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Reduction of Shrinkage in Epoxy Resins

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Synopsis

Volume changes during curing of an unfilled epoxy resin using a series of anhydrides were measured. It was shown that a significant reduction in shrinkage could be achieved by proper choice of structure.

Shrinkage occurs generally in polymerizations as a logical consequence of forming large molecules from small ones. It amounts to 34% in vinyl polymerization[1] and is as low as 1% when rings are converted to chains.[2] It is fairly low (5–6%) in typical unfilled epoxy resins,[3] but in no case does it appear to be absent. At present there are three general ways to combat this contraction problem. The first[4,5] is to use an inert filler to dilute the effect. The second is to use materials that are liquid at high molecular weights so there will be less change in molecular size going from liquid to solid. Use of Thiokol–epoxy blends affords an example of this type.[4] The third comprises adding a gas-forming agent[4] like isocyanate and a little water to form a slightly foamed polymer. All pay some penalty for the lowered shrinkage.

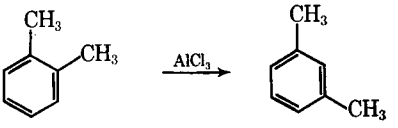
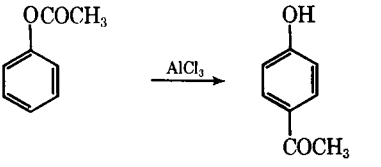
This work was undertaken to determine whether the structure of a crosslinking agent in a typical unfilled epoxy resin could be altered to minimize shrinkage. It is obvious that a low-shrinkage crosslinking reaction must not split off volatile by-products and therefore should be of the type:

$$A + B \rightarrow C$$

A survey of the literature showed that all addition reactions led to contraction, especially where saturation of multiple bonds was involved. In all these cases we are exchanging a double bond for two single bonds, as well as reducing the number of molecules. A few rearrangements as shown in Table I do lead to modest expansion, but it would be difficult to combine a curing reaction with rearrangement. A more practical approach took advantage of the fact that when a ring opens the parts become much more flexible and occupy a larger volume. This should also be the case when a fused cyclohexane ring is converted to a monocyclic form.

Some of these principles were incorporated in a crosslinking agent, and density measurements were made before and after cure. Table II shows

TABLE I[a]

Reaction	Expansion, %
$CH_3CH_2CH_2CH_3 \xrightarrow{AlBr_3} CH_3CH(CH_3)CH_3$	3.4
$CH_3CH(O)CH_2 \xrightarrow{H+} CH_3CH_2CHO$	3.0
$HC(COOEt)=HC(COOEt) \rightarrow EtOOC(CH)=HC(COOEt)$	1.5
	2.0
	ca. 1.5

[a] Densities for reactants and products were obtained from *Lange's Handbook* or Beilstein.

TABLE II

Shrinkage with Various Curing Agents using EPI-Rez 510[a]

Curing agent	Temp., °C.	Density, g./cc.[b] Reactants	Density, g./cc.[b] Product	Shrinkage, %	Hardness[c]
Phthalic anhydride	105	1.1526	1.2229	5.8	24
Tetrahydrophthalic anhydride	105	1.1263	1.1898	5.4	30
Hexahydrophthalic anhydride	105	1.1088	1.1651	4.8	33
Hexahydrophthalic anhydride	80	1.1258	1.1830	4.9	29
Succinic anhydride	105	1.1361	1.2010	5.4	12
Glutaric anhydride	105	1.1206	1.1677	4.0	5
Hexahydrohomophthalic anhydride	80	1.1367	1.1700	2.8	35
Dodecahydrodiphenic anhydride	80	1.1056	1.1334	2.5	27
4-Ketopimelic acid dilactone	80	1.1691	1.2077	3.1	6

[a] One mole of epoxide per mole of curing agent. All samples were cured 20 hr. with 1% pyridine.

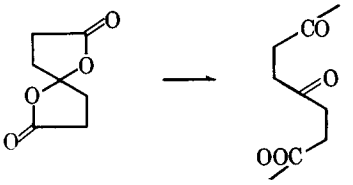
[b] Densities of the liquids were determined by a pycnometer and those of the solids by determining the displaced mercury in a wide mouth pycnometer. All densities were run at curing temperature.

[c] Hardness determined on a Barcol Impressor model GY ZJ 934-1.

the results in the anhydride series. Six-membered glutaric anhydride gave less shrinkage than succinic. In the phthalic anhydride series shrinkage decreased from phthalic to tetrahydrophthalic to hexahydrophthalic, indicating that the cyclohexane ring increased in flexibility when the anhydride opened, occupying a larger volume, whereas the rigid benzene ring did not change. Combination of these two effects was roughly additive, as shown by the low shrinkage of hexahydrohomophthalic anhydride.[6]

A slightly better case, though one which turned out to be rather difficult to synthesize, was perhydrodiphenic anhydride.[7] This compound incorporated formation of two free cyclohexane rings as well as opening a seven-membered anhydride.

4-Ketopimelic acid dilactone, prepared from 4-ketopimelic acid by distillation, has been used as an epoxy curing agent[8] and also causes a reduction in shrinkage. This result may be attributed to the opening of a compact molecule:



These low-shrinkage curing agents have not as yet been used on filled epoxy resins but presumably they will work equally well.

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Résumé

Les variations de volume au cours du traitement d'une résine époxy (non-chargée) au moyen d'une série d'anhydrides ont été mesurées. On montre qu'une réduction significative de retrait peut être obtenue par un choix approprié de la structure.

Zusammenfassung

Volumsänderungen während der Härtung ungefüllter Epoxyharze mit einer Reihe von Anhydriden wurden gemessen. Durch Wahl einer geeigneten Struktur konnte eine wesentliche Herabsetzung der Schrumpfung erreicht werden.

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