresponding linear polymer.

INTRODUCTION

On the basis of mechanical,[1-4] water absorption,[5,6] gas diffusion,[7,8] or density[4,5,9] measurements, it has been suggested that the free volume fraction would increase, or more generally, the packing density would decrease with the crosslink density, for certain tridimensional polymers in glassy state.

This is a relatively unexpected result since it is well known that the glass transition temperature increases with the crosslink density,[10,11] which should coincide, according to the free volume theory, with a decrease of the free volume fraction at a given temperature, below T_g.

It should be observed that the above cited physical properties possibly depend on many structural parameters, for instance aromatic content (i.e., chain stiffness), cohesive energy density, etc., not only on packing density ρ^*. Moreover, this latter, which can be well represented by the ratio, Van der Waals volume/molar volume,[12] is not necessarily an increasing function of the density ρ, but depends on the composition of the monomer unit, as shown by the following example: PMMA: $\rho = 1.18$, $\rho^* = 0.662$; PVC: $\rho = 1.39$, $\rho^* = 0.637$.

It seemed interesting to us to determine the packing density of various epoxide–amine stoichiometric systems, and to compare their values with those of common linear polymers, in order to appreciate an eventual effect of crosslinking.

EXPERIMENTAL

Epoxides and Amines. The following epoxides were used: DGEBA (diglycidyl ether of bisphenol A); DGEBF (diglycidyl ether of bisphenol F: the isopropylidene of DGEBA is replaced by a methylene); TGAP (triglycidyl

amino phenol); TGMDA (tetraglycidyl methylene dianiline). A previously published result on a diglycidyl ether of butane diol (DGEBD) system[13] will also be used.

The amines were DDM (diamino diphenyl methane), DDS (diamino diphenyl sulfone), PDA (paraphenylene diamine), and DAk (polymethylene diamines $H_2N(CH_2)_kNH_2$ with $k = 4, 6,$ or 12).

In the case of DGEBF and TGAP, the experimental epoxide index corresponded to its theoretical value. In the case of DGEBA, it was used to determine the average degree of polymerization j. In the case of TGMDA it was 84% of its theoretical value.

Samples. In all cases, epoxide and amine were mixed in stoichiometric ratio (taking into account the experimental value of epoxide index). The mixing and curing conditions were optimized in order to obtain the highest possible value of the glass transition temperature (T_g), which is generally in close agreement with the available literature data. No residual cure exotherm was found in DSC traces which were used to determine T_g (sample weight: 5 ± 1 mg; scanning rate: 20 K min^{-1}).

Measurements. Density measurements were made by picnometry, flotation in heptane–carbon tetrachloride mixtures, and column density gradient measurements which gave results in good agreement. The cubic expansion coefficient αg was determined for some systems from the linear coefficient of expansion measured by the classical method (AFNOR NFT 51221), in the 20–100°C range, e.g., at least 50°C below T_g.

DETERMINATION OF THE PACKING DENSITY

"Monomer Unit". For the calculations, we chose the smallest structural unit containing an integer of groups, for instance, two DGEBA and one diamine units or four TGAP and three diamine units. In the case of TGMDA systems, it was supposed that the TGMDA impurities are mainly oligomers containing ether links or molecules with a similar structure as previously found.[14] Two alternative hypothesis were taken to determine their crosslink density n:

(i) All impurities are oligomers which participate in crosslinking (CH crosslink points resulting from the epoxide–epoxide reaction). In this case,

$$n_1 = \frac{4}{M_e + xM_a}$$

where M_e is the molar weight of pure TGMDA, M_a the molar weight of the diamine, and x the molar fraction of diamine ($x = 0.84$ since the epoxide index is 84% of its theoretical value).

(ii) All the impurities are inactive in crosslinking. Then,

$$n_2 = \frac{4x}{M_e + xM_a}$$

Both hypotheses will be considered.

Van der Waals Volume V_w. V_w was obtained by summation of the molar group contributions given by Bondi.[12] No decrement for hydrogen bonding ($\delta V_w \leq 2$ cm^3/mol) was applied.

Packing Density at 293 K. It is given by

$$\rho^* = \rho \frac{V_w}{M}$$

where ρ is the density measured at 293 K and M the molar weight of the "monomer unit."

Packing Densities at 0 K and T_g. They were determined by extrapolation using the linear model of volume expansion:

$$\rho^*_{(0\,K)} = \rho^*_{(T)}(1 + \alpha T)$$

Linear Polymers. The packing densities at 293 K, 0 K, and T_g were determined from the data of several authors and suppliers; the corresponding references can be found in the tables of results.

Some characteristics of the systems under study are given in Table I.

RESULTS AND DISCUSSION

The results are summarized in Table II. The packing density at 293 K of epoxy networks is higher than for linear polymers except hydrogen-bonded ones. It seems to increase with the crosslink density (Fig. 1) and reaches the level of crystalline linear polymers-average value ρ^*_c (298 K) $\simeq 0.69$.[15] These data cannot be interpreted in terms of structure–property relationships since the glass transition temperature, the expansivity, and the presence of hydrogen bonds have an obvious influence on the packing density at 293 K.

We determined for some samples the packing densities at 0 K and T_g (Table II). These results call for the following comments:

(a) The packing densities of linear polymers are in the following order: poly(vinyl alcohol) > polyamide > non-hydrogen-bonded polymers. It seems clear that the hydrogen bond or the cohesive energy density play an important role.

(b) Practically the same hierarchy is found at T_g, but the differences are attenuated, which is not surprising if we consider the well-known rules based on the pseudoconstancy of the free volume excess at T_g.[16] For the chosen series, $\rho^*(T_g)$ is an almost linear function of $\rho^*(0$ K) (Fig. 2). However, considering the small number of polymers under study, this could be fortuitous.

(c) The packing densities at 0 K of the networks under study are higher than those of non-hydrogen-bonded polymers and practically equal or slightly lower than those of polyamides. $\rho^*(0$ K) is higher for networks containing aliphatic segments (DGEBA–DAk) than for the corresponding aromatic systems.

(d) The packing densities at T_g of networks are noticeably higher than those of linear polymers having comparable packing densities at 0 K. In a $[\rho^*(T_g)–\rho^*(0$ K)] plot (Fig. 2) networks and linear polymers constitute well-distinguishable families. It can be thus presumed that crosslinking has a

TABLE I
Degree of Polymerization of the Diepoxide; Theoretical Concentration of Hydrogen Bonding Groups and Crosslink Density; Molar Weight and Van der Waals Volume of the Monomer Unit: Expansivity in Glassy State and Glass Transition Temperature[a]

System	j	[NH] or [OH] (mol/kg)	n (mol/kg)	M (g/mol)	V_w (cm³/mol)	α (10^6 K^{-1})	T_g (K)
DGEBA–DDM	0.14	4.47	2.09	958	541	177	451
DGEBA–PDA	0.14	4.93	2.30	868	487	—	451
DGEBA–DDS	0.14	4.25	1.98	1008	551	—	490
DGEBA–DDS	0.38	4.16	1.75	1145	628	153	453
DGEBA–DA4	0	5.21	2.60	768	440	260 (21)	392
DGEBA–DA6	0	5.03	2.51	796	461	272 (21)	380
DGEBA–DA12	0	4.54	2.27	880	522	281 (21)	368
DGEBF–DDM	0	4.87	2.43	822	455	144	430
DGEBF–DDS	0	4.51	2.29	872	465	144	456
DGEBD–DDS	0	6.13	3.07	652	353	—	351
TGAP–DDM	—	7.05	5.88	1702	945	144	494
TGAP–DDS	—	6.48	5.40	1852	976	—	523
TGMDA–DDM	—	5.71	6.25 ± 0.5	588	333	144	505
TGMDA–PDA	—	6.55	7.1 ± 0.7	513	288	144	507
PS	—	0	0	104	62.85	180 (22)	370
PVAC	—	0	0	86	45.88	214 (22)	303 (22)
PVC	—	0	0	62.5	28.63	210 (22)	353
PMMA	—	0	0	100	56.10	269 (15)	398
PC	—	0	0	254	136.21	200 (23)	423
PSU	—	0	0	442	231.65	168 (24)	463
PESU	—	0	0	232	110.64	165 (25)	483
PA12	—	5.08	0	197	132.31	376 (15)	310 (15)
PA11	—	5.46	0	183	122.08	363 (15)	314 (15)
PA8	—	7.09	0	141	91.39	322 (15)	324 (15)
PA6	—	8.85	0	113	70.93	292 (15)	348 (15)
PVAL	—	22.72	0	44	25.05	378 (15)	372 (15)

[a] The references are given in parentheses. Abbreviations: for epoxy systems, see Experimental part. PS = polystyrene; PVAC-poly(vinyl acetate); PVC = poly(vinyl chloride); PMMA = poly(methyl methacrylate); PC = polycarbonate; PSU = polysulfone containing the bisphenol A unit; PESU-polyethersulfone; PAj = polyamide j; PVAL = poly(vinyl alcohol).
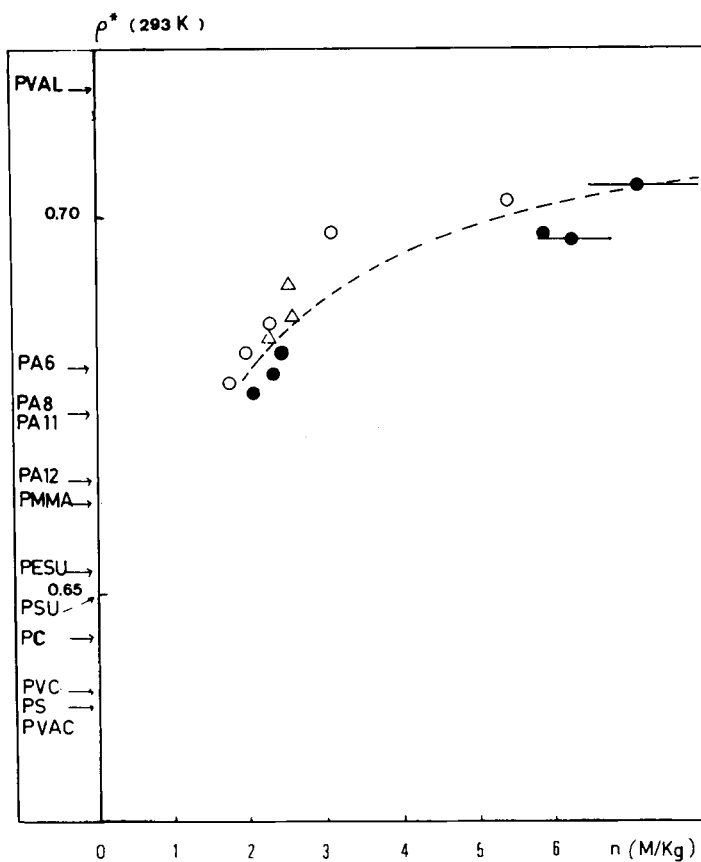
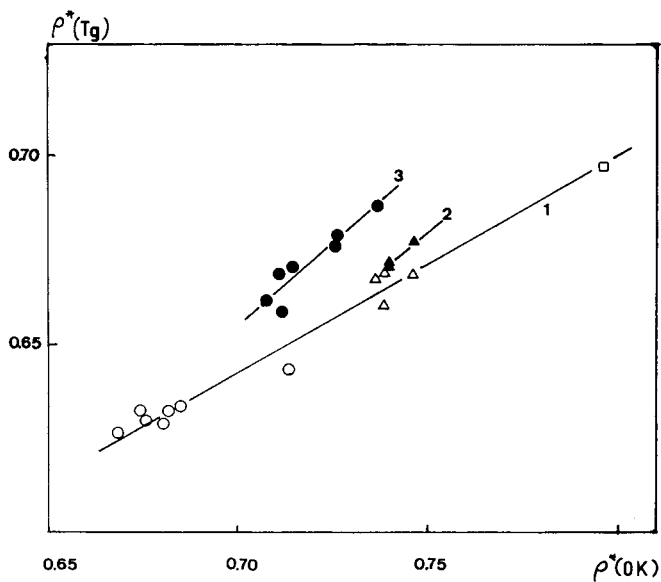Fig. 1.   Packing density at 293 K vs. crosslink density: (●) DDM and PDA systems; (○) DDS systems; (△) DAk systems.

Fig. 2.   Packing density at T_g vs. packing density at 0 K: (1) linear polymers; (2) DGEBA–DAk; (3) other networks; (○) non-hydrogen-bonded polymers; (△) polyamides; (□) PVAL.

TABLE II
Density at Ambient Temperature; Packing Density at 293 K, 0 K, and T_g

System	ρ	ρ^* (293 K)	ρ^* (0 K)	ρ^* (T_g)
DGEBA–DDM	1.199	0.677	0.712	0.659
DGEBA–PDA	1.210	0.679	—	—
DGEBA–DDS	1.247	0.682	—	—
DGEBA–DDS	1.236	0.678	0.708	0.662
DGEBA–DA4	1.199	0.687	0.740	0.672
DGEBA–DA6	1.206	0.691	0.746	0.678
DGEBA–DA12	1.153	0.684	0.740	0.671
DGEBF–DDM	1.232	0.682	0.711	0.669
DGEBF–DDS	1.285	0.686	0.715	0.671
TGAP–DDM	1.256	0.698	0.727	0.679
TGAP–DDS	1.332	0.702	—	—
TGMDA–DDM	1.233	0.697	0.726	0.677
TGMDA–PDA	1.255	0.704	0.737	0.687
DGEBD–DDS	1.287	0.698	—	—
PS	1.05 (15)	0.635	0.669	0.627
PVAC	1.19 (15)	0.635	0.675	0.632
PVC	1.39 (15)	0.637	0.676	0.630
PMMA	1.18	0.662	0.714	0.644
PC	1.20 (23)	0.644	0.681	0.629
PSU	1.24 (24)	0.650	0.682	0.633
PESU	1.37 (25)	0.653	0.685	0.634
PA12	0.99 (15)	0.665	0.738	0.661
PA11	1.01 (15)	0.674	0.746	0.669
PA8	1.04 (15)	0.674	0.736	0.668
PA6	1.084 (15)	0.680	0.738	0.670
PVAL	1.26 (15)	0.717	0.796	0.698

[a] The references are given in brackets. Same abbreviations as in Table I.

specific influence on the volumetric properties. It must be observed that the application of a negative decrement δV_w for hydrogen bonding[12] would displace the representative points of epoxies and polyamides in the plot of Figure 2, but would preserve the differences existing between both families.

Since the effects of hydrogen bonding seem to be important and since, in the networks under study, the concentration in groups able to establish hydrogen bridges (hydroxyls) increases more or less regularly with the cross-link density (Table I), it is relatively difficult to determine the specific influence of this latter parameter. It seemed to us interesting to plot in Figure 3 $\rho^*(T_g)$ and $\rho^*(0$ K) against the concentration in species able to establish hydrogen bonds: —OH or >NH. No significant influence of crosslinking can be seen on $\rho^*(0$ K) which seems to depend essentially on hydrogen bonding and aromatic content (DA 12 > DDM). In contrast, $\rho^*(T_g)$ is slightly higher for the networks than for the corresponding linear polymers and the difference increases with the crosslink density. Such an approach could be questioned since the nature of hydrogen bonding groups and the strength of hydrogen bonds were not taken into account. However, considerations of cohesive energy density (e.g., of solubility parameter[15,17]) would lead to similar conclusions.
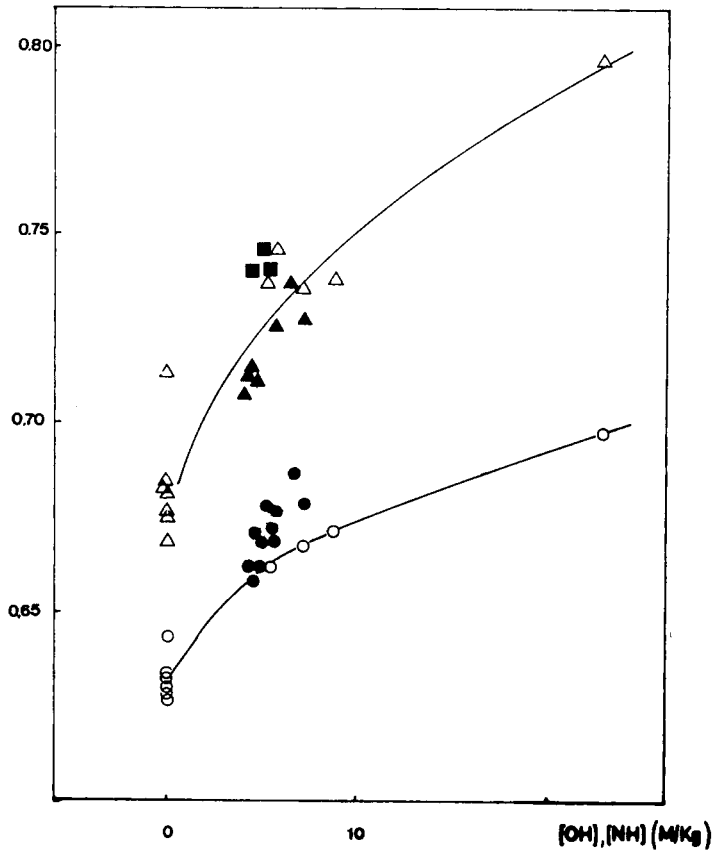
Fig. 3. Packing density at T_g (○,●) and at 0 K (△,▲,■) for linear polymers (○,△) and networks (●,▲, ■): (■) DGEBA–DAk.
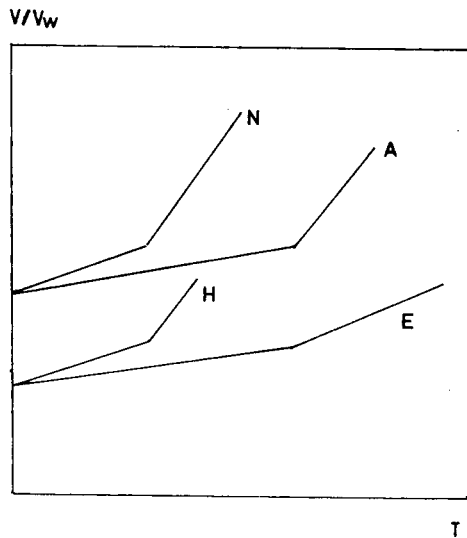

Fig. 4. Schematic representation of the $(V/V_w - T)$ plot for four types of polymers having the same glass transition temperature or the same packing density at 0 K: (E) epoxide–amine network; (H) hydrogen-bonded aliphatic polymer; (A) aromatic skeleton linear polymer without hydrogen bonds; (N) aliphatic linear polymer without hydrogen bonds.

Finally, the differences between the volumetric properties of epoxide–amine networks (E), aromatic skeleton linear polymers having almost the same glass transition temperature (A), and aliphatic linear polymers with (H) or without (N) hydrogen bonds are schematically represented on Figure 4. It should be noted that the packing densities of networks are 4–8% higher than those of aromatic linear polymers having the same T_g, whereas these latter (for instance, polysulfones) have in certain cases higher densities.

The crosslinking was shown to have a small increasing effect (relatively hydrogen bonding), on the packing density at T_g. Indeed, such an effect will be enhanced at ambient temperature, due to the fact that crosslinking increases T_g and decreases expansivity. These results seem contradictory with those of density measurements on incompletely cured or nonstoichiometric systems.[4,5,9] However, the following remarks can be made concerning these latter:

(i) A density decrease is not necessarily lacking in consistency with a packing density increase as shown by calculation for the DGEBA–PDA system.[18]

(ii) For homologue series based on completely crosslinked systems in which the crosslink density is varied by using diepoxides differing by their degree of polymerization[19] or aniline a chain extender,[20] the density increases with the crosslink density.

Our results put in evidence an important peculiarity of epoxide–amine networks: Their cohesive properties, in which hydrogen bonding plays probably a very important role, increase at the same time as their crosslink density, at least for the most common structural series, making difficult any study of structure–property relationships in glassy state. Other problems can arise from the possible existence of a morphological heterogeneity[19] and the occurrence of a volume relaxation (physical aging), which can lead to variations of the packing density from one sample to another one, differing by their thermal history. It can be, however, observed that, for a given system, the density values differ slightly from an author to another, for instance, Ref. 19 and this work for DGEBA–DDM, or Ref. 4 and 20 for DGEBA–PDA. Moreover, density measurements during physical aging showed variations at the third decimal level only.[13]

Thus, it can be concluded that epoxide–amine networks are densely packed and that their packing density increases mainly with hydrogen bonding (or cohesive energy density), but also with the crosslink density which seems to have a specific influence on the glass transition temperature.

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