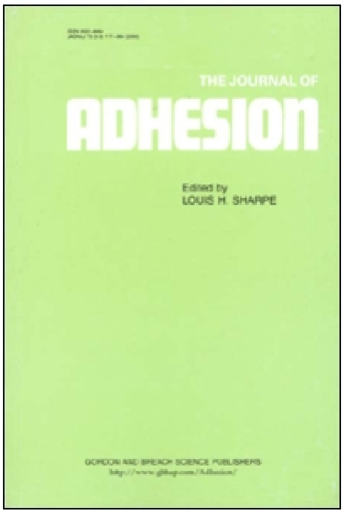


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Thermoset Matrices for Structural Adhesives: Imidazole-Catalysed Curing of Epoxy Resins

Jürgen Vogt[a]
[a] Ciba-Geigy SA, Research Centre Plastics and Additives, Fribourg, Switzerland

To cite this Article Vogt, Jürgen(1987) 'Thermoset Matrices for Structural Adhesives: Imidazole-Catalysed Curing of Epoxy Resins', The Journal of Adhesion, 22: 2, 139 — 151

To link to this Article: DOI: 10.1080/00218468708074997

URL: http://dx.doi.org/10.1080/00218468708074997

J. Adhesion, 1987, Vol. 22, pp. 139–151
Photocopying permitted by license only

Printed in the United Kingdom

Thermoset Matrices for Structural Adhesives: Imidazole-Catalysed Curing of Epoxy Resins†

JÜRGEN VOGT

Ciba-Geigy SA, Research Centre Plastics and Additives, CH 1701 Fribourg, Switzerland

(Received October 24, 1986)

The thermoset epoxy systems of diglycidyl ether of bisphenol-A (DGEBA) and different imidazoles (unsubstituted imidazole, N-methyl-im., 2-methyl-im., 4(5)-methyl-im., 2-ethyl,4-methyl-im., 2-ethyl-im., 2-phenyl-im.) as catalytical curing agents were characterized. From microcalorimetric experiments it was deduced that each molecule of imidazole induces more than 20 epoxy groups to undergo polyaddition. Therefore, optimum glass transition temperature-ranges can be obtained with 0.025 to 0.05 mol of catalyst/equivalent of epoxy. The different alkyl- and aryl-substituted imidazoles show rather similar catalytic effects, with the kinetics differing by a factor of 3 at most. Mechanical properties (flexural modulus and strength, ultimate strain and fracture toughness) at ambient temperature do not correlate with the crosslinking density of the polymer network.

KEY WORDS Imidazoles; catalysed curing; epoxy resins; mechanical properties; structural adhesives; thermoset matrices.

INTRODUCTION

Structural bonding with organic adhesives is now accepted in many industries as a viable joining method. Adhesives based on epoxide resins are versatile materials mainly because of the following

---

† Presented at the Tenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 22–27, 1987.

advantages:

- —good adhesion to many substrates
- —cure without evolution of volatiles
- —adaptable, by formulation, to various application forms, cure conditions and performance properties
- —good resistance to chemical and environmental exposure.

With the great number of possible combinations of formulation components and their relative amounts on one hand, and the legion of possible applications, substrates and designs on the other hand, a countless number of tests would be necessary to find the optimal adhesive system for a specific application. To avoid unlimited testing, some sort of basis set of material data for each principal adhesion formulation might be sufficient to choose an appropriate system and to supply property data for computer-aided construction and design programs.

In this work, the basic physico-chemistry of a rather simple thermoset epoxy resin system is correlated with its materials science data. Some more practical-application-oriented adhesive systems are dealt with in an accompanying paper.[1]

EXPERIMENTAL

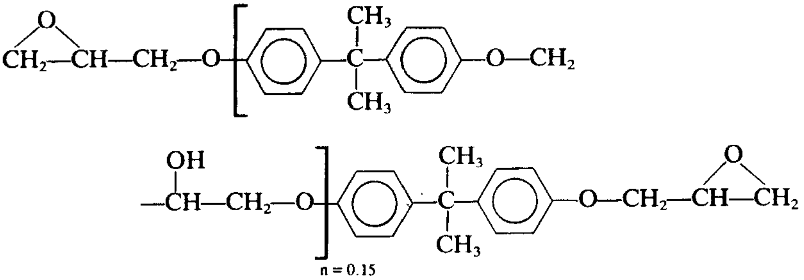
Materials and methods

DGEBA (Araldite GY 250, Ciba-Geigy), Im (Fluka), N–Me–Im (Araldite DY 070, Ciba-Geigy), 2-Me–Im, 4(5)-Me–Im, 2-Et,4-Me–Im, 2-Et–Im (Aldrich) and 2-Phe–Im (Merck) were used as supplied. Resin/catalyst mixtures were prepared at 30 to 50°C, vacuum degassed and cured in aluminum moulds using a forced air circulation oven. Microcalorimetric measurements were performed on a DuPont TA 9000 Thermoanalyser System, dynamic scans at 10 K/min. For dynamic mechanical analysis, a Lonza Torsional Pendulum was used at a heating rate of 1 K/min. Mechanical tests were performed at room temperature on a Schenck servohydraulic testing equipment. Test specimens were cut from 1 and 4 mm sheets. Fracture toughness was determined on the compact tension specimen[8] of dimension 26 × 26 × 4 mm.

RESULTS

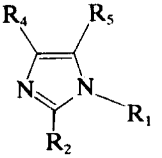
Imidazole-catalysed cure of epoxy resin

In order to illustrate the dependence of polymer physical and mechanical properties on formulation and cure cycle parameters, we studied the thermoset system of a basic commercial epoxy resin, diglycidyl ether of bisphenol-A (DGEBA, Araldite GY 250, Ciba-Geigy),



(1)

and a series of catalytic hardeners, in our case several substituted imidazoles (Table I).



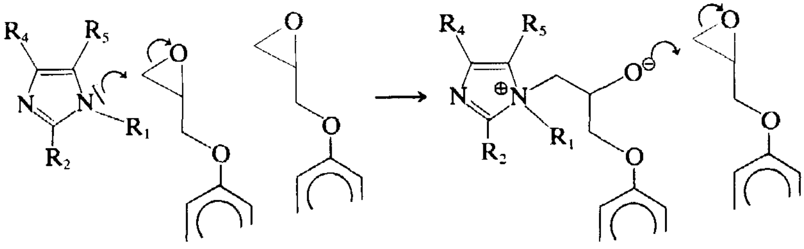
(2)

TABLE I
Substituted imidazoles used as catalytic curing agents

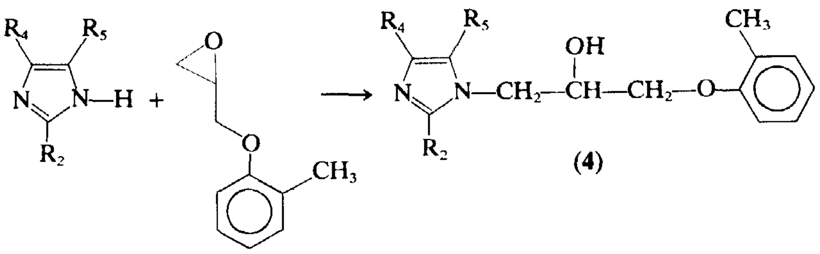
Designation	R_1	R_2	R_4	(R_5)
Im	H	H	H	H
N-Me-Im	CH_3	H	H	H
2-Me-Im	H	CH_3	H	H
4(5)-Me-Im	H	H	CH_3	H
2-Et,4-Me-Im	H	C_2H_5	CH_3	H
2-Et-Im	H	C_2H_5	H	H
2-Phe-Im	H	C_6H_5	H	H

Although the imidazoles are well known epoxy curing agents, systematic work has been published predominantly on the reaction with non-crosslinking, monofunctional epoxies such as phenyl glycidyl ether[2–4] or *p*-cresol glycidyl ether[5] with emphasis on the elucidation of the reaction mechanism. Some data were published on the imidazole cure of technically relevant epoxies,[6] mainly discussing the kinetics, but giving only few data on their mechanical behaviour.

Polyaddition of glycidyl ether compounds is induced by imidazole through nucleophilic addition to the epoxide ring, thereby forming the t-amine-alcoholate intermediate 3 as chain propagating species.[3] For N-unsubstituted imidazoles, the primary reaction is the addition of the imidazole to an epoxy ring to form the N-substituted imidazole 4, which then acts as the catalytically active species.[1,3] This primary addition of N-unsubstituted imidazoles can be detected in the dynamic DSC-experiment as an exothermic peak at lower temperatures than the onset of the principal polyaddition reaction (Figure 1, upper trace). This extra peak disappears (Figure 1, lower trace), if a 1:1 molar adduct of the unsubstituted imidazole and a monofunctional epoxy compound such as *o*-cresol glycidyl ether is used as catalyst 4. The secondary hydroxyl groups in, *e.g.*, 1 and 4 act as co-catalysts.[5]



(3)



(4)

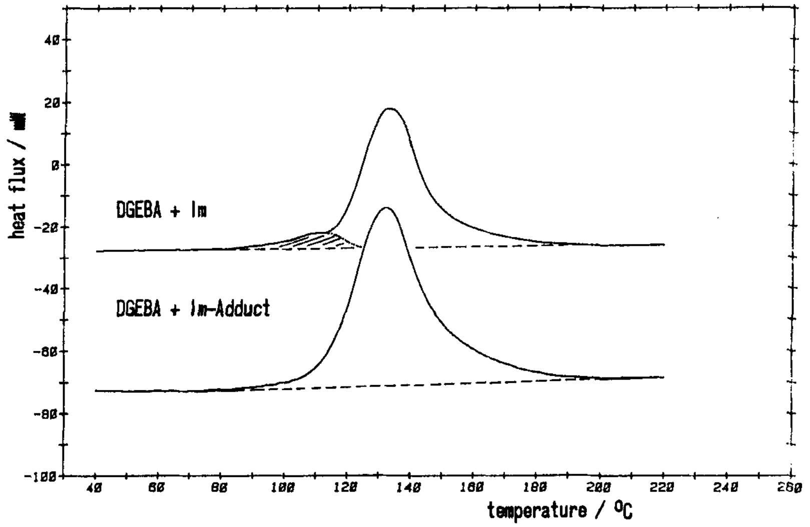


FIGURE 1 Differential scanning calorimetric characterization of the DGEBA polyaddition induced by Im (upper trace) and the Im/o-cresol glycidyl ether adduct (lower trace).

Dynamic cure (10 K/min), in the DSC instrument, of DGEBA with different amounts of catalyst, reveal that under these conditions up to about 20 epoxy groups can be induced to undergo polyaddition by one molecule of imidazole. This ratio corresponds to a catalyst concentration of 0.05 mol/equiv. of epoxy. As can be deduced from the dependence of heats of reaction on catalyst concentration (Figure 2), more than 0.05 mol catalyst/equiv. of epoxy give fully cured systems yielding 99 ± 5 kJ/equiv. of epoxy (*cf.* dotted curve in Figure 2). This value is rather close to 92 kJ/equiv. of epoxy reported for the t-amine catalyzed epoxy polyaddition.[7]

Below the optimum catalyst concentration, the heat of reaction per mol of catalyst remains rather constant near 2000 kJ/mol, indicating that although more than 20 reactive epoxy groups are present per molecule of imidazole, the excess remains unreacted. This is accompanied by a decrease in the glass transition temperature-range Tg (Figure 3). The Tg also decreases at catalyst concentrations higher than 0.05 mol/equiv. of epoxy (Figure 3), due

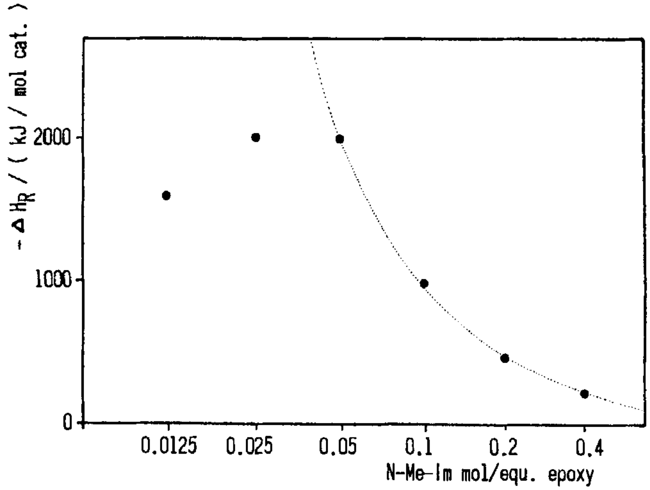


FIGURE 2 DGEBA polyaddition catalysed by N—Me—Im. Heats of reaction per mol catalyst in function of catalyst concentration.

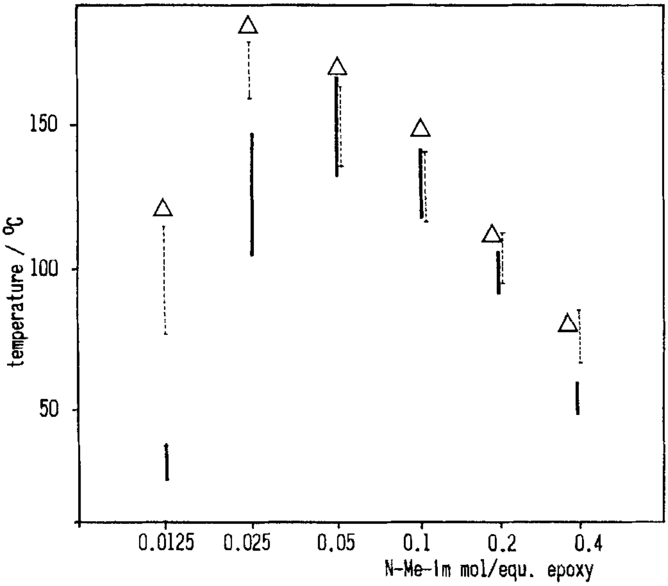


FIGURE 3 DGEBA polyaddition catalysed by N—Me—Im. Glass transition temperatures after dynamic cure (10 K/min, ———), after cure cycle 6h 80°C + 4h 180°C determined by DSC (- - - -) and DMA (max. of loss factor, Δ).

to the fact that each molecule of imidazole acts as a chain end group, thereby lowering the crosslinking density.

With a different curing cycle (slow gelation at 80°C, 6 h, and post-cure at 180°C, 4 h), slightly higher Tg values can be obtained. The conversion per mol of catalyst can be increased, resulting in high Tg ranges with 0.025 mol cat./equiv. of epoxy (Figure 3).

For comparison, the dynamic mechanical characterizations of DGEBA resin cured with different concentrations of N–Me–Im are given in Figure 4. These results are in agreement with the microcalorimetric data discussed above. As expected, the increasing crosslinking density leading to a higher Tg is also reflected in an increased shear modulus above Tg. Furthermore, the maximum of the loss factor with temperature essentially coincides with the corresponding upper limit of the calorimetrically determined Tg-range (*cf.* Figure 3). For all catalyst concentrations a broad β-relaxation is observed near −60°C.

This type of catalyst-concentration effect on the cure of DGEBA is typical of all imidazoles studied. The Tg ranges obtained after dynamic cure with 0.05 mol cat./equiv. of epoxy are depicted in Figure 5. The rather similar Tg ranges indicate that the different alkyl or aryl substituents do not have an important influence on the

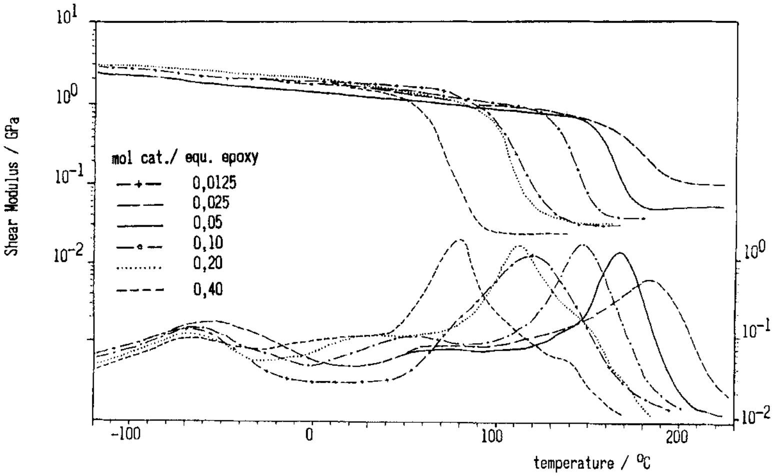


FIGURE 4 DGEBA polyaddition catalysed by N—Me—Im. Effect of catalyst concentration on complex shear modulus.

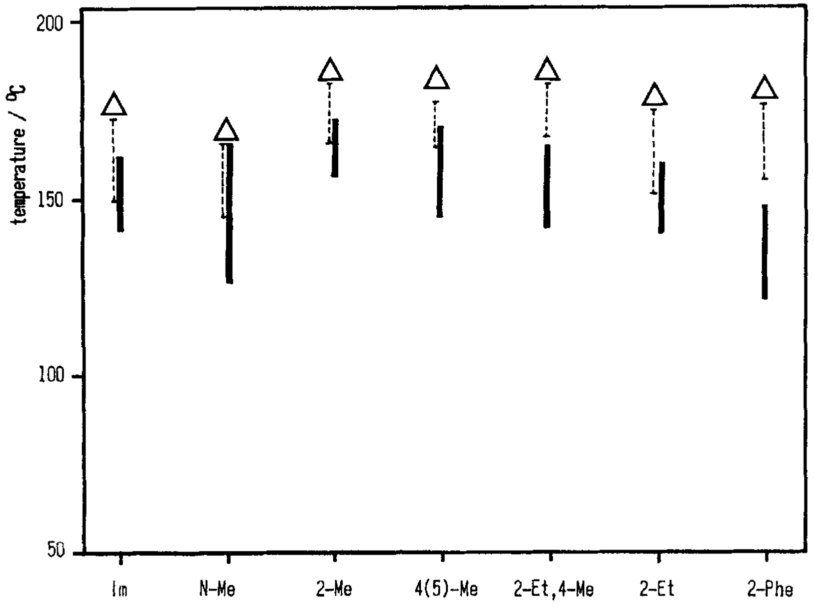


FIGURE 5 DGEBA polyaddition catalysed by different imidazoles. Glass transition temperatures obtained with 0.05 mol cat./equ. epoxy (designation as in Fig. 3).

network structure. Some minor substituent effects were observed on the polyaddition kinetics, resulting in gel times differing at most by a factor of 3 (Figure 6). From the Arrhenius plot of the temperature dependence of gel times (Figure 6), overall activation energies for gelation can be determined (Table II). The close similarity of the activation energies observed using various imidazole derivatives is taken to indicate a common reaction mechanism.

The similarity of cure induced by the different imidazoles also becomes evident from the corresponding dynamic mechanical analysis data. In Figure 7, the temperature dependence of shear modulus and loss factor of the DGEBA/imidazole systems are shown. These data reveal that up to 150°C the complex shear modulus is essentially independent of the type of imidazole. Only above this temperature do small differences in Tg differentiate the systems under study.

Most often the glass transition temperature is chosen as the main criterion for the development of thermosets, although their usual

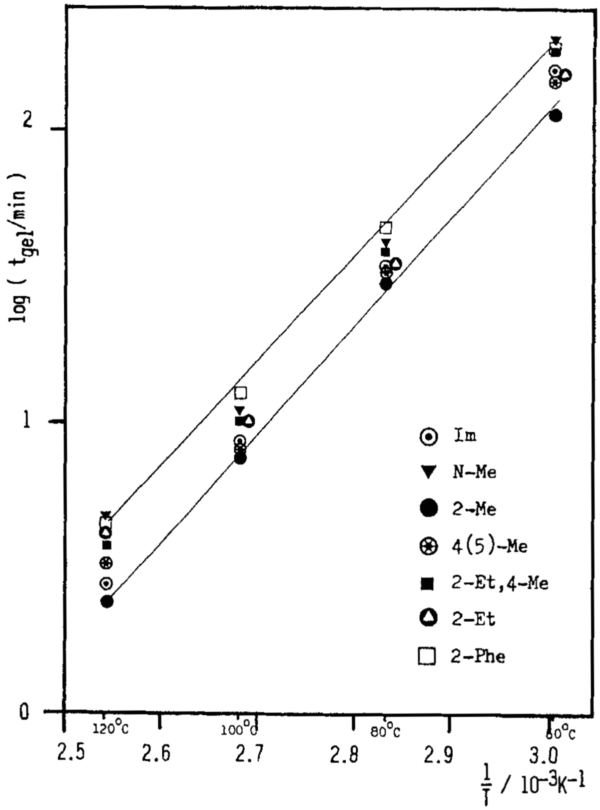


FIGURE 6 Arrhenius-plot of gel times (DGEBA + 0.05 mol. cat./equ. epoxy).

TABLE II
Activation energies for imidazole-catalyzed epoxy polyaddition from gel times (*cf.* Figure 6)

Catalyst	E_a/kJ/mol
Im	70
N–Me–Im	71
2-Me–Im	74
4(5)-Me–Im	75
2-Et,4-Me–Im	71
2-Et-Im	66
2-Phe-Im	68

application in adhesives or engineering plastics occurs at temperatures much below Tg. As is demonstrated with the series of different concentrations of N–Me–Im and DGEBA, quite a range of different Tgs and, therefore, different polymer network properties are "adjustable". Though, important material properties such as the flexural modulus E and the flexural strength σ show a non-monotonic dependence on Tg, as becomes evident from the data in Figure 8. E and σ have a common behaviour in dependence on catalyst concentration with an apparent local minimum at 0.025mol cat./equiv. of epoxy, where the Tg has its maximum. Below that concentration, E and σ rise, although the polymer network is poorly crosslinked due to more unreacted epoxy groups. Both E and σ reach their local maximum at 0.2 mol cat./equiv. of epoxy, where Tg has an intermediate value. Surprisingly enough, the specific mass ρ (Figure 8) of the cured resin follows the catalyst concentration dependence of E and σ, indicating that at temperatures much below Tg, the packing density of polymer segments determines E and σ. The packing density in this temperature range depends only rather indirectly on the crosslinking density.

At the highest crosslinking density (slow cure, 0.025 mol cat./equiv. of epoxy, maximum Tg), the free volume reaches its

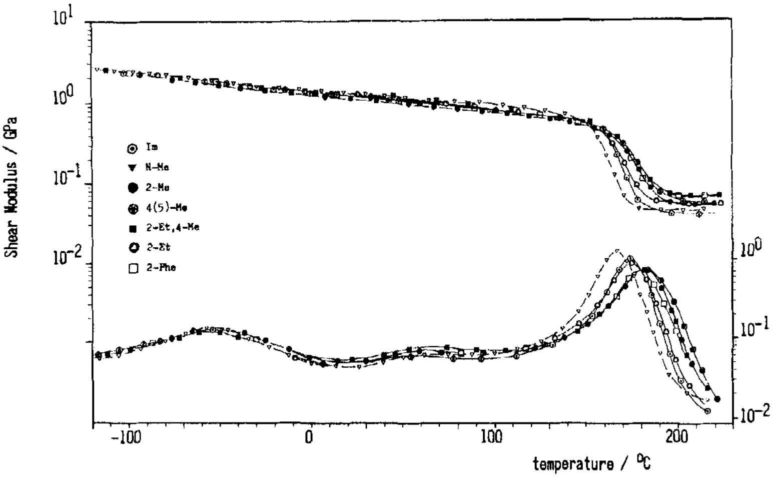


FIGURE 7 DGEBA polyaddition catalysed by different imidazoles. DGEBA + 0.05 mol cat./equ. epoxy, cure 6h 80°C + 4h 180°C, dynamic mechanical analysis.

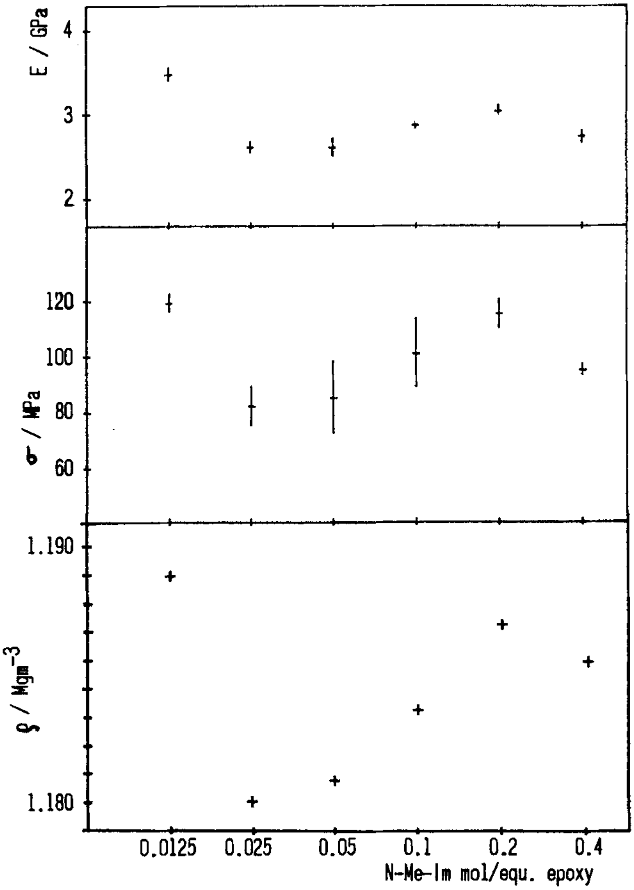


FIGURE 8 DGEBA/N—Me—Im, cure 6h 80°C + 4h 180°C. Effect of catalyst concentration on flexural modulus E, flexural strength σ and specific mass ρ.

maximum due to the high built-in disorder of the polymer network. With decreasing cross-linking density, obtained at higher or lower catalyst concentrations, the polymer segments can relax, due to their higher mobility, into a more closely packed structure. Above 0.2 mol cat./equiv. of epoxy, the specific mass of the cured resin drops again, most probably due to the large portion of the low density catalyst ρ(N–Me–Im, 23°C) = 1.04 Mg/m^3, against ρ(DGEBA, 23°C) = 1.17 Mg/m^3.

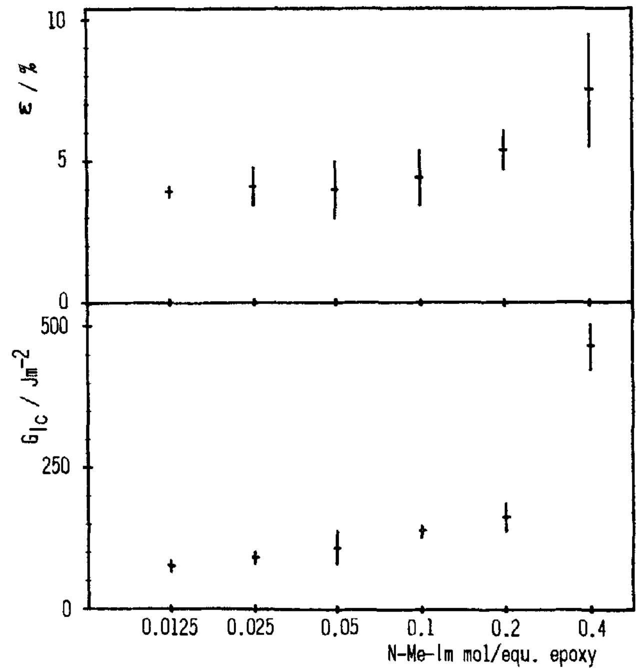


FIGURE 9 DGEBA/N—Me—Im, cure 6h 80°C + 4h 180°C. Effect of catalyst concentration on ultimate strain ε and fracture toughness G_{Ic}.

The effect of catalyst concentration upon ultimate strain and fracture toughness takes again a different course (Figure 9). Both properties are fairly constant or only slowly rising over the range 0.025 to 0.1 mol cat./equiv. of epoxy, with a sharp increase above 0.2 mol cat./equiv. of epoxy. This behaviour can be rationalized considering the increasing number of imidazole-terminated polymer segments fixed to the network only with one end. They increase the plasticity through orientation and chain sliding during deformation while simultaneously lowering the Tg, as discussed above.

CONCLUSIONS

In conclusion, the seemingly simple system of DGEBA and different amounts of imidazole catalysts reveal rather complicated dependencies between the polymer physical data and the macroscopic mechanical properties. Since practical applications need well-chosen optimizations of several material properties, the knowledge of such dependencies and their intercorrelations help considerably to reduce effort and time for the development of adhesives or engineering plastics specifically adapted to a certain performance profile.

Acknowledgement

Specimen preparation and careful measurements by Mrs. C. Irrgang, Mrs. E. Pürro and Dr. K. Jud are gratefully acknowledged.

References

1. U. T. Kreibich and A. F. Marcantonio, paper presented at the Tenth Annual Meeting of The Adhesion Society, Williamsburg, Virginia 1987, *J. Adhesion* **22,** 153–165 (1987).
2. A. Farkas and P. F. Strohm, *J. Appl. Polym. Sci.* **12,** 159 (1968).
3. F. Ricciardi, M. M. Jouille, W. A. Romanchick and A. A. Griscavage, *J. Polym. Sci. Polym. Lett. Ed.* **20,** 127 (1982).
4. F. Ricciardi, W. A. Romanchick and M. M. Jouille, *J. Polym. Sci. Polym. Chem. Ed.* **21,** 1475 (1983).
5. J. Berger and F. Lohse, *J. Appl. Polym. Sci.* **30,** 531 (1985).
6. W. A. Harding and S. H. Christie, *Amer. Chem. Soc., Div. of Organic Coatings and Plastics Chemistry Preprints* **24**(2), 309 (1964); T. J. Dearlove, *J. Appl. Polym. Sci.* **14,** 1615 (1970); C. A. Glandt and J. K. Gillham, *Amer. Chem. Soc., Div. of Polym. Chem. Preprints,* **16**(1), 694 (1975).
7. H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw-Hill, New York, 1967), Chap. 6.
8. A. J. Kinloch and R. J. Young, *Fracture Behaviour of Polymers* (Elsevier, London, 1983), Chap. 3.