

PATENT SPECIFICATION

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(19)



(54) METHOD OF CURING EPOXY-POLYMERS

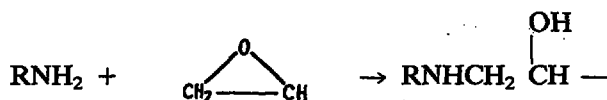
(71) We, THE UNIVERSITY OF MALAYA, a Body Corporate of Malaysia, of Kuala Lumpur, Malaysia do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a method of curing epoxy polymers and epoxidised polymers.

Generally epoxy prepolymers are crosslinked (hardened) with reagents of the type:

- (1) Tertiary amines
- (2) Mono- and poly-functional primary and secondary amines
- (3) Acid anhydrides.

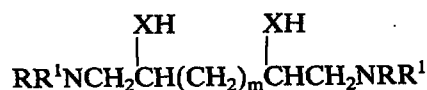
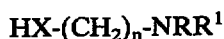
The present invention relates to crosslinking by classes (1) and (2) above. In both classes crosslinking is initiated by ring opening of an epoxy group, e.g.:

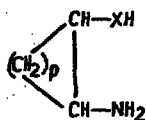


The initial epoxide ring opening reaction also occurring with secondary and tertiary amines.

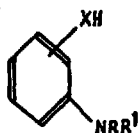
It is well known that such reactions can be accelerated by proton donors such as hydroxy groups in the epoxy resin, or by water or by added donors such as phenols. This invention concerns the activation of the above reaction and is brought about by proton donors which are an integral constituent of the amine hardener, specifically by amines containing weakly acidic α , β or γ substituents.

The present invention provides a method of curing an oligomer or polymer containing epoxy groups which method comprises mixing the oligomer or polymer with, as a curing agent, an effective amount of a compound having a primary, secondary or tertiary amino group and in a position α , β or γ to the amino group, a weakly acidic group selected from -OH, -SH, -SeH, and -CONH₂ and maintaining the mixture until curing has taken place, wherein the curing agent is a compound having the general formula chosen from the following:-

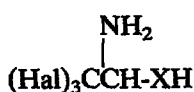




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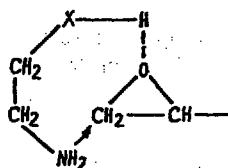
(VI)



(VII)

Wherein $n = 0, 1, 2$, or 3 ; $m = 0-8$; $p = 3-5$; $-\text{XH}$ is $-\text{OH}$, $-\text{SH}$, $-\text{SeH}$, $-\text{CONH}_2$, R and R' are each independently H , alkyl or aryl group, with the proviso that in compound (I), when $-\text{XH}$ is $-\text{OH}$ and n is 2 or 3 and R and R' cannot both be H or an ethyl group; Hal is Cl or Br .

The mode of action of the catalysis appears to involve nucleophilic attack at the epoxide carbon by the amine moiety with concomitant protonation by the weakly acidic functional group, e.g.:



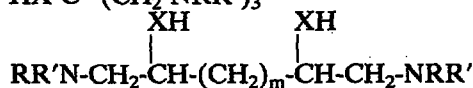
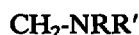
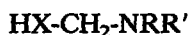
This activation is peculiar to compounds containing the activation group as an integral constituent of the molecule. Thus mixtures of compounds such as $\text{RNH}_2 = \text{RXH}$ are much less reactive towards epoxide than compounds of the type:



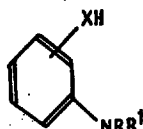
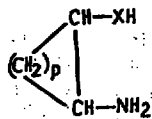
where $n = 0, 1, 2$ or 3 .

A particular example of this type of substituted amine, which has a significant accelerating effect is 2-aminoethanethiol wherein in the formula (1) $n = 2$ and $\text{X} = \text{S}$. Other examples of this type are those wherein $n = 0$ and X is O or S .

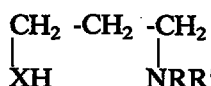
The following types of compound, wherein XH is a weakly acidic group e.g. OH , SH , SeH , $-\text{CONH}_2$; R and R' are each independently hydrogen or an alkyl or aryl group, Hal is Cl or Br , $m = 0-8$, $p = 3-5$, are examples of curing agents which may be used in the present invention:-



(11)



XH

(Hal)₃C-NH₂

A particularly preferred amine for use as a curing agent in the method of the present invention is 2-aminoethanethiol.

The curing reaction may advantageously be carried out at ambient temperature although it can also be induced at higher temperatures. The time taken to effect cure ranges from 1/2 hour to 8 hours depending upon the temperature at which the reaction is conducted. The amount of curing agent used may vary with the molar ratios of curing agent to polymer or prepolymer being from 0.5:1 to 5:1. The preferred ratio is about 2:1.

The following example illustrates the invention.

Example 1

A commercial epoxy resin (CIBA ref: ACACA 17e gy 257) having epoxy equivalent 175 was mixed with 2-aminoethanethiol in the proportions 0.22g of hardener per g of resin. The subsequent adhesive strength was measured on aluminium test pieces having an area of overlap of 1 sq.m. The bond strength was measured by stretching the test sample perpendicularly to the bond in an INSTRON (Registered Trade Mark) tensometer at a pulling rate of 0.5 cm min⁻¹. The results are shown in Table I.

TABLE I

Hardener	Cure Time	Strength
2-aminoethanethiol	6 hours	455 kgf
	2 days	460 kgf

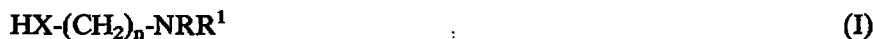
Table I shows that a 2-aminoethanethiol is an effective and rapid hardener for commercial epoxy prepolymers. Comparison with the data for the adhesive formed by use of a conventional amine hardener with the same resin (Table 2) emphasises the effectiveness of the modified hardener for ambient temperature cures.

TABLE 2

Hardener	Cure Time	Strength
Conventional	6 hours	7 kgf
polyamine	2 days	165 kgf
hardener	7 days	260 kgf

WHAT WE CLAIM IS:-

1. A method of curing an oligomer or polymer containing epoxy groups which method comprises mixing the oligomer or polymer with, as a curing agent, an effective amount of a compound having a primary, secondary or tertiary amino group and in a position α , β or γ to the amino group, a weakly acidic group selected from -OH, -SH, -SeH, and -CONH₂ and maintaining the mixture until curing has taken place, wherein the curing agent is a compound having the general formula chosen from the following:-



Wherein $n = 0, 1, 2$, or 3 ; $m = 0-8$; $p = 3-5$; -XH is -OH, -SH, -SeH, -CONH₂, R and R¹ are each independently H, alkyl or aryl group, with the proviso that in compound (I), when -XH is -OH and n is 2 or 3 R and R¹ can not both be H or an ethyl group; Hal is Cl or Br.

2. A method as claimed in Claim 1 wherein the curing agent is 2-aminoethanethiol.
3. A method as claimed in either Claim 1 or Claim 2, wherein the molar ratio of curing agent to polymer or prepolymer is from 0.5:1 to 5:1.
4. A method of curing an oligomer or polymer as claimed in Claim 1 substantially as hereinbefore described.
5. Cured epoxy polymers or epoxy oligomers whenever made by the method claimed in any one of claims 1 to 4.

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