CORRELATION OF PHYSICAL AND CHEMICAL PROPERTIES OF ANHYDRIDE-CURED EPOXY RESINS WITH THEORETICAL STRUCTURE

by

Ronald E. Johnson

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
and State University
in partial fulfillment for the degree of
DOCTOR OF PHILOSOPHY

in

Materials Engineering Science

APPROVED:

Dr. A. L. Fricke, Chairman

Dr. J. H. Steele, Jr.

Dr. H. L. Brinson

Dr. C. R. Houska

Dr. T. P. Floridis

September, 1971

Blacksburg, Virginia

ACKNOWLEDGEMENTS

It is impossible to acknowledge all of the many people who have aided this research endeavor by their support and cooperation, but certainly an outstanding few deserve special recognition. This research was made possible with moral, equipment, and financial support of Corning Glass Works, Blacksburg, Virginia; in particular that of Walter Johnston, Process Engineering Supervisor, who permitted me to allocate many hours towards this project. Recognition should also go to Polytron Corporation for unlimited use of their testing equipment, as well as to Humphrey Chemical Company for their special preparation of the alkyl succinic anhydrides. Above all I owe a sincere obligation for the advice and support of Dr. A. L. Fricke who has spent innumerable hours in assistance on this project over the last two years, and for the assistance and cooperation of my wife without whose love and understanding any endeavor on my part would be fruitless.

TABLE OF CONTENTS

TABLES

FIGURES

PREFACE

Epoxy resins are used commercially in a wide variety of applications including floor coatings, adhesives, castings, filament winding, chemical-resistant coatings, and foams. As a class the resins are characterized by their natural adhesiveness, their inherent toughness, and their formulation flexibility which allows the formulator a wide range of properties determined by selection of curing agent, catalyst, gel temperature, and post cure temperature.

Anhydride cured epoxy resins, as compared to epoxy resins cured by other curing agents, are characterized by long pot lives, low exotherm, low toxicity, low viscosity, and a high degree of chemical and thermal resistance. Due to the sluggishness of the epoxy-anhydride reaction, even when a tertiary amine catalyst is employed, the anhydride cured epoxies generally require a two stage heat cure. A lower-temperature cure (50-120°C) for gelation and an elevated-temperature cure (120-250°C) for obtainment of a high cross-linking density. For some low-temperature applications not requiring a high degree of chemical resistance, the post cure is omitted. For chemical-resistant applications and use temperatures in excess of 100°C, however, the post cure is considered essential. Applications for anhydride cured epoxies are, therefore, limited to those for which a two stage heat cure is practical. Major applications include casting, encapsulation, high temperature adhesives, filament wound pipe and tanks, compression molding, preimpregnated fiberglass laminates, tooling, and chemical resistant coatings.

INTRODUCTION

This investigation is an attempt to correlate the theoretical structure of alicyclic dicarboxylic acid anhydride cured epoxy resins with their physical and chemical properties, as well as the maintenance of these properties after elevated temperature exposure. The ultimate goal of such a study is to develop low viscosity resin formulations suitable for use as filament winding resins where long-time maintenance of chemical and physical properties after temperature exposures up to 200°C is of primary importance. It is well established in epoxy resin technology that an increase in cross-linking density or system functionality will generally increase the high temperature strength, chemical resistance, and heat stability of a resin system. Such systems of high cross-linking density, however, are also highly rigid with tensile elongations often one percent or less. For many applications a certain degree of flexibility is required in a resin system and failure at elevated temperatures is often a result of embrittlement rather than thermal degradation. The high rigidity adversely affects such properties as flexural strength and toughness (area under the stress-strain curve) due to increased flaw sensitivity. Rather than judge, therefore, a resin's suitability for high temperature service on the basis of heat distortion temperatures or elevated temperature weight losses, this investigation judges formulations on their ability to maintain flexural properties after high temperature heat aging.

In order to specifically study the effect of the anhydride structure, the basic resin structure, catalyst concentration, and cure temperatures are held constant, while the anhydride structure is systematically varied. A tertiary amine catalyst is employed throughout the investigation so that the mole anhydride to epoxy equivalent ratio can be maintained at 1/1. The anhydrides investigated are related to the basic succinic anhydride structure. Substituted side chains are added to this basic structure; the simplest of which yields methyl succinic anhydride. More complex structures are formed by substituting alkenes onto the basic succinic anhydride structure through reaction with maleic anhydride, thus forming the alkenyl succinic anhydrides. Subsequent hydrogenation of the alkenyl succinic anhydrides yields a second homologous anhydride series, the alkyl succinic anhydrides. Besides variation in the length of these side chains, the chains can be linear or branched depending on the structure of the substituent. When tetrapropylene is reacted with maleic anhydride, for instance, the product is methyl branched dodecenyl succinic anhydride, but when dodecene is the substituent the product is linear dodecenyl succinic anhydride. The alkenyl succinic anhydrides contain inherent unsaturation which can influence anhydride reactivity, as well as the cross-linking density of the cured system. Unsaturation can also be present in the anhydride ring itself as in maleic anhydride. In addition to the single ring alicyclic anhydrides, multi-ring anhydrides are formed which bear definite structural relationships to the single ring anhydrides. These include hexahydrophthalic anhydride, which can be considered the multi-ring equivalent of succinic anhydride; tetrahydrophthalic, the multi-ring equivalent of maleic; and methyl tetrahydrophthalic, the multi-ring equivalent of citraconic. The structure of methyl tetrahydrophthalic anhydride is further modified by the presence of a methylene bridge to create methyl endomethylene tetrahydrophthalic anhydride. Unsaturation inherent in any of the above anhydrides can be reacted with vinyl monomers either thermally or upon addition of an organic peroxide. The vinyl monomer serves the function of a viscosity reducing reactive diluent. Another purpose of this investigation is to determine the effect of these monomers on theoretical structure, as well as on measured properties.

The basic approach of this investigation can be summarized as follows:

a. Testing of the alicyclic dicarboxylic anhydride cured systems of varying structure in regard to their density, flexural strength, flexural modulus, toughness, chemical resistance, and heat distortion temperature. These properties are related to structure in terms of substituted chain length, chain branching, reactivity, unsaturation, etc.. Tensile strength, tensile modulus, and relaxation constants are measured for compositions with heat distortion temperatures too close to room temperature for meaningful flexural property determinations.

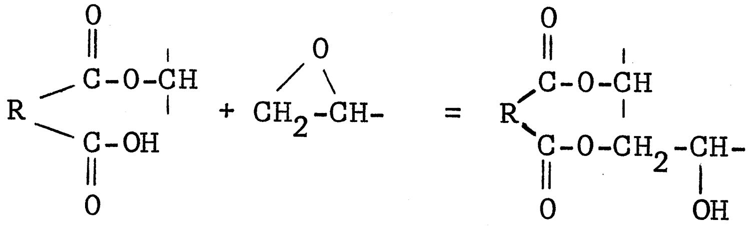
b. Investigation of possible flexibilization of the more brittle structures by utilization of the saturated anhydrides and substituted succinic anhydrides as co-curing agents with the unsaturated anhydrides, such as maleic and methyl tetrahydrophthalic which give highly cross-linked structures. Properties determined are density, flexural strength, flexural modulus, toughness, chemical resistance, and heat distortion temperature.

c. Investigation of the effect of viscosity reducing vinyl monomers reacted into the structure, through the addition of a peroxide catalyst, on cured unsaturated systems. Effect of monomer on viscosity is determined as well as effect on heat distortion temperature, flexural strength, flexural modulus, toughness, density, and chemical resistance.

d. Determination of the effect of aging on the as-cured properties of those formulations which exhibit some potential for high temperature applications. The aging characteristics are also interpreted in terms of the structure of the cured system.

LITERATURE REVIEW

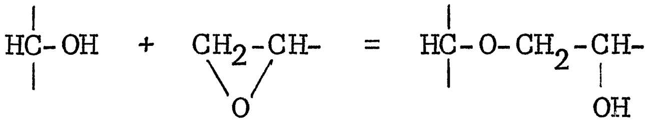
Anhydrides were recognized early in epoxy technology as suitable hardners for glycidyl ether resins.[1] The epoxide-anhydride reaction itself, as well as its catalyzation by tertiary amines, was known even earlier.[2] It was not until the fifties and early sixties, however, that the reaction became thoroughly understood.[3,4,5,6] The reaction with a cyclic dicarboxylic anhydride is begun with opening of the anhydride ring to form a monoester by a hydroxyl group present in the commercial resin. The monoester thus formed reacts with an epoxide group to give an additional ester linkage and a free hydroxyl:



---

1. P. Castan, U. S. 2,324, 483, (17)
2. C. Weinschank, *Chem. Ztg.*, (1905), p. 1311, (50)
3. W. Fisch and W. Hofmann, *Plastic Tech.*, (Aug. 1961), pp. 28-32, (30)
4. E. C. Dearborn et. al., *Ind. Eng. Chem.*, vol. 45 (1953), pp. 2715-2721, (22)
5. L. Shechter and J. Wynstra, *Ind. Eng. Chem.*, vol. 48, (1956), pp. 86-93, (46)
6. W. Fisch et. al., *J. Applied Chem.*, vol. 6, (1956), p. 429, (31)

As a competing reaction there is also the possibility for self condensation of the epoxy resin by reaction of a hydroxyl group directly with an epoxide group:



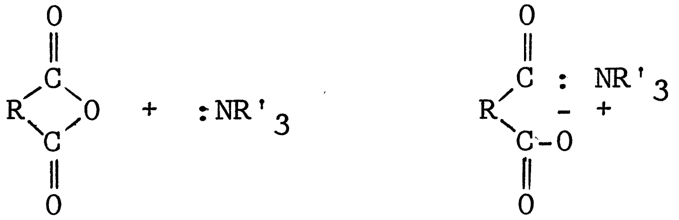
$$\mathrm{\overset{|}{\underset{|}{HC}}{-}OH} + \underset{\diagdown\,O\,\diagup}{\mathrm{CH_2{-}CH{-}}} = \mathrm{\overset{|}{\underset{|}{HC}}{-}O{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}}$$

This reaction is known as etherification, and the former reaction as esterification. The amount of etherification which occurs depends on the nature of the anhydride, the reaction temperature, and the concentration of the hydroxyls.[7] Acid catalyzation promotes etherification, while the esterification reaction is base catalyzed. The optimum epoxide to anhydride ratio (A/E) depends, therefore, on the amount of etherification and varies from .4/1 for a strongly acid catalyzed system to 1/1 for a weakly acid or base catalyzed system.[8] The presence of a basic accelerator, such as the tertiary amines, promotes the esterification reaction to almost complete exclusion of etherification.[9,10,11,12] The tertiary amines are Lewis bases, i.e., compounds containing an atom with an unshared electron pair in its outer

---

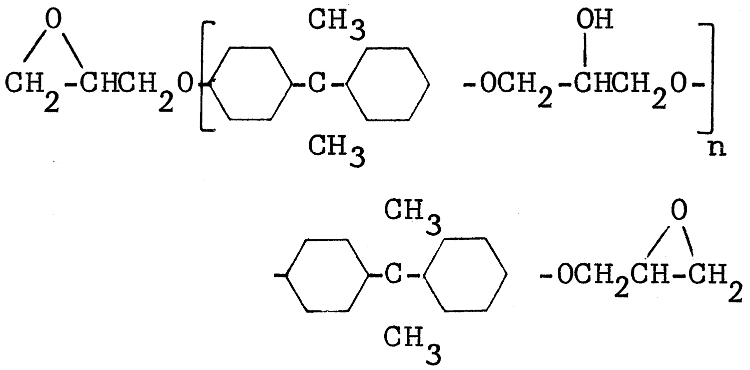
7. H. Lee and K. Neville, *Handbook of Epoxy Resins*, p. 5.13, (40)
8. *Ibid.*, p. 5.22
9. *Anhydride Hardners for Epoxy Resins*, p. 39, (3)
10. E. C. Dearborn, R. M. Fuoss, and A. F. White, *J. Poly. Sci.*, vol. 16, (1955) pp. 201-208, (23)
11. R. Fischer, *Ind. Eng. Chem.*, vol. 52, (1960), pp. 321-322, (33)
12. W. Fisch and W. Hofmann, *loc. cit.*

orbital, which react preferentially with an anhydride to generate a carboxyl ion:



The carboxyl ion then reacts with an epoxide group, generating an ion which opens another anhydride ring. These reactions continue to alternate, consuming anhydride and epoxide groups in a 1/1 stoichiometric ratio, and the reaction rate is dependent on the accelerator concentration.[13,14]

The most commonly used epoxy resin is diglycidyl ether of bisphenol-acetone (DGEBA):



which is obtained by reacting epichlorohydrin with bisphenol-acetone in the presence of sodium hydroxide. The

---

[13] R. Fischer, loc. cit.

[14] J. Feltzin et. al., A.C.S. Symposium, (1964) p. 282, (29)

reaction occurs in two steps:

a. formation of a chlorohydrin intermediate,

b. dehydrohalogenation of the intermediate to the gylcidyl ether.

The length of the molecular chain is controlled by addition of calculated amounts of monofunctional reactants, which terminate the reaction at the desired molecular weight.[15] Resins of increased functionality can be manufactured by replacing the bisphenol-acetone with a novolac resin.[16,17] This epoxidized novolac is available commercially with functionalities ranging from 2.4 to 3.6.[18] The advantages of epoxidized novolac over DGEBA are generally recognized as: better heat resistance, higher A.S.T.M. heat distortion temperatures, better chemical resistance, better electrical properties, and improved adhesion.[19,20,21]

Several types of anhydrides are used commercially as hardners for these epoxy resins:[22]

---

[15] Anhydride Hardners for Epoxy Resins, p. 10

[16] H. Lee and K. Neville, op. cit., p. 2.10

[17] A. Meath, "Chemistry, Properties and Applications of Epoxy Novolac, Flexible Epoxy and Flame Retardent Epoxy Resins", in Epoxy Resin Technology, P. Bruins, ed., pp. 31-36,(15)

[18] D.E.N. Epoxy Novolac Resins, p.1, (5)

[19] Ibid.

[20] A. Meath, loc. cit.

[21] Ciba EPN 1139, (4)

[22] H. Lee and K. Neville, op. cit., chap. 12

- a. aliphatic (linear)
- b. alicyclic
    - 1. single ring
    - 2. multi-ring
- c. aromatic

The cyclic dicarboxylic anhydrides are by far of the greatest commercial significance and their use as hardners is summarized in the literature.[23,24,25,26] Although numerous studies have been made to determine effects of gel time, post cure temperature, catalyst concentration, and A/E ratio,[27,28,29] no significant attempt has been made to relate the characteristics of the anhydride to cured properties. The alicyclic dicarboxylic anhydrides utilized commercially include succinic, methyl succinic, alkenyl substituted succinic, maleic, hexahydrophthalic, tetrahydrophthalic, methyl tetrahydrophthalic, and methyl endomethylene tetrahydrophthalic.

Succinic and methyl succinic anhydrides are saturated, single ring, alicyclic, dicarboxylic anhydrides used

---

23. Ibid.
24. R. Perez, "Commercial Resin Curing Agents," in Epoxy Resin Technology, P. Bruins, ed., pp. 66-71, (15)
25. Anhydride Hardners for Epoxy Resins, (3)
26. I. Skeist, Epoxy Resins, pp. 45-58, (47)
27. A. Bolson, A.C.S. Symposium, (1960), (14)
28. S. Christie, Modern Plastics, vol. 42, (Aug., 1965) pp. 134-142, (19)
29. T. Levitan, RIP division of S.P.I., (1965), (41)

primarily to impart toughness and flexibility to cured compositions.[30,31] The former is restricted in use somewhat by its high melting temperature (118.3-119°C). The unsaturated counterpart of succinic anhydride, maleic anhydride, is reported to produce brittle castings with the rigid epoxies and is generally used with a flexibilizer or in blends with other anhydrides. Infrared studies on the maleic-DGEBA reaction indicate a temperature sensitive cis-trans isomerization. Low temperature gels followed by post cures at 150°C yield very little trans form, whereas initial cures at 150-180°C cause a considerable amount of trans in the cured resin. At cure temperatures in the 180°C range it is suggested that the double bonds in the maleate structure undergo addition polymerization and thermal oxidation simultaneously, resulting in the formation of additional crosslinks and new carboxyl and hydroxyl groups.[32] The anhydride may be employed in excess with addition polymerization of the anhydride occurring through the unsaturation. The Vicat softening temperature after prolonged aging rises with increasing amounts of anhydride up to a ratio of 5/1. The weight loss also increases rapidly; however, it remains less than the

---

[30] Anhydride Hardners for Epoxy Resins, p. 9, (3)
[31] A. Bavley et. al., U. S. 2,938,014, (9)
[32] H. Lee and K. Neville, op. cit., pp. 12.7-12.9

calculated excess weight of the anhydride.[33] In the absence of a catalyst, the A/E ratio that provides minimum weight loss is .4/1. If maleic anhydride is used with an unsaturated epoxy, such as epoxidized polybutadiene, a peroxide catalyst may be employed to increase the heat distortion temperature (HDT) from 120 to 200°C.[34] When compared to succinic anhydride, maleic anhydride was found to have higher vicat softening temperatures, and the difference was found to increase with aging.[35] Due to the high reactivity of this anhydride, precautions must be taken to avoid foaming; when blended with other anhydrides it acts as an accelerator of epoxy cure. Maleic anhydride is used to obtain high compressive strengths where some sacrifice can be made in tensile and flexural properties.[36,37] Maleic anhydride is a particularly useful curing agent for epoxidized novolac, because it exhibits a low viscosity at room temperature (5,000 cps at 36 phr with novolac of 3.3 functionality).[37]

The multi-ring counterparts of succinic and maleic are hexahydrophthalic (cyclohexane 1,2 dicarboxylic) and tetrahydrophthalic (cis-4-cyclohexene 1,2 dicarboxylic), respectively. Hexahydrophthalic, like succinic, is used

---

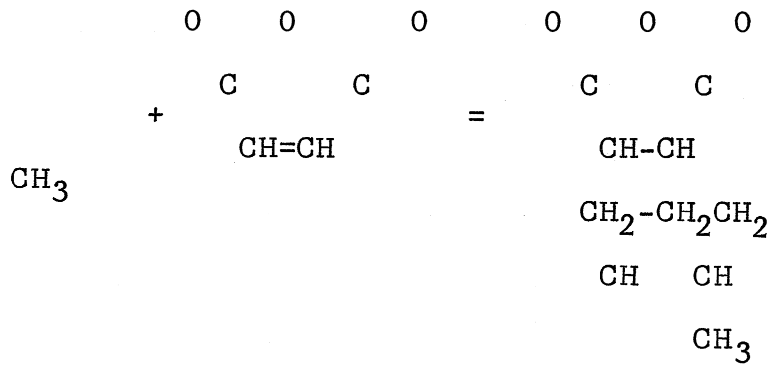
[33] G. Ehlers, Polymer, vol. 1, (1960),pp. 304-314, (26)
[34] H. Lee and K. Neville, loc. cit.
[35] G. Ehlers, loc. cit.
[36] Anhydride Hardners for Epoxy Resins, p. 9, (3)
[37] R. Perez, op. cit. p. 69
[38] H. Lee and K. Neville, op. cit., p. 12.9

to add resilence to cured epoxies without any appreciable strength loss.[39,40] However, hexahydrophthalic yields both higher strengths and heat distortion temperatures than its single ring counterpart. Hexahydrophthalic anhydride finds wide use as an epoxy hardner where low viscosity, good pot life, and moderate heat resistance are required. It also reaches its optimum mechanical properties at relatively short cure times.[41] Tetrahydrophthalic anhydride is reported to give generally the same properties as hexahydrophthalic annhdride, but it is restricted in use because of its high melting temperature (99-101°C). It is a low cost anhydride and is often blended with other anhydrides for economic reasons alone.[42,43] Tetrahydrophthalic anhydride is also available as a liquid mixture of isomers,[44] as is methyl tetrahydrophthalic anhydride; properties as indicated in their respective technical data sheets appear to be similar for both isomeric mixtures.[45,46] Lee and Neville[47] claim, however, that the properties of methyl tetrahydrophthalic anhydride closely parallel those of methyl endomethylene

---

[39] Anhydride Hardners for Epoxy Resins, p. 9, (3)
[40] R. Perez, op. cit., pp. 67-68
[41] Technical Service Notes 96, (7)
[42] Anhydride Hardners for Epoxy Resins, p. 9, (3)
[43] R. Perez, op. cit., p. 69
[44] Ibid., p. 86
[45] Nadic 200 Acid Anhydride, (6)
[46] Vanderide Liquid Anhydrides, (8)
[47] H. Lee and K. Neville, op. cit., p. 12.11

tetrahydrophthalic anhydride, and report a heat distortion temperature 30°C above that listed for the isomeric mixture. Methyl endomethylene tetrahydrophthalic anhydride (methyl-5-norbornene 2,3 dicarboxylic) differs structurally from methyl tetrahydrophthalic by the presence of a methylene bridge. The anhydride is synthesized commercially by a Diels-Alder reaction from methycyclopentadiene and maleic anhydride:



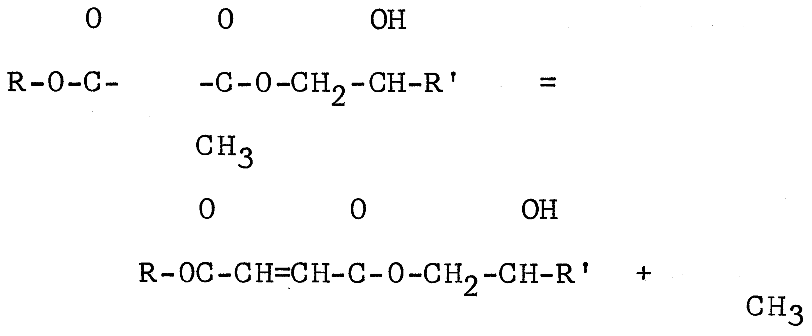
The commercial product is a mixture of stereo and structural isomers; the main isomer being the adduct from 2 methyl cyclopentadiene and maleic anhydride.[48]

Methyl endomethylene tetrahydrophthalic anhydride cured epoxies have high distortion temperature, good strength retention at elevated temperatures, and low

---

[48] G. Fleming, J. App. Poly. Sci., vol. 10, (1966), pp. 1813-1830, (34)

weight losses on aging.[49,50] In general the high temperature aging characteristics are considered outstanding.[51] There have been several statistical optimization studies done on methyl endomethylene tetrahydrophthalic anhydride cured systems in regard to catalyst concentrations, A/E ration,and cure cycles.[52,53,54] Thermograms of this anhydride and other bridged Diels-Alder anhydride adducts have recently revealed unusual thermal properties for these materials as compared to non-bridged Diels-Alder anhydride adducts (such as tetrahydrophthalic) and single ring anhydrides (such as maleic).[55] It was found that the bridged Diels-Alder anhydride adducts undergo a reverse Diels-Alder reaction prior to main resin degradation:



$$R\text{-}O\text{-}\overset{O}{C}\text{-} \qquad \text{-}\overset{O}{C}\text{-}O\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}R' \quad = \qquad CH_3$$

$$R\text{-}O\overset{O}{C}\text{-}CH{=}CH\text{-}\overset{O}{C}\text{-}O\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}R' \quad + \qquad CH_3$$

---

49. H. Lee and K. Neville, *op. cit.*, p. 12.10
50. J. Delmonte, *Chem. Eng. Progr.*, vol. 58, (1962), pp. 51-54, (24)
51. *Anhydride Hardners for Epoxy Resins*, p. 7, (3)
52. H. Lee and K. Neville, *op. cit.*, p. 12.9
53. H. Weiss, S.P.E. RETEC, (1958), (51)
54. A. Mack, *Ind. Eng. Chem. Prod. Res. Develop.*, vol. 3, (1964), p. 213, (42)
55. G. Fleming, *J. App. Poly. Sci.*, vol. 13, (1969), pp. 989-997, (35)

This reaction does not rupture the main backbone of the resin system, but leaves an activated olefinic bond which is capable of undergoing cross-linking reactions during degradation by free radicals produced therein. This increased cross-linking results in lower rates of weight loss and higher char yields than in systems where reverse Diels-Alder reactions do not occur before main resin degradation. The maximum rates of weight loss for the bridged Diels-Alder adducts are similar to that for maleic anhydride (see Figure 1) due to their identical polymeric structures after the reverse reaction occurs. Under vacuum the diene liberated is removed before further reaction can occur, but under atmospheric environments it may polymerize, adding to the olefinic double bond in the polymer backbone,and thereby increasing the cross-link density. The initial weight loss to 350°C for systems cured with tetrahydrophthalic and maleic anhydrides is accounted for by the regeneration and subsequent loss of original anhydride from incompletely cured monoester-monoacid.[56]

Both maleic and methyl endomethylene tetrahydrophthalic anhydrides are known to give highly rigid systems and it is often recommended that a flexibilizer be used with them.[57] Flexibilization is accomplished by addition

---

[56] Ibid.

[57] H. Lee and K. Neville, op. cit., pp, 12.7, 12.10

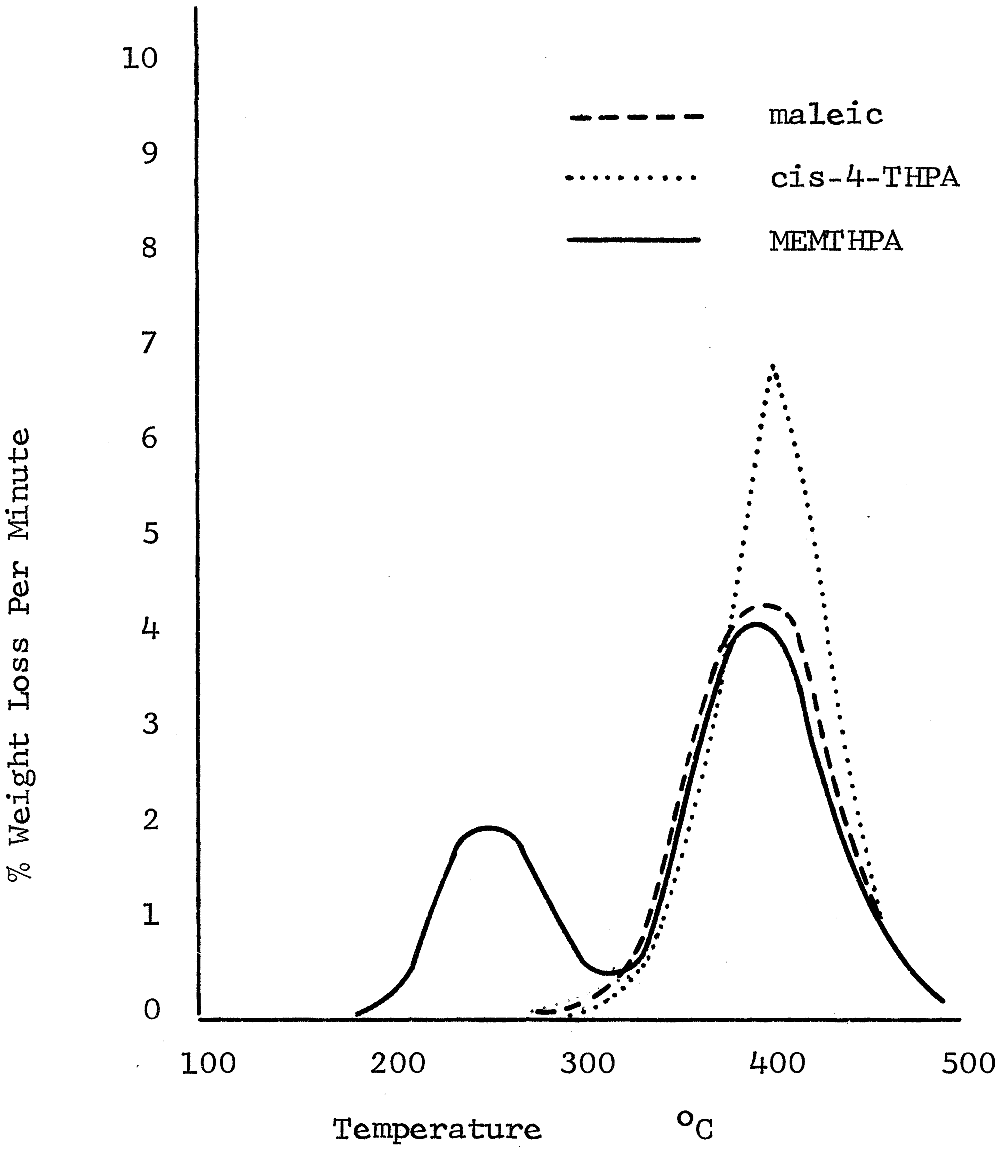


FIGURE I <u>RATE OF WEIGHT LOSS PLOT FOR ANHYDRIDE CURED RESORCINOL DIGLYCIDYL ETHER</u>[58]

---

[58] G. Fleming, *Ibid*.

to the epoxy-anhydride mixture of various long chained organic compounds:

a. saturated dicarboxylic acids containing 4 to 12 carbon atoms,[59]

b. higher aliphatic monocarboxylic acids (at least 8 carbon atoms),[60]

c. phenols containing 2 to 4 hydroxyl groups[61]

d. monohydric alcohols and polyols of varying molecular weight,[62,63,64,65]

e. hydroxyl terminated polyesters,[66]

f. aliphatic digylcidyl ethers.[67]

These flexibilizing additives react with either the anhydride or the epoxide groups and increase the distance between cross-linking points. Flexibility increases as the molecular weight or distance between reactive sites increase.[68,69] The same effect is often accomplished by utilizing an anhydride with a long aliphatic chain inherent in the anhydride structure.

---

[59] N. Canaan et. al., U.S. 2,801,232, (16)

[60] W. Belanger et. al., U.S. 2,934,506, (11)

[61] W. Belanger et. al., U.S. 2,934,521, (10)

[62] W. Belanger et. al., U.S. 2,934,506, (11)

[63] J. Delmonte, U.S. 3,188,362, (25)

[64] B. Phillips et. al., U.S. 2,890,196, (45)

[65] W. Belanger and J. Masters, U.S. 2,947,717, (12)

[66] W. Binningen, U.S. 2,830,031, (13)

[67] L. Harry and R. Helmreich, S.P.E. J., vol. 17, (1961), pp. 583-587, (36)

[68] W. Binningen, loc. cit.

[69] W Belanger et. al., U.S. 2,934,506, (11)

Branched dodecenyl succinic anhydride, a branched alkenyl substituted succinic anhydride, is the most common of there materials, and its use as a flexibilizing agent is covered in the literature.[70,71,72,73] The alkenyl substituted succinic anhydrides are available with both branched and linear chains.[74] Anhydrides with branched chains are preferred, those having 8 to 11 carbon atoms in the linear portion being liquids. Branched nonenyl and dodecenyl are typical and both give essentially the same properties when used as epoxy curing agents.[75] The long hydrocarbon chains in these curing agents produce solvent sensitive epoxy systems.[76] Although suggested as curing agents,[77] there is no information in the literature on the properties of linear alkyl substituted succinic anhydride cured materials. "Flexibilization" is a loosely defined term throughout the literature, being used to infer, among other things, softening of the material,[78] improvement in thermal shock resistance,[79] improvement in insert crack resistance,[80] higher flexural strengths,[81] increased

---

[70] H. Lee and K. Neville, op. cit., p. 12.5
[71] Anhydride Hardners for Epoxy Resins, p. 7, (3)
[72] R. Perez, op. cit.,pp. 68-69
[73] S. Christie, loc. cit.
[74] Aliphatic Chemicals, (2)
[75] H. Lee and K. Neville, loc. cit.
[76] R. Perez, loc. cit.
[77] Aliphatic Chemicals, (2)
[78] J. Delmonte, loc. cit.
[79] N. Canaan et. al., U. S. 2,801,232, (16)
[80] Ibid.
[81] L. Harry and R. Helmreich, loc. cit.

impact values,[82] and increased tensile elongation.[83] It has even been used interchangebly with "elasticity".[84] At one extreme the term refers to a reduction in rigidity to any degree, while at the other extreme it refers solely to increases in elongation.[85]

Besides flexibilizers, other reactive organic compounds are often added to the epoxy-anhydride system. The majority of these are added as diluents to reduce the viscosity of the uncured mixture. The types of reactive diluents are generally grouped as:

a. monofunctional epoxy
b. polyfunctional epoxy
c. non-epoxy

The latter classification includes olefinic monomers which can react with unsaturated double bonds in the resin[87,88] or the anhydride.[89,90,91] In the case of DGEBA or epoxidized novolac, the olefinic unsaturation must occur in the anhydride. When the anhydride epoxy-monomer mixture is cured, the dicarboxylic anhydride containing the unsaturation undergoes a copolymerization with the

---

[82] S. Christie, loc. cit.
[83] H. Lee and K. Neville, op. cit., p. 16.2
[84] W. Binningen, loc. cit.
[85] H. Lee and K. Neville, loc. cit.
[86] Ibid., pp. 13.10-13.20
[87] C. Wheelock, U. S. 3,028,370, (52)
[88] H. Lee and K. Neville, op. cit., p. 13.18
[89] F. Eirich, U. S. 2,848,433, (48)
[90] I. Updegraff, U. S. 2,781,333, (48)
[91] H. Lee and K. Neville, op. cit., p. 12.7

olefinic unsaturated monomer, concurrently with cross-linking through esterification.[92] Properties of the final resin may be varied considerably by changing the sequence of the epoxide-anhydride and olefinic reactions. This can be achieved by the use of different epoxides and different cure cycles. Peroxide catalysts may be employed to accelerate the reaction. Improved flexibilities are obtained when the monomer is above two parts per hundred parts resin, but above forty parts per hundred parts resin the cured products are soft.[93] Anhydrides which contain olefinic unsaturation include maleic, tetrahydrophthalic, methyl tetrahydrophthalic, methyl endomethylene tetrahydrophthalic, and alkenyl substituted succinic.

Any of the saturated or unsaturated alicyclic dicarboxylic anhydrides can be blended with one another in varying mole ratios to achieve intermediate properties. In general the properties from anhydride blends are felt to be additive rather than synergistic.[94] Methyl endomethylene tetrahydrophthalic anhydride is often added to other anhydride systems to upgrade the temperature

---

[92] F. Eirich, loc. cit.

[93] Ibid.

[94] S. Christie et. al., S.P.E. Tech. Papers, vol. 12, (1966) pp. 1-5, (18)

resistance.[95,96] Anhydrides are also blended to achieve low melting eutectic mixtures.[97,98,99] Data of any of these binary or tertiary anhydride mixtures, however, is exceedingly scarce in the literature.

Evaluation of cured epoxy systems is, of course, based on the measurement of various physical and chemical properties. Although a full discussion of all the aspects of these properties is beyond the scope of this review, the facets of those that have significance to this research are discussed individually below:

Density - During an investigation of various epoxide resin systems, some cases were found in which the room temperature density decreased with increasing cure temperature and degree of cure.[100,101] Three distinct types of density dependence on cure temperature were observed:

a. density decreased with cure temperature over the entire temperature range (80-180°C),

b. density decreased up to a certain temperature and then became constant,

---

[95] H. Lee and K. Neville, op. cit., p. 12.35

[96] J. Warburton, U. S. 3,218,288, (49)

[97] H. Lee and K. Neville, p. 12.33

[98] Anhydride Hardners for Epoxy Resins, pp. 39-41, (3)

[99] R. Perez, op. cit., p. 71-72

[100] W. Fisch and W. Hofmann, loc. cit.

[101] W. Fisch, W. Hofmann and R. Schmid, J. App. Poly. Sci., vol. 13, (1960, pp. 295-308, (32)

c. density was independent of curing temperature.

The same types of dependence were found inversely between cure temperature and glass transition temperature. When density decreased with cure temperature, the glass transition temperature was always higher than the cure temperature by a constant amount. Post curing a sample cured at a lower temperature was found to reduce the density considerably without, however, reaching the value obtained by direct curing at the higher temperature. This unique behavior was attributed to a decrease of the contraction coefficient with increasing cure temperature and degree of cure. The decrease in density of the resin on heating outweighed all increases of density, i.e., isothermal cure shrinkage and contraction, on cooling.[102]

Cured epoxy systems were found to be two phased systems with roughly spherical floccules arranged in layers in an interstitial fluid resembling the starting materials.[103,104] An analogy can be drawn to grains and grain boundaries in a metallic system. The density of an epoxy system was found to increase linearly with average floccule diameter. The floccule size was related

---

[102] Ibid.

[103] H. Lee and K. Neville, op. cit., p. 6.5

[104] R. Cuthrell, J. App. Poly. Sci., vol. 10, (1966) pp. 949-952, (21)

inversely to cure temperature.[105]

Heat Distortion Temperature - This A.S.T.M. test is widely used as a measure of the extent of cure or degree of cross-linking.[106,107] Excellent correlation has been obtained between the HDT and other methods of estimating cross-linking density.[108,109]

Tensile and Flexural Properties - Several recent studies of these properties, although on polyamide cured epoxies, reached some significant conclusions concerning ductile epoxy materials in general:[110,111,112]

a. Linearity was found between the yield stresses of tension, compression, and flexure and the log strain rate. The same applied to yield stresses and log yield time.

b. Stress-strain curves all exhibited the same characteristics: A linear region followed by a curved region terminating in a flat maximum at yield.

c. At a given temperature and strain rate, the

---

[105] R. Cuthrell, J. Appl. Poly. Sci., vol. 11, (1967), pp. 955-967, (20)
[106] H. Lee and K. Neville, op. cit. p. 6.5
[107] Anhydride Hardners for Epoxy Resins, p. 25, (3)
[108] G. Ehlers, A.S.T.M. Bulletin, (Feb., 1959(, (26)
[109] H. Lee and K. Neville, op. cit., pp. 6.17-6.19
[110] O. Ishai, J. App. Poly. Sci., vol. 11, (1967), pp. 963-981, (39)
[111] O. Ishai, J. App. Poly. Sci., vol. 11, (1967), pp. 1863-1879, (38)
[112] A. Moehlenpah et. al., J. App. Poly. Sci., vol. 13, (1969), pp. 1231-1245, (43)

yield stress determined in compression is 1.28 times as great as that in tension over the entire temperature and strain rate region tested.

d. Flexural yield stress can be used to accurately predict the yield stress in tension and compression.

e. Yield strain, unlike yield stress, is not simply related to temperature and strain rate.

f. The flexural test is not a good method to determine the yield strain of a cross-linked material that is near the glass transition temperature due to inadequacy of the simple beam theory at high flexural strains.

g. At a given temperature and strain rate the initial elastic moduli and stress relaxation moduli determined in tension, compression and flexure are the same.

h. Tangent moduli plotted against the reciprocal of the strain rate can be used to predict stress relaxation and vice-versa.

i. Initial elastic moduli, stress relaxation moduli and yield stress data can be correlated by the time-temperature superposition principle.

j. Creep strain versus time curves revealed a distinct delayed yielding region of constant minimum rate (secondary creep) followed by

> a post yielding region of increasing slope (tertiary creep). In all cases, results indicate linearity between creep stress and log secondary creep rate.

Many highly cross-linked epoxy systems, however, do not reach a yield stress, but exhibit brittle failure on the positive slope of stress-strain curve. This flaw sensitivity adversely affects attempts to correlate tensile strength with cross-linking density.[113] Tests have indicated that for these brittle materials cracks are initiated at bubbles, inclusions and surface scratches.[114]

Chemical Resistance - The chemical resistance of anhydride cured epoxies in general id discussed in the literature.[115,116] Comparisons have also been made between the various anhydrides.[117] Often overlooked in chemical resistance determinations is the necessity of removing the surface if differences in matrix properties are to be determined. The surface layer in epoxy polymers is always dissimilar to the matrix, with a gradient of properties extending several hundred microns into the bulk.[118] It is possible during cure to evaporate from

---

113. S. Christie, op. cit., p. 138
114. H. Lee and K. Neville, op. cit., p. 6.23
115. R. Perez, op. cit., pp. 67-68
116. Anhydride hardners for Epoxy Resins, pp. 30-31, (3)
117. Ibid.
118. R. Cuthrell, J. App. Poly. Sci., vol. 10, (1966), pp. 949-952, (21)

the surface not only the anhydrides, but practically the whole monoester content, by disturbing the anhydride-monoester equilibrium.[119]

Heat Resistance - The most common methods used for determining a resin's comparative heat resistance are:

a. heat distortion temperature,[120]
b. differential thermal analysis (DTA),[121]
c. thermogravimetry (TGA),[122]
d. weight loss on aging,[123]
e. retention of HDT after aging,[124,125]
f. retention of mechanical properties after aging.[126,127]

The first of these methods is the least effective and should be used only for screening purposes.[128] The latter two provide the most meaningful data in terms of relation to actual service conditions. With elevated temperature aging, there is generally a progressive loss of strength and an overall reduction in properties. As aging continues

---

[119] W. Fisch and W. Hofmann, loc. cit.
[120] H. Lee and K. Neville, op. cit., pp. 6.20-6.21
[121] Ibid., pp. 6.33-6.34
[122] Ibid., pp. 6.35-6.37
[123] Ibid., p. 17.21
[124] Ibid.
[125] D.E.N. Epoxy Novolac Resins, p. 10, (5)
[126] Ibid., p. 11
[127] H. Lee and K. Neville, loc. cit.
[128] D.E.N. Epoxy Novolac Resins, p. 10., (5)

surface charring will occur followed by cracking and decomposition. Reduction in properties may result from degradation or progressive embrittlement; thus when elevated temperature service is involved, data from as-cured samples are inadequate. Meaningful data for selection of materials can be obtained only after long time aging tests at temperatures substantially in excess of the service temperature.[129]

---

[129] H. Lee and K. Neville, *op. cit.*, p. 17.19

PROCEDURE

Alicyclic dicarboxylic anhydride cured systems tested in this research were succinic, methyl succinic, maleic, hexahydrophthalic (cyclohexane 1,2 dicarboxylic), tetrahydrophthalic (cis-4-cyclohexene 1,2 dicarboxylic and isomeric mixture), methyl tetrahydrophthalic (isomeric mixture), methyl endomethylene tetrahydrophthalic (isomeric mixture), n-octenyl succinic, n-dodecenyl succinic, n-hexadecenyl succinic, branched octenyl succinic, branched nonenyl succinic, branched dodecenyl succinic, n-octyl succinic, n-dodecyl succinic, and n-hexadecyl succinic. Properties determined were flexural strength, flexural modulus, toughness, density, heat distortion temperature, and chemical resistance. Tensile and stress relaxation data were also measured for the succinic and substituted succinic anhydride cured systems. Flexural properties were not determined for the linear chain substituted succinic anhydrides with 12 or more carbon atoms in the substituted chain because of excessive slippage between supports. Co-anhydride cured systems investigated were maleic/branched octenyl succinic, maleic/branched dodecenyl succinic, hexahydrophthalic/maleic, hexahydrophthalic/tetrahydrophthalic, hexahydrophthalic/

methyl tetrahydrophthalic, and hexahydrophthalic/methyl endomethylene tetrahydrophthalic. Ratios tested were 1/0, 3/1, 1/1, 1/3, and 0/1 for the substituted succinic binary systems and 1/0, 1/1, and 0/1 for the hexahydrophthalic binary systems. Properties tested were flexural strength, flexural modulus, toughness, density, heat distortion temperature, and chemical resistance. Vinyl toluene at a monomer/anhydride mole ratio of .5/1 was added to each unsaturated system, as well as the saturated hexahydrophthalic and hexahydrophthalic/maleic binary system. Variable vinyl toluene concentrations were also tested in the methyl tetrahydrophthalic cured system, at monomer/anhydride ratios of .25/1, .5/1, and 1/1. Monochlorostyrene and vinyl toluene were both tested in a maleic anhydride cured system at monomer/anhydride ratios of .3/1 and .5/1. Properties tested in each case were flexural strength, flexural modulus, toughness, density, heat distortion temperature, and chemical resistance.

Resin formulations were cast into 8" x 16" sheets (thickness .125" - .150" nominal) in glass shielded aluminum molds using a fluorocarbon release (Miller-Stephenson MS-122) on the aluminum surface. A few highly flexible formulations, i.e., the linear alkenyl and linear alkyl substituted succinic anhydride cured materials, were found to tear on cooling in the aluminum molds and were, therefore, cast in self-releasing silicone rubber molds (General Electric RTV 630). The anhydrides were mixed into the resin at room temperature, or where necessary, at a temperature slightly in excess of the melting point of the anhydride. Other additives were mixed into the resin after the addition of the anhydride and prior to the addition of the tertiary amine catalyst. If heating was necessary to melt the anhydride, the resin-anhydride mixture was cooled below the casting temperature before the other constituents were added. The resin used in all cases, except one, was diglycidyl ether of phenol formaldehyde novolac (Dow Chemical D.E.N. 431); the epoxy equivalent weight was determined on each lot by the hydrogen bromide titration method.[130] The single exception was a diglycidyl ether of bisphenol-acetone (Ciba 6005) formulation cured with methyl endomethylene tetrahydrophthalic anhydride, included for purposes of comparison. The hydrogen bromide titration was also used to determine the epoxy equivalent weight of the diglycidyl ether of bisphenol-acetone. The tertiary amine catalyst used throughout this investigation was benzyldimethylamine (Ciba accelerator 062); the concentration of which was kept constant at .02 moles of benzyl-

---

130. Ibid., p. 4.17

dimethylamine for each epoxy equivalent. The mole anhydride to epoxy equivalent ratio was held constant at 1/1; the molecular weights of the individual anhydrides were determined from their theoretical structures. These structures, along with the commercial sources of the anhydrides tested in this investigation, are given in Appendix A. The casting temperature in all cases was 100°C, except for formulations containing maleic anhydride, in which case the resin was allowed to gel at a lower temperature prior to the 5 hour cure at 100°C. Attempts to cast maleic anhydride formulations at 100°C resulted in badly crazed sheets due to the high exotherm of the resin mix; therefore, these formulations were allowed to gel slowly at 50°C. For formulations containing both maleic anhydride and vinyl monomers, however, the 50°C temperature was found to allow excessive volatile loss (greater than 10 percent), since the gel time was markedly increased. For these formulations the gel temperature was increased to 75°C where the gel time was sufficiently short to prevent undue loss of the vinyl monomers, but not rapid enough to cause exothermic crazing. The peroxide catalyst used in all formulations containing vinyl monomers was tertiary butyl perbenzoate at a catalyst to anhydride molar ratio of .01/1. Attempts to use a peroxide with a shorter half life at 100°C, such as lauroyl peroxide, resulted in foaming of the resin mix at 75°C and 100°C. At 50°C there were indications of immiscibility, i.e., layering, especially with systems containing hexahydrophthalic anhydride. Attempts to use dicumyl peroxide with a longer 100°C half life than tertiary butyl perbenzoate resulted in excessive monomer loss.

After 5 hours at 100°C, the cast sheets were removed from the molds and the test specimens were cut with a saw along templets according to the dimensions given in Table I. All samples were subsequently post cured for 15 hours at 200°C (250°C where noted), and furnace cooled below 100°C before removal from the oven. Flexural, tensile, and stress relaxation samples were sanded and conditioned (A.S.T.M. D618-61, Procedure A) prior to testing. Flexural samples were fine polished with a 500-grit emery cloth and tested so that the top surface of the original cast sheet was always placed in tension. The flexural strength determined was the flexural yield strength or in the case of brittle failure, the ultimate flexural strength. The flexural modulus was determined as the tangent modulus and the toughness as the area under the stress-strain curve. The same applies to tensile samples where applicable. Unless otherwise noted the deflection rate for flexural testing was 2"/ minute and the strain rate for tensile testing was .2"/

TABLE I

DIMENSIONS OF TEST SPECIMENS

Test	Specimen Dimensions *
Flexural	.450"± .050" x .125" ± .015" x 3.0" minimum
Tensile	A.S.T.M. D638-61T (Type I) d=.150" ± .025"
Stress Relaxtion	A.S.T.M. D1708-59T d=.150" ± .025"
Heat Distortion	.500" ± .050" x .150" ± .025" x 5.0" minimum
Chemical and Density	1 ± .5 gram squares d=.125" ± .025"

* d (depth) dimension had a maximum variation of ± .001" for a given specimen; w (width) dimension ± .002"

inch/minute. Stress relaxation samples were strained at a .2"/inch/minute rate to a stress value less than 50 percent of the tensile yield stress and held at constant strain. The reduction of modulus was recorded as a function of time for a minimum of 1000 minutes. The relaxation spectrum was determined from a graphical plot of the first derivative of the relaxation modulus curve.[131] Further details on the stress relaxation calculations are discussed in Appendix B. Tensile testing was done in accordance with A.S.T.M. D638-61T and flexural testing in accordance with A.S.T.M. D790-63 (except for deflection rate and dimensional specifications). Flexural, tensile, and stress relaxation testing were all done on an Instron testing machine at 72 ± 2°F and 60 ± 10 percent relative humidity.

Heat distortion data was taken in accordance with A.S.T.M. D648-56 (264 psi load). For 250°C post cured and aged maleic anhydride cured formulations, however, deflection of the specimen bar under load was so gradual that compensation had to be made for thermal expansion of the specimen and test apparatus. The thermal expansion was determined from a supported specimen as .001" per 35°C. For those few formulations with heat distortion

---

131. R. A. Andrews, Ind. Eng. Chem., vol. 44, (1952), pp. 707-710, (1)

temperatures over 265°C (the upper limit of the test apparatus) the heat distortion temperature was estimated from a deflection versus temperature curve which was extended graphically above 265°C. Heat distortion tests were rerun if agreement between samples were not within ± 1°C below 150°C or ± 2°C above 150°C.

Chemical resistance data was taken as the average weight change for three specimens after total immersion in a reagent for a specified time and temperature. Unless otherwise noted chemical resistance samples were all sanded prior to testing and immersed in the reagent for 240 hours at 25°C. Reagents were all laboratory grade purchased from Baker Chemical Company. Densities were determined from the difference between weight in air and the weight in water; reported values are the average of two samples, agreement being at least ± .001 gram/cm^3. Viscosities were measured at the laboratory temperature (23.5°C), utilizing a Brookfield viscometer. Measurements were taken just prior to the tertiary amine addition.

Aged samples were all post cured for 15 hours at 200°C prior to aging for 960 hours at 250°C. Weight loss data on aging was determined from the specimens cut for the heat distortion test. Aged samples were not repolished after aging, except for the chemical resistance specimens, which were tested in both the repolished and non-repolished conditions. The aging was done in a circulating air oven with the temperature controlled to within ± $2^{o}C$. All specimens were placed between two sheets of glass to prevent warpage. Heat distortion specimens were aged for all formulations except the linear substituted succinic anhydrides with 12 or more carbon atoms in the substituted chain (exempted because of softness). Flexural, density, and chemical resistance specimens were aged for all single anhydride formulations with heat distortion temperatures over $100^{o}C$, two representative hexahydrophthalic binary formulations, and all the formulations containing vinyl toluene at a monomer/anhydride mole ratio of .5/1.

Sample calculations of all the properties determined from measurements taken in the above tests are given in Appendix B for the succinic anhydride formulation. Exceptions are viscosity calculations, which are for the methyl tetrahydrophthalic / vinyl toluene system, and the stress relaxation calculations for soft materials, which is for the n-hexadecyl succinic cured system.

RESULTS AND DISCUSSION

Alicyclic dicarboxylic anhydrides were found to be amazingly versatile as epoxy curing agents. Variations in anhydride structure produce cured systems of markedly different properties. Heat distortion values range from below room temperature to over 250°C, strength properties from hard and brittle to soft and weak, tensile elongations from a few percent to over 30%, etc. The anhydride structure was found to influence properties primarily through its effect on physical density, cross-linking density, and extent of reaction, all of which are, of course, inter-related.

Table II illustrates the properties of the major commercial anhydrides in the as-cured state. Several generalizations can be made at first glance: The multi-ring anhydrides tend to have higher strengths and moduli, but lower densities, than their single ring counter-parts; and the saturated anhydrides tend to have higher toughness, but lower densities and moduli than their unsaturated counter-parts. The division of the heat distortion temperatures is less consistent, as apparently several conflicting factors are affecting cross-linking density.

TABLE II

PHYSICAL PROPERTIES OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT
	gms/cm^3	psi	10^5 psi	10^3 psi	° C
succinic	1.295	20,950	4.50	1.4	106
methyl succinic	1.258	20,750	4.42	1.2	98
maleic	1.304	22,700	4.63	.90	156
hexahydrophthalic	1.242	25,900	5.02	1.5	136
cis-4-tetrahydrophthalic	1.264	25,750	5.12	1.1	126
methyl tetrahydrophthalic	1.244	25,500	5.42	.93	121
methylendomethylene tetrahydrophthalic	1.250	24,650	5.23	.79	145

The two most obvious of these are, of course, extent of the epoxide-anhydride reaction and degree of cross-linking occurring through ethylenic unsaturation. A more complete discussion of these anhydrides can be made if we look at other aspects of the anhydride cured materials as illustrated in Tables III through IX.

It is apparent on aging that the carbon-carbon double bond reacts wherever present at 250°C, and contributes to a marked increase in modulus and heat distortion temperature. In the as-cured state, however, saturated hexahydrophthalic anhydride has a higher heat distortion temperature than unsaturated cis-4-tetrahydrophthalic anhydride, indicating that the extent of the epoxide-anhydride reaction is very significant before aging. The difference in as-cured properties between maleic and succinic, which is usually attributed solely to the addition polymerization of maleic anhydride through its unsaturation,[132] is also at least partially due to a difference in the extent of the epoxide-anhydride reaction. The succinic anhydride formulation has a 58°C rise in heat distortion temperature upon aging, on the other hand saturated hexahydrophthalic rises only 4°C. Since there is no ethylenic double bond in succinic to react, apparently succinic anhydride has a lower extent to epoxide-

---

[132] F. Eirich, _loc_. _cit_.

TABLE III

AGED PHYSICAL PROPERTIES OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT
	gms/cm^3	psi	10^5 psi	10^3 psi	^oC
succinic	1.288	10,950	4.74	.12	164
methyl succinic	1.256	10,650	4.88	.10	128
maleic	1.270	8,800	5.68	.067	285
hexahydrophthalic	1.240	9,850	5.28	.084	140
cis-4-tetrahydrophthalic	1.253	8,800	5.72	.058	248
methyl tetrahydrophthalic	1.230	9,750	6.12	.075	167
methylendomethylene tetrahydrophthalic *	1.241	3,550	4.86	.013	266

* crazed

TABLE IV

EFFECT OF AGING ON PHYSICAL PROPERTIES OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY gm/cm^3	FLEXURAL STRENGTH RETENTION %	FLEXURAL MODULUS 10^5 psi	TOUGHNESS T_a/T_i	HDT °C	WEIGHT LOSS @ 250°C %
succinic	-.007	52.5	+.24	.09	+58	13.7
methyl succinic	-.002	51.4	+.46	.08	+30	12.5
maleic	-.034	38.8	+1.05	.07	+129	19.5
hexahydrophthalic	-.002	38.1	+.26	.06	+4	12.1
cis-4-tetrahydrophthalic	-.011	34.2	+.60	.05	+122	10.0
methyl tetrahydrophthalic	-.014	38.2	+.70	.08	+46	14.8
methylendomethylene tetrahydrophthalic *	-.009	14.4	-.37	.02	+121	8.4

* crazed

TABLE V

COMPARISON OF DGEBA AND EPOXIDIZED NOVOLAC CURED WITH METHYL ENDOMETHYLENE TETRAHYDROPHTHALIC ANHYDRIDE

PROPERTY		DGEBA	NOVOLAC	AGED DGEBA*	AGED NOVOLAC*
DENSITY gms/cm^3		1.219	1.250	1.213	1.241
FLEXURAL STRENGTH psi		25,500	24,650	7050	3550
FLEXURAL STRENGTH RETENTION %		—	—	27.6	14.4
FLEXURAL MODULUS 100,000 psi		5.07	5.23	4.82	4.86
TOUGHNESS 1000 psi		1.1	.79	.048	.013
HDT	200°C post cure	139	145	—	—
	250°C post cure	179	211	—	—
	aged	—	—	262	266
WEIGHT LOSS @ 250°C		—	—	7.1	8.4
WEIGHT GAIN %	acetone	4.5	2.1	.62	.47
	ethylene dichloride	7.2	1.0	.49	.38
	water boil **	1.4	1.4	.59	.60
	HBr in acetic ***	7.7	3.8	-.20	-.50

* crazed
** 24 hours at 100°C
*** 24 hours at 70°C

TABLE VI

COMPARISON OF CIS-4-TETRAHYDROPHTHALIC ANHYDRIDE WITH TETRAHYDROPHTHALIC ISOMERS

PROPERTY		Cis-4-THPA	THPA ISOMERS
DENSITY gms/cm^3		1.264	1.264
FLEXURAL STRENGTH psi		25,750	25,300
FLEXURAL MODULUS 10^5 psi		5.12	5.19
TOUGHNESS 10^3 psi		1.1	1.1
HDT	200°C post cure	126	122
	250°C post cure	136	125
	aged	248	189
% WEIGHT LOSS @ 250°C		10.0	14.2
% WEIGHT GAIN	acetone	1.0	1.7
	ethylene dichloride	.52	2.6
	water boil *	1.4	1.5
	1 N HBr in acetic **	1.6	3.0

* 24 hours at 100°C
** 24 hours at 70°C

TABLE VII

CHEMICAL PROPERTIES OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	PERCENT WEIGHT GAIN			
	acetone	ethylene dichloride	water boil*	HBr in acetic**
succinic	2.0	2.0	1.7	1.9
methyl succinic	3.4	5.9	1.1	2.4
maleic	.45	.27	1.9	...
hexahydrophthalic	1.2	1.4	1.0	1.6
cis-4-tetrahydrophthalic	1.0	.52	1.4	1.6
methyl tetrahydrophthalic	1.6	1.2	1.1	2.3
methylendomethylene tetrahydrophthalic	2.0	1.0	1.4	3.8

* 24 hours at 100°C
** 24 hours at 70°C (1 N HBr)

TABLE VIII

EFFECT OF OXIDIZED SURFACE ON WEIGHT GAIN MEASUREMENTS AFTER AGING

Anhydride	Percent Weight Gain *			
	Polished		Unpolished	
	acetone	ethylene dichloride	acetone	ethylene dichloride
succinic	.43	.42	.98	-.02
maleic	.21	.22	1.29	-.01
tetrahydrophthalic	.17	.43	1.05	...
hexahydrophthalic	.47	.85	1.19	-.02

* 240 hours total immersion

TABLE IX

CHEMICAL PROPERTIES OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC AFTER AGING

ANHYDRIDE	PERCENT WEIGHT GAIN			
	acetone	ethylene dichloride	water boil*	HBr in acetic **
succinic	.43	.42	.68	.84
methyl succinic	1.4	1.6	.28	1.8
maleic	.21	.22	.68	-.82
hexahydrophthalic	.47	.85	.26	3.0
cis-4-tetrahydrophthalic	.17	.43	.62	-.42
methyl tetrahydrophthalic	.16	.10	.29	.81
methylendomethylene tetrahydrophthalic	.47	.38	.60	-.50

* 24 hours at 100°C
** 24 hours at 70°C (1 N HBr)

anhydride reaction. This is further supported by succinic anhydride's higher weight gain in boiling water (Table VII) and higher weight loss on aging (Table IV) than hexahydrophthalic, both of which are indicative of the presence of unreacted anhydride. The succinic anhydride cured material also has greater solvent sensitivity than hexahydrophthalic (Table VII), in spite of its higher physical density. Since succinic has a low extent of reaction by comparison with hexahydrophthalic anhydride, there is no reason why not to conclude that maleic anhydride also has a low extent of epoxide-anhydride reaction which is counteracted in its effect on properties by a high degree of cross-linking occurring through addition polymerization of the double bond. This is seemingly supported by the high weight gain in boiling water and the high weight loss on aging for the maleic anhydride cured formulation; however, the weight gain in the HBr-acetic reagent, which should be high if unreacted epoxide is present, is nil, indicating a high extent of epoxide reaction. How then do we account for the presence of unreacted anhydride in the maleic anhydride cured material? Maleic anhydride is a well known hydroscopic material,[133] and in the process of handling for melting and mixing, some moisture pick-up can be considered inevitable. This moisture readily

---

[133] Anhydride Hardners for Epoxy Resins, p. 42, (3)

converts maleic anhydride to cis-2-butenedioic acid (maleic). The four carbon atoms in this acid, having electrons in p orbitals, form a pi bond system (resonance hybrid). The creation of a negative charge on either hydroxyl oxygen by the loss of a hydrogen ion can be readily delocalized to create a highly stable carboxyl ion. Butenedioic acid is, therefore, a strong Bronsted acid (proton donor) and can readily protonate an epoxide. The facility of butenedioic acid in losing a proton is substantiated by its acid dissociation constant in water; $k_a = 1.42 \times 10^{-2}$, as compared to 6.89×10^{-5} for butanedioic (succinic), 7.4×10^{-5} for 2-methyl butanedioic (methyl succinic) and 3.55×10^{-4} for cyclohexane dicarboxylic (hexahydrophthalic).[134] The delocalization of charge is substantiated by the marked decrease in the dissociation constant for the second carboxyl group after the butenedioic acid has lost one proton ($k_a = 8.57 \times 10^{-7}$). For succinic acid, on the other hand, delocalization of charge through resonance cannot occur and the decrease in k_a for the second carboxyl group is relatively small ($k_a = 2.47 \times 10^{-6}$).[135] The protonation of the epoxide by acid causes a partial charge difference across an oxygen-carbon sigma bond in the epoxide group. A partial positive charge, therefore, develops on the carbon

---

[134] C. D. Hodgman, Handbook of Chemistry and Physics, pp. 1753-1756, (37)

[135] Ibid.

atom which can most readily support it. The 2^o carbon atom in the epoxide group can best support this positive charge, and for epoxidized novolac this ability to support the partial charge is enhanced by the presence of an adjacent aromatic ring. Based on the evidence of acid catalyzed epoxide clevage reactions, protonation does not proceed all the way to the formation of a carbonium ion, as the reaction remains primarily SN2.[136] The protonated epoxide can subsequently react with a carboxyl ion which is attracted to the partial positive charge on the 2^o carbon atom; thus, forming a monoester, and generating a hydroxyl group. This reaction eliminates the negative charge on the pi bond system of the maleic acid, thereby making it easier for the remaining carboxyl group to protonate a second epoxide. Our attention, however, transfers here from the carboxyl group to the hydroxyl group generated by the acid catalyzed esterification reaction. This hydroxyl functional group is a potential reaction site and can react with an anhydride through a termolecular transition state giving rise to further esterification,[137] or it can react with a protonated epoxide giving rise to etherification. In the etherification reaction a new hydroxyl group and a hydrogen ion are generated, the latter in turn which protonates another epoxide, therefore, the reactive

---

[136] R. T. Morrison and R. N. Boyd, Organic Chemistry, p. 891, (44)

[137] H. Lee and K. Neville, op. cit., p. 5.23

groups, a protonated epoxide and a hydroxyl group, are not consumed in the reaction. This can certainly explain why a relatively small water pick-up can lead to considerable etherification, if the dicarboxylic acid is a strong Bronsted acid. In the absence of the strong acid, the esterification reaction can be expected to dominate. In the presence of a tertiary amine, carboxyl ions are generated which can react directly with a non-protonated epoxide to generate an ion which opens another anhydride ring. The increase in carboxyl ions due to the tertiary amine will tend to shift the equilibrium between maleic acid and protonated epoxide, thereby reducing potential for etherification. Only for the strongest Bronsted acids, therefore, should any substantial etherification occur in the presence of a Lewis base. Of the anhydrides in Table II only maleic anhydride should form an acid of sufficient strength to promote etherification. The properties of the maleic anhydride cured formulation, as tabulated in Tables II, III, IV, VII, and IX, show that etherification has in fact occurred. The high weight loss on aging and high weight gain in boiling water show substantial excess anhydride, while there is no evidence of excess epoxide base on the weight gain in the HBr-acetic reagent. Based solely on its ability to form carboxyl ions, however, we could deduce that the epoxide-anhydride reaction should be relatively high for maleic anhydride. Kinetic studies have found that for a given anhydride the reaction rate is primarily a function of the tertiary amine concentration.[138] The rate determining step is, therefore, the formation of the carboxyl ions by the action of the Lewis base on the anhydride. The more stable carboxyl ions should be expected to be more readily formed. Again using the acid dissociation constants as a guide we would expect the relative reactivity of the anhydrides to be: maleic, hexahydrophthalic, methyl succinic, and succinic, in that order. Neglecting maleic anhydride because of the etherification complications, the results of this investigation indicate that the reaction order indicated by the differences in acid dissociation constants is correct. The weight loss on aging, the weight gain in boiling water, and the change in heat distortion temperature on aging all tend to show that hexahydrophthalic is more highly reacted than methyl succinic which in turn is more highly reacted than succinic. Solvent sensitivities are complicated by the presence of the methyl group on methyl succinic which lowers the physical density and increases the weight gain in both acetone and ethylene dichloride relative to succinic anhydride. The weight gain in the HBr-acetic reagent is also complicated by the methyl group. Apparently the weight gain caused by absorption of acetic acid into the

---

138. J. Feltzin et. al., *loc. cit.*

methyl succinic material outweighs the weight gain caused by reaction of epoxide with HBr for the succinic material. In general the HBr-acetic reagent is a less accurate indicator of excess epoxide than boiling water is of excess anhydride. For the latter case, the reaction of water with excess anhydride greatly outweighs the weight gain caused by absorption of water as a solvent. For the HBr-acetic reagent, however, the weight gains caused by the HBr reaction with the epoxide and the absorption of acetic acid are both significant. This is further complicated by leaching out of the unreacted unsaturated anhydrides, as evidenced by the weight losses in Table IX.

Upon aging, all the anhydride cured formulations embrittle such that the toughness is only a fraction of its former value and the effect of aging on toughness is expressed accordingly as the ratio of the aged toughness to the as-cured toughness (Table IV). For methyl endomethylene tetrahydrophthalic anhydride, however, the embrittlement caused by aging is especially severe. The sharp decrease in flexural strength, and subsequent loss in toughness, was caused by severe crazing of the resin surface. Crazing was observed on all formulations containing methyl endomethylene tetrahydrophthalic anhydride in this research, including the hexahydrophthalic/methyl endomethylene tetrahydrophthalic binary formulation. Obviously then, the crazing can be attributed directly to the presence of the methyl endomethylene tetrahydrophthalic anhydride (MEMTHPA). Additives to MEMTHPA cured systems which tend to decrease cross-linking density also were found to decrease crazing. An example of this behavior is illustrated in Table V. The diglycidyl ether of bisphenol A formulation, although also crazed, has better flexural strength retention than the epoxidized novolac. In fact, the diglycidyl ether formulation shows almost as much flexural strength retention as the uncrazed cis-4-THPA formulation. Increased cross-linking of the novolac system is apparent from differences in solvent sensitivities. The heat distortion temperature after aging is less significant because crazing would tend to increase the load on the uncrazed portion of the test specimen and suppress the recorded heat distortion temperature. High cross-linking resulting from ethylenic reaction of the double bond or a high extent of reaction is not sufficient; however, to explain the crazing as both maleic and cis-4-THPA cured systems cross-link to high degrees without any evidence of crazing. There is, moreover, no evidence in this investigation to indicate that MEMTHPA cured systems have a particularly high extent of epoxide-anhydride reaction unless we use weight loss on aging as the sole guide. Some researchers claim in fact that extent of reaction for MEMTHPA is less than for cis-4-THPA.[139] The peculiar behavior of MEMTHPA cured systems is,

---

[139] G. J. Fleming, loc. cit.

therefore, apparently related to the methylene bridge in its structure. The tendency for bridged Diels-Alder adducts to undergo reverse Diels-Alder reaction at high temperatures is the one property that differentiates it from the other anhydrides. The liberated diene in the presence of oxygen could undergo clevage similar to that encountered in ozonolysis and subsequently react with the regenerated maleic anhydride to significantly increase the cross-linking density. Special note should be made that the aging temperature in this investigation exactly corresponds to the temperature at which the weight loss from the reverse Diels-Alder reaction is at a maximum (see Figure I). Such a reaction with the subsequent addition polymerization accounts, therefore, for both the surface crazing and the low weight loss on aging.

Inspection of Tables III and IV reveal that aging separates the unsaturated anhydrides from the saturated anhydrides in terms of heat distortion temperature, modulus (if MEMTHPA is neglected due to the effect of crazing), and change in physical density. These different effects are, of course, due to addition polymerization of the double bond. The latter effect is due to a decrease in the contraction coefficient of the material which, like both the modulus and heat distortion temperature, results from increased resistance to molecular motion. It is also interesting to note, however, that the modulus is also markedly affected by the presence of the methyl group on the anhydride structure. In Table III where extents of reaction are all relatively high due to the long heat age, the modulus for methyl succinic as compared to succinic is 4.88×10^5 to 4.74×10^5 and for methyl tetrahydrophthalic as compared to cis-4-tetrahydrophthalic, 6.12×10^5 to 5.72×10^5. This relationship is in spite of the fact that other effects of the methyl group are to decrease heat distortion temperature and decrease density; effects which should indicate facilitated molecular motion. Apparently then the resistance to deformation caused by the presence of the methyl group is confined to conditions of limited molecular motion, i.e., low strains. The methyl group is evidently increasing resistance to bond distortion and rotations from equilibrium conformations about carbon-carbon bonds. At higher temperatures, however, the energy required for conformational interrotation can be supplied thermally and the effect of the methyl group is less important, and the resistance to flaw or deformation is controlled by other factors, notably the extent of cross-linking. Another effect of the methyl group is to decrease physical density and thereby increase solvent sensitivity by increasing the ability of the solvent to diffuse into the material.

For the unsaturated multi-ring anhydrides the position of the double bond on the cyclohexene ring can also have an effect on final properties. As is apparent from Table VI, an isomeric mixture can give both reduced epoxide-anhydride reaction, as well as reduced cross-linking through ethylenic unsaturation. The effect on the double bond reaction is the most pronounced with a 59°C difference in heat distortion temperatures existing after aging. The double bond is most reactive in the cis-4-position, so the above effect of isomerization on cross-linking through unsaturation should be expected. A lower extent of epoxide-anhydride reaction is, however, also apparent from solvent sensitivities and weight gains in both the boiling water and HBr-acetic reagents. This effect unlike the former requires a detailed analysis of relative proportions of each isomer in the isomeric mixture for proper explanation. Some isomers, such as the cis-1 isomer, could be expected to have a greater degree of epoxide-anhydride reaction due to the formation of a more stable carboxyl ion. With the double bond in the cis-1 position, the same resonance effects would occur as in maleic anhydride. Unfortunately such an analysis is currently unavailable. It can be inferred, however, that the cis-4-MTHPA isomer would have a greater double bond reactivity than the MTHPA isomeric mixture utilized in this research, but the epoxide-anhydride reactivity could be either greater or less depending on the relative proportions of the isomers in the isomerized mixture. Now that the importance of this isomerization on final properties is recognized, it would certainly be recommended in any future reserach to avoid the isomeric mixtures and utilize only the pure isomers for which it would accordingly be much easier to relate properties to structure since the structure is more completely known.

The dependence of solvent sensitivity on physical density leads to another attribute of the presence of a double bond in the anhydride structure. Even when reaction through unsaturation is neglected, a double carbon-carbon bond can improve solvent resistance. The density of the overall system increases due to a reduction in the carbon-carbon bond length, as compared to a carbon single bond, and the absence of two hydrogen atoms which of course take up atomic volume. This effect accounts for the improved solvent sensitivities of cis-4-THPA as compared to HHPA (Table VII) in spite of a reduced extent of reaction. It also accounts in part for the vast difference in solvent sensitivity between maleic and succinic (other factors as already discussed are also important in this case). The increase in density due to the double bond may also have a negative effect on the toughness of the unsaturated materials in Table II.

The chain deformation and motion required for stretching of the polymer at high stress levels will tend to be more severely restricted in a denser medium. The double bond, however, also inhibits rotation between conformers and bond distortions; thus, it is similar to the effect of the methyl group. MTHPA which has both a methyl group and a double bond has the highest modulus measured in both the as-cured and aged conditions. A third structural condition which inhibits bond rotation is the presence of a cyclohexane (or cyclohexene) ring. The multi-ring anhydrides, have accordingly higher moduli than their single ring counterparts. This factor also affects MTHPA and helps contribute to its extraordinarily high modulus. The methyl group, double bond, and cyclic structure also account for the relatively high modulus of MEMTHPA. The modulus remains, however, lower than MTHPA in the as-cured state, possibly due to a lower extent of reaction (Table VII). After aging crazing adversely affects an accurate measurement of MEMTHPA's modulus due to the difficulty in measuring the true cross-sectional area. It is interesting to note that, thus far, all the factors which adversely affect free rotation about carbon-carbon bonds (i.e., pi bonds, methyl groups, and cyclic structures) have a significant affect on the modulus.

The presence of the ethylenic double bond also appears to favor low weight losses on aging. This is not surprising as any reaction which tends to link the anhydride to the polymer structure will tend to decrease its volatility. Self polymerization between anhydride molecules also tends to increase molecular weight and thereby reduce volatility. This latter effect is expected to be relatively minor unless a vinyl monomer is added to enhance polymerization through the double bond. This will be discussed in more detail later when the effect of vinyl monomers is considered. As shown in Table IV, THPA does have a lower aging weight loss than HHPA: MEMTHPA is even lower for reasons already discussed. Isomerization of THPA by decreasing double bond reaction, also increases weight loss (Table IV). Maleic anhydride is, of course, adversely affected in this respect due to the complications of etherification.

The overall results as depicted in Tables II through IX, reveal HHPA as an excellent anhydride in the as-cured condition for combining high toughness with good heat distortion temperatures and solvent resistance. Succinic anhydride is a close second in toughness although adversely affected in other properties by its low extent of reaction. Aging of the materials reveal succinic and methyl succinic to be superior in retention of properties, although all the materials embrittle severely, with MEMTHPA having the lowest property retentions due to crazing.

Before discussing the properties of the binary anhydride systems, perhaps more should be said about the comparison of DGEBA and epoxidized novolac as illustrated in Table V. The DGEBA formulation is very significantly affected by its low density. Solvent sensitivities, in particular that of the density sensitive ethylene dichloride, markedly increase when compared to epoxidized novolac. Toughness, however, improves significantly resulting from the same factors which are adversely affecting other properties, i.e., low density, and reduced cross-linking due to lower resin functionality. In the aged condition, the severe crazing of the novolac samples makes comparison difficult. The increased surface exposure due to crazing could account for the slight difference noted in weight loss. Selection of epoxidized novolac over DGEBA in an application would depend on whether toughness or chemical resistance and heat distortion temperatures were more important.

Properties of the hexahydrophthalic binary anhydride systems are illustrated in Tables X through XIII. The properties for the most part lie, as should be expected, between the two anhydrides which form the binary system. In the as-cured state, however, properties of the anhydrides proved too similar to be able to determine whether the properties of the binary systems are additive or synergistic.

TABLE X

PROPERTIES OF EPOXIDIZED NOVOLAC CURED WITH A BINARY MIXTURE OF SATURATED HEXAHYDROPHTHALIC ANHYDRIDE AND AN UNSATURATED ANHYDRIDE

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT	WEIGHT GAIN * %	
	gms/cm^3	psi	10^5 psi	10^3 psi	^{o}C	acetone	edc **
HHPA	1.242	25,900	5.02	1.5	136	.63	.82
HHPA:THPA 1:1	1.252	24,250	5.08	1.3	131	.22	.57
cis-4-THPA	1.264	25,750	5.12	1.1	126	.19	.51
HHPA:MTHPA 1:1	1.244	25,600	5.26	.97	129	.15	.81
MTHPA	1.244	25,500	5.42	.93	121	.14	.70
HHPA:MA 1:1	1.268	22,950	4.72	.95	141	.33	.35
MA	1.304	22,700	4.63	.90	156	.11	.20
HHPA:MEMTHPA 1:1	1.246	25,950	5.29	.99	129	.37	.41
MEMTHPA	1.250	24,650	5.23	.79	145	.29	.38

* unpolished samples
** ethylene dichloride

TABLE XI

AGED PROPERTIES OF EPOXIDIZED NOVOLAC CURED WITH BINARY MIXTURE OF SATURATED HEXAHYDROPHTHALIC ANHYDRIDE AND AN UNSATURATED ANHYDRIDE

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT	WEIGHT GAIN %	
	gms/cm^3	psi	10^5 psi	10^3 psi	^{o}C	acetone	edc *
HHPA	1.240	9860	5.28	.084	140	.47	.85
HHPA:THPA 1:1	1.246	9250	5.50	.063	171	.22	.52
cis-4-THPA	1.253	8800	5.72	.058	248	.17	.43
HHPA:MA 1:1	1.256	9100	5.56	.068	211	.17	.29
MA	1.270	8800	5.68	.067	285	.21	.22

* ethylene dichloride

TABLE XII

EFFECT OF AGING ON EPOXIDIZED NOVOLAC CURED WITH A BINARY MIXTURE OF SATURATED HEXAHYDROPHTHALIC ANHYDRIDE AND AN UNSATURATED ANHYDRIDE

ANHYDRIDE	DENSITY gms/cm^3	FLEXURAL STRENGTH RETENTION %	FLEXURAL MODULUS 10^5 psi	TOUGHNESS T_a/T_i	HDT °C	WEIGHT LOSS @ 250°C %
HHPA	-.002	38.1	+ .26	.06	+4	12.1
HHPA:THPA 1:1	-.006	38.1	+ .42	.05	+4-	9.9
cis-4-THPA	-.011	34.2	+ .60	.05	+122	10.0
HHPA:MA 1:1	-.012	39.6	+ .84	.07	+70	12.8
MA	-.034	38.8	+1.05	.07	+129	19.5

TABLE XIII

EFFECT OF POST CURE TEMPERATURE ON HEAT DISTORTION TEMPERATURE

ANHYDRIDE	HDT (°C)	
	200°C post cure	250°C post cure
succinic	106	108
methyl succinic	98	97
maleic	156	243
hexahydrophthalic	136	134
cis-4-tetrahydrophthalic	121	123
methylendomethylene tetrahydrophthalic	145	211
HHPA:THPA 1:1	131	136
HHPA:MTHPA 1:1	129	131
HHPA:MEMTHPA 1:1	129	155
HHPA:MA 1:1	141	164

In cases where the double bond reaction is unimportant, and the primary reaction is the epoxide-anhydride reaction, properties are expected to be additive. Data in Table X for the HHPA/THPA and HHPA/MTHPA systems in which the double bond reaction is not yet significant, tend to support this hypothesis. Values of heat distortion temperature, flexural modulus, density, and toughness for the HHPA/THPA formulation all tend to fall midway between HHPA and THPA. The HHPA/MTHPA system behaves similarly except for the toughness value. Flexural strengths in both cases are too close to reach any conclusions. The tendency for the toughness to be closer to the more brittle material in every case where one of the anhydrides forming the binary system does not yield, but fails by brittle failure on the positive slope of the stress-strain curve, is not surprising. As HHPA is added to MTHPA, for instance, the ultimate flexural strength becomes progressively closer to the theoretical yield stress. The toughness values are accordingly increased slightly. At some concentration of HHPA, however, the yield stress is reached and the material yields, with toughness values rising sharply. Toughness values, therefore, can be expected to be synergistic whenever one of the anhydrides forming the binary system fails by brittle failure. If both anhydrides fail by brittle failure, or if both yield as in the HHPA/THPA system, then the toughness values can be expected to be additive.

When the double bond reaction of a saturated/unsaturated binary system becomes significant, the properties of the intermediate compositions may or may not become synergistic, depending on the effect of the saturated anhydride on the reactivity of the double bond. The most likely case, in fact, would be for the properties to become synergistic. The ability of the double bond to cross-link in the polymer system depends on the close proximity of two unsaturated sites on the polymer chain, unless a bridging agent, such as excess anhydride or a vinyl monomer, is present. The addition of the saturated anhydride to such a system, as evidenced by Table XII, decreases both the number of unsaturated sites and the potential for reaction between remaining unsaturated sites. However, when a bridging agent, such as the excess unsaturated anhydride in the MA/HHPA system is available, the decrease in reaction potential of the unsaturated sites need not occur until the distance between sites becomes large. Two unsaturated sites on the polymer chains which were separated too far for mutual reaction in the HHPA/THPA case, can in the HHPA/MA case react by formation of a maleic bridge due to the presence of excess unsaturated anhydride. In this case the potential for reaction of an unsaturated site is not reduced substantially until the distance between unsaturated sites increases beyond the ability of maleic anhydride to bridge between them; thus, a positive deviation from linearity occurs. Judging from the heat distortion data in Table XIII after the 250°C post cure, the MEMTHPA/HHPA system can be expected to have the same synergistic behavior as the HHPA/THPA system. Of course, this would be expected, based on the previous discussions, as there is no significant excess anhydride in the MEMTHPA/HHPA material. The heat distortion data for the MTHPA/HHPA system remain too close even after the 250°C post cure to permit any conclusions to be drawn.

Tables XIII and XIV illustrate an interesting point which has been mentioned briefly earlier. The tendency for the density of some anhydride cured epoxy systems to decrease with increasing post cure temperature, due to a decrease in the contraction coefficient of the thermoset resin, may cause a decrease in heat distortion temperatures with increasing post cure if no significant increase in cross-linking has occurred at the higher temperature. This undoubtedly accounts for the lower heat distortion values for both the HHPA and MSA cured materials in Table XIII. The decrease in density also accounts for the relatively small increases in heat distortion temperatures recorded for the MTHPA, MTHPA/HHPA and SA formulations. For these materials, therefore, there is no advantage in increasing post cure temperature for the purpose of increasing cross-linking density. Long heat ages are required to signifi-

TABLE XIV

EFFECT OF POST CURE TEMPERATURE AND AGING ON DENSITY

ANHYDRIDE	DENSITY gms/cm^3			
	100°C	200°C	250°C	aged
succinic	1.286	1.295	1.286	1.288
methyl succinic	1.258	1.258	1.255	1.256
maleic	1.312	1.304	1.298	1.270
hexahydrophthalic	1.246	1.242	1.239	1.240
cis-4-tetrahydrophthalic	1.265	1.264	1.254	1.253
methyl tetrahydrophthalic	1.249	1.244	1.240	1.230
methylendomethylene tetrahydrophthalic	1.256	1.250	1.250	1.241
DGEBA methylendomethylene tetrahydrophthalic	1.222	1.219	1.216	1.213

cantly affect cross-linking density and are, commercially, at least, impractical. Table XIV also illustrates the tendency for unsaturated systems to have a more significant decrease in contraction coefficient with increasing post cure temperature and aging. The very large decrease for maleic anhydride is also due in part to the diffusion of unreacted maleic anhydride out of the polymer without subsequent shrinkage occurring. The saturated anhydride systems have densities which are evidently comparatively independent of cure temperature and aging. The increase in density for succinic anhydride when increasing the post cure from 100° to $200^{\circ}C$ is further evidence of its low reactivity, as the increase is indicative of cure shrinkage.

The use of branched alkenyl succinic anhydrides as flexibilizers for rigid systems is a common practice in epoxy technology, as was discussed in the literature review. Table XV and Figures II through VIII illustrate the effect of branched octenyl and dodecenyl succinic anhydrides on a rigid maleic system. Density, flexural strength, toughness, aged weight loss, and solvent sensitivities tend to be synergistic with significant negative deviations from linearity. No improvement in flexibility is noted for the maleic system if either flexural strength or toughness is used as a measure of system flexibility. It is more accurate to call the effect weakening of the material since both ultimate flexural

TABLE XV

EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDES SUBSTITUTED FOR MALEIC ANHYDRIDE

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT °C			WEIGHT LOSS**	WEIGHT GAIN***	
	gms/cm^3	psi	10^5 psi	10^3 psi	200*	250	aged	%	ace.	edc
maleic	1.304	22,700	4.63	.90	156	243	285	19.5	.11	.20
MA:OSA 3:1	1.251	20,200	4.52	.66	136	191	256	12.8	.91	.67
MA:OSA 1:1	1.208	19,600	4.28	.63	114	161	191	11.8	3.8	5.3
MA:OSA 1:3	1.174	18.150	4.07	.56	94	120	142	11.3	14.0	22.
OSA	1.143	17,200	3.98	.63	79	85	104	9.4	23.	D
MA:DDSA 3:1	1.228	20,250	4.34	.73	116	152	200	13.5	2.6	6.4
MA:DDSA 1:1	1.186	18,800	4.14	.70	98	110	134	12.4	12.	23.
MA:DDSA 1:3	1.138	17,250	3.95	.76	77	86	78	8.6	D	D
DDSA	1.110	16,050	3.63	.81	68	65	52	10.1	D	D

* post cure temperature
** weight loss on aging
*** unpolished samples; ace.=acetone, edc=ethylene dichloride, D=disintergrated

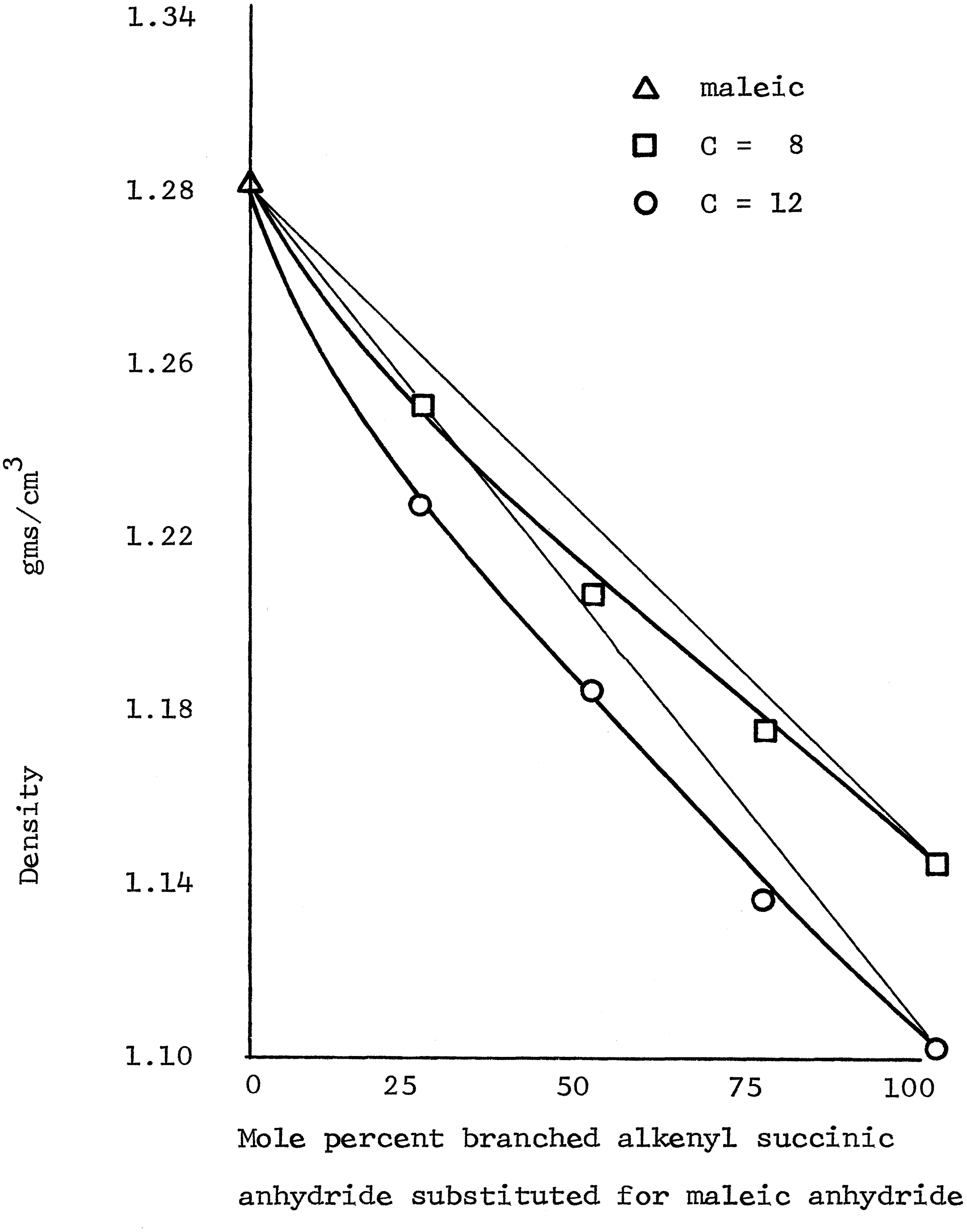


FIGURE II EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDE ON THE DENSITY OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

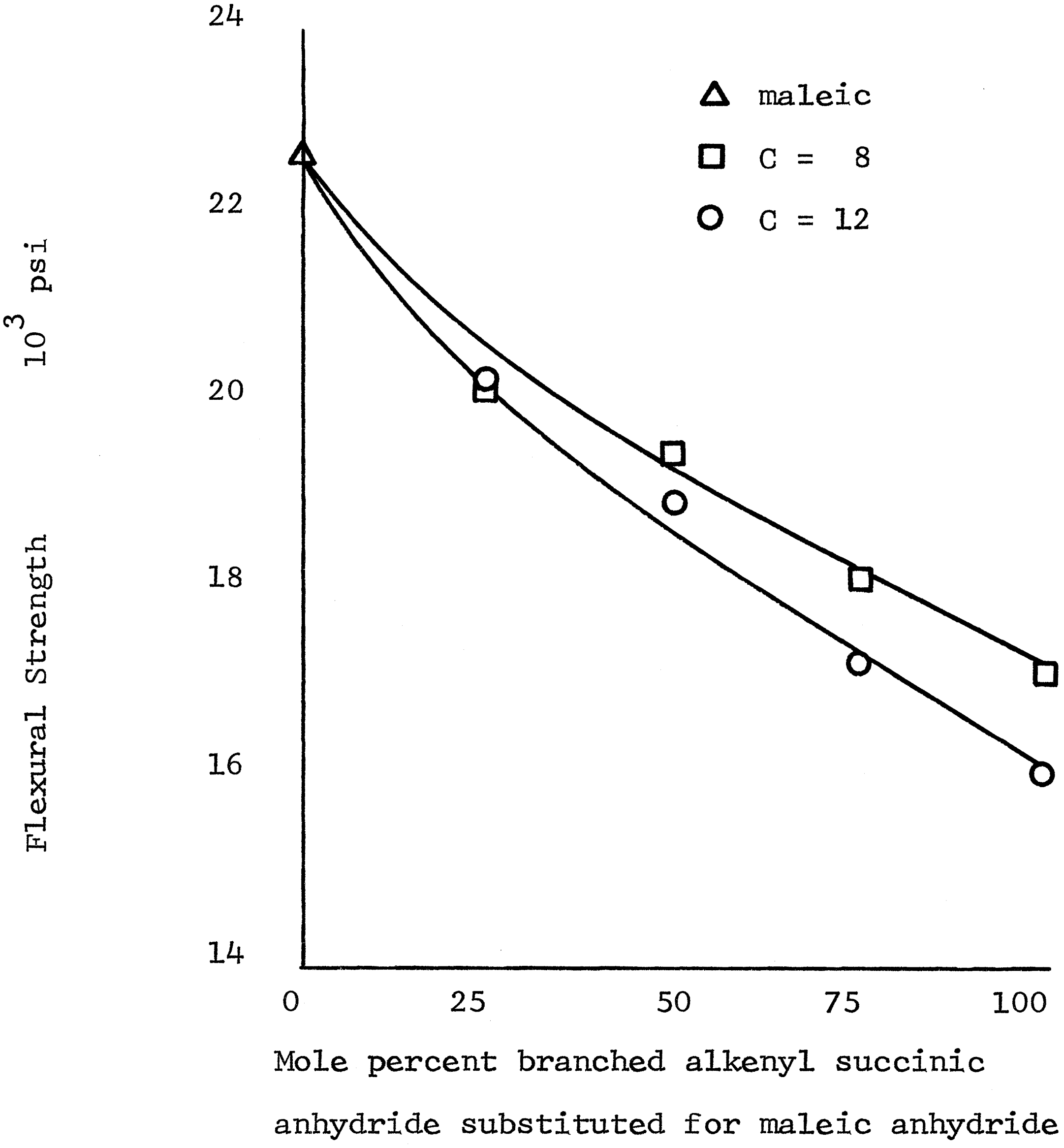


FIGURE III EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDE ON THE FLEXURAL STRENGTH OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

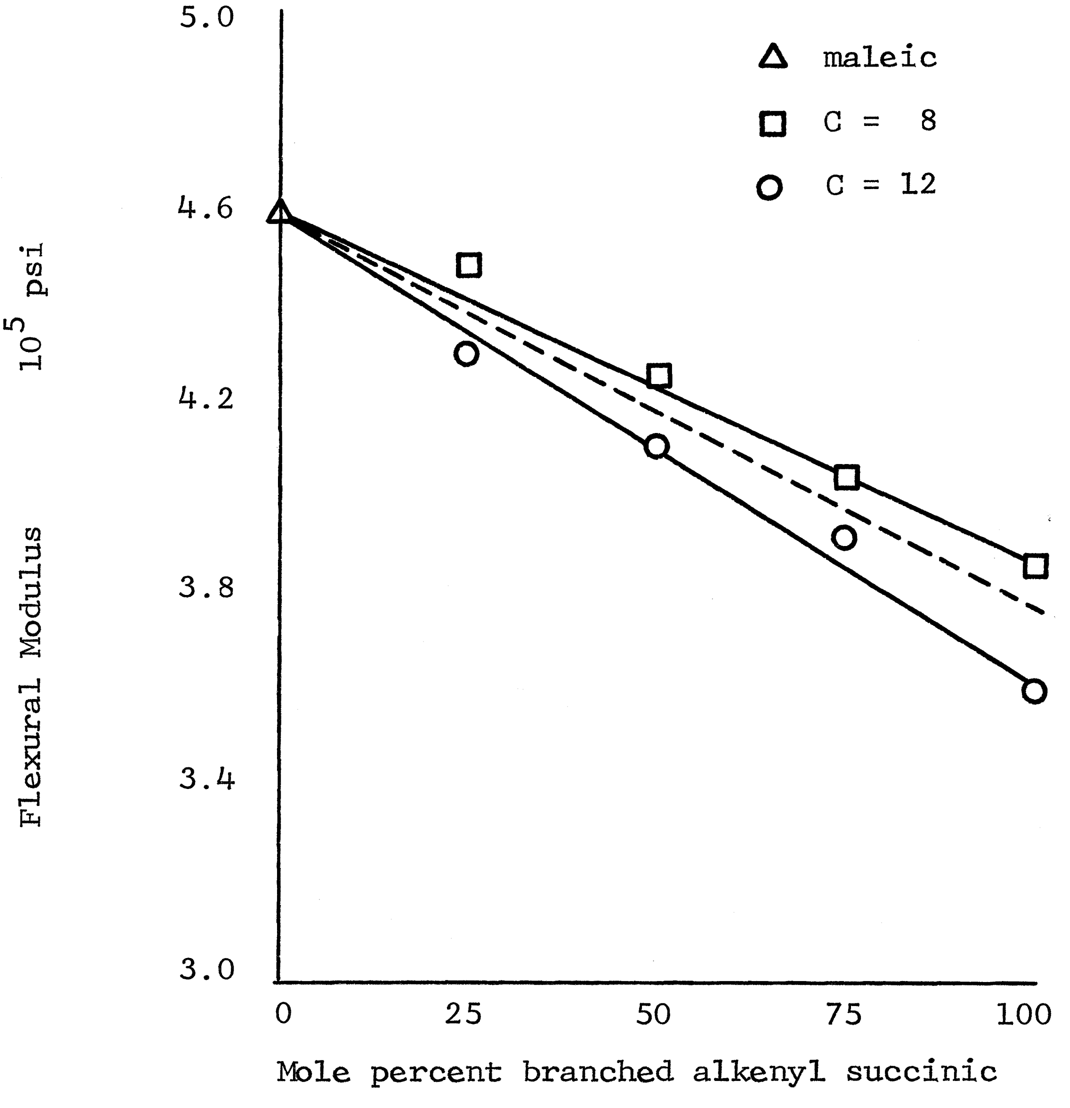


FIGURE IV EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDE ON THE FLEXURAL MODULUS OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

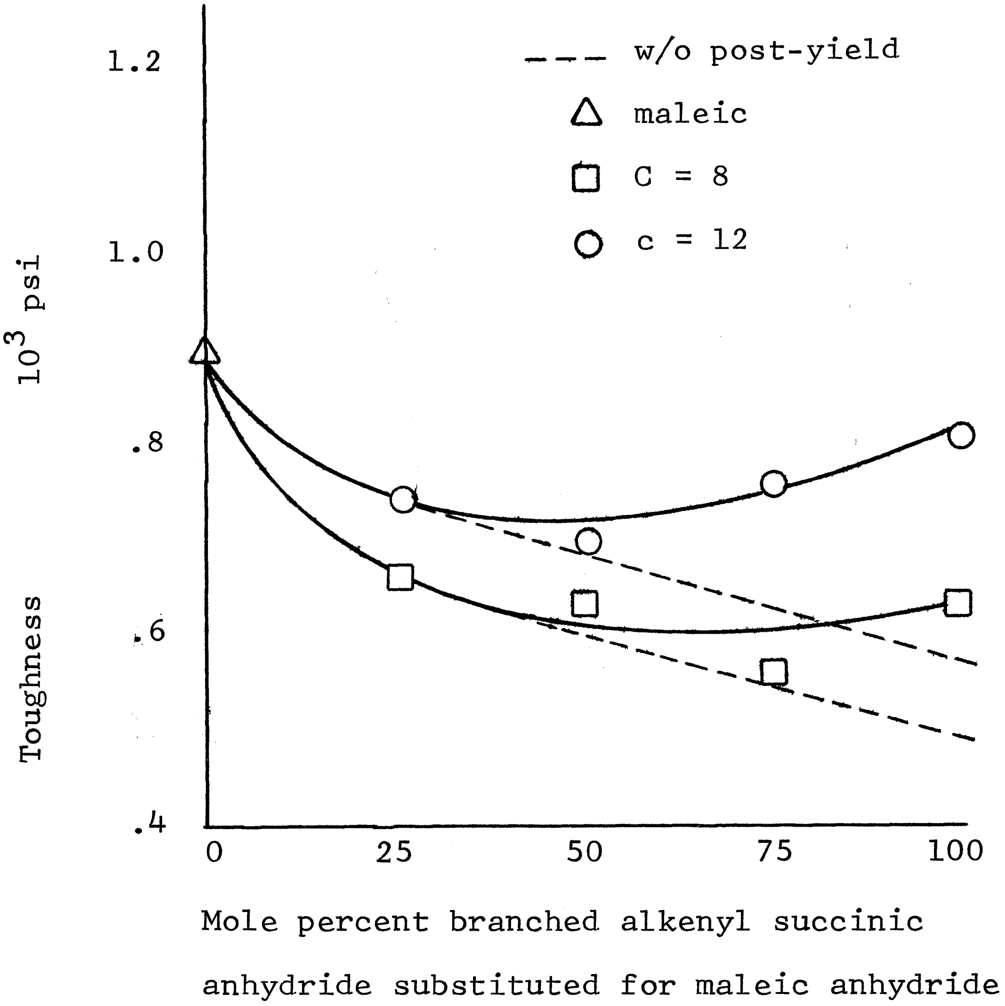


FIGURE V <u>EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDE ON THE TOUGHNESS OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC</u>

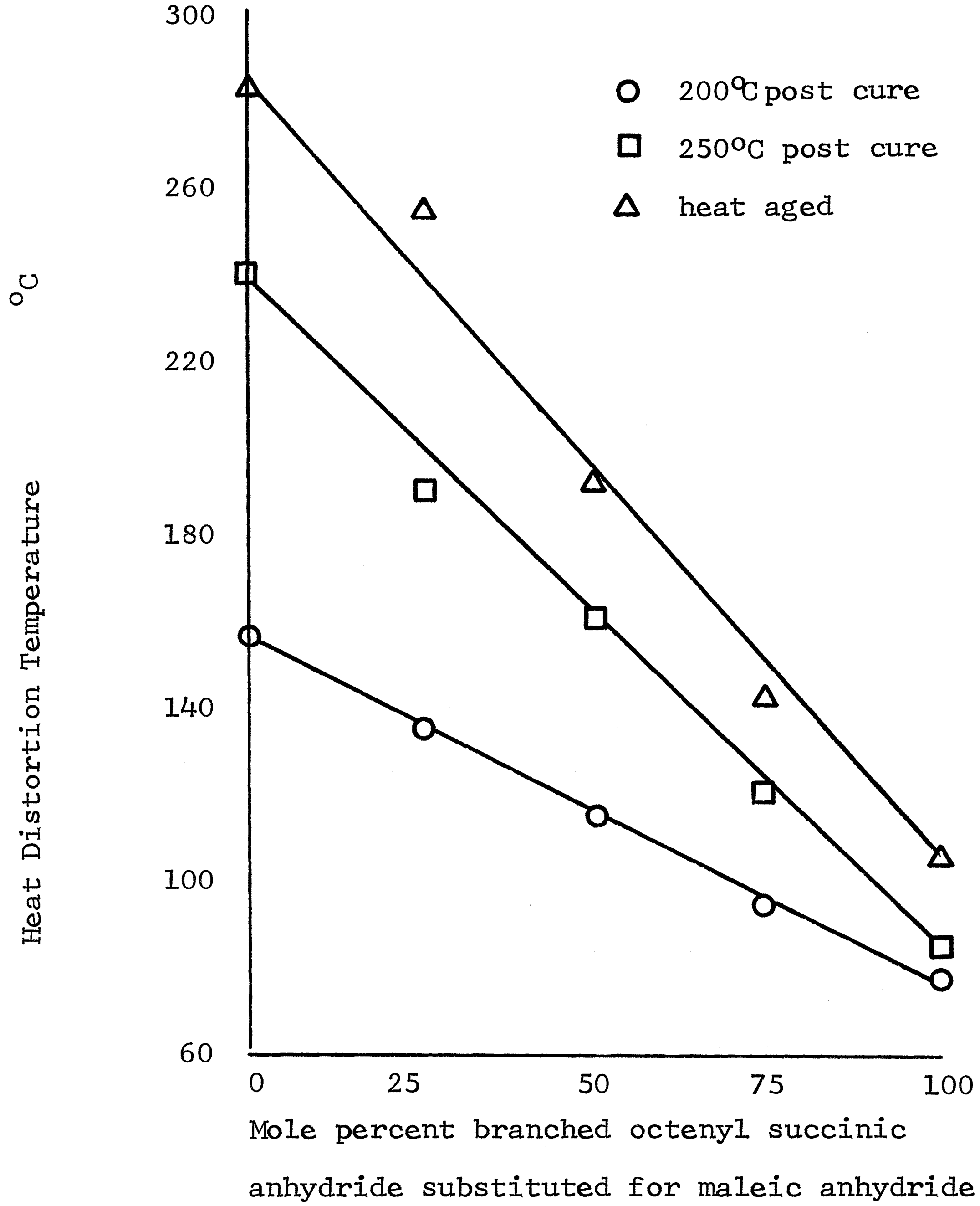


FIGURE VI EFFECT OF BRANCHED OCTENYL SUCCINIC ANHYDRIDE ON THE HEAT DISTORTION TEMPERATURE OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

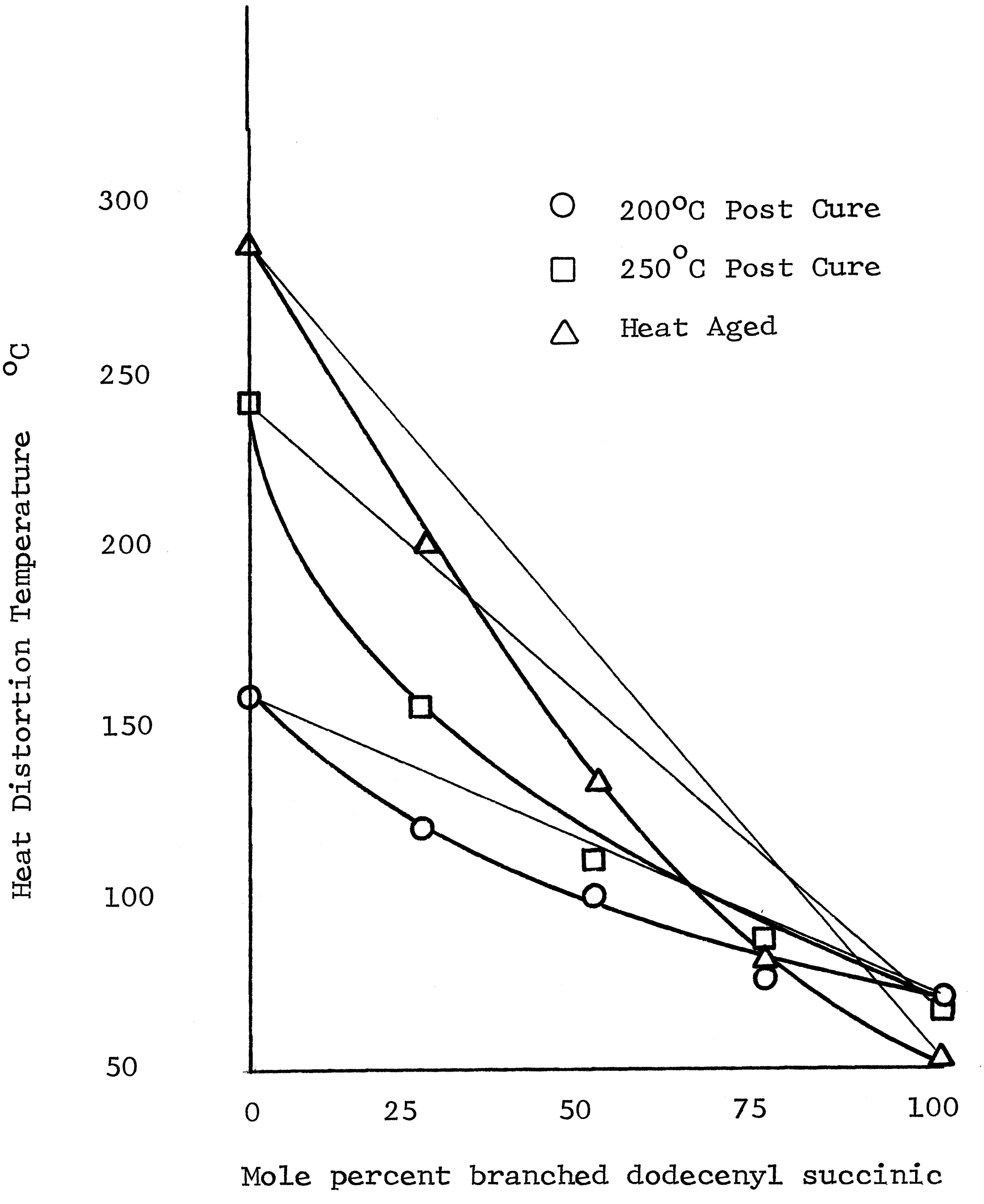
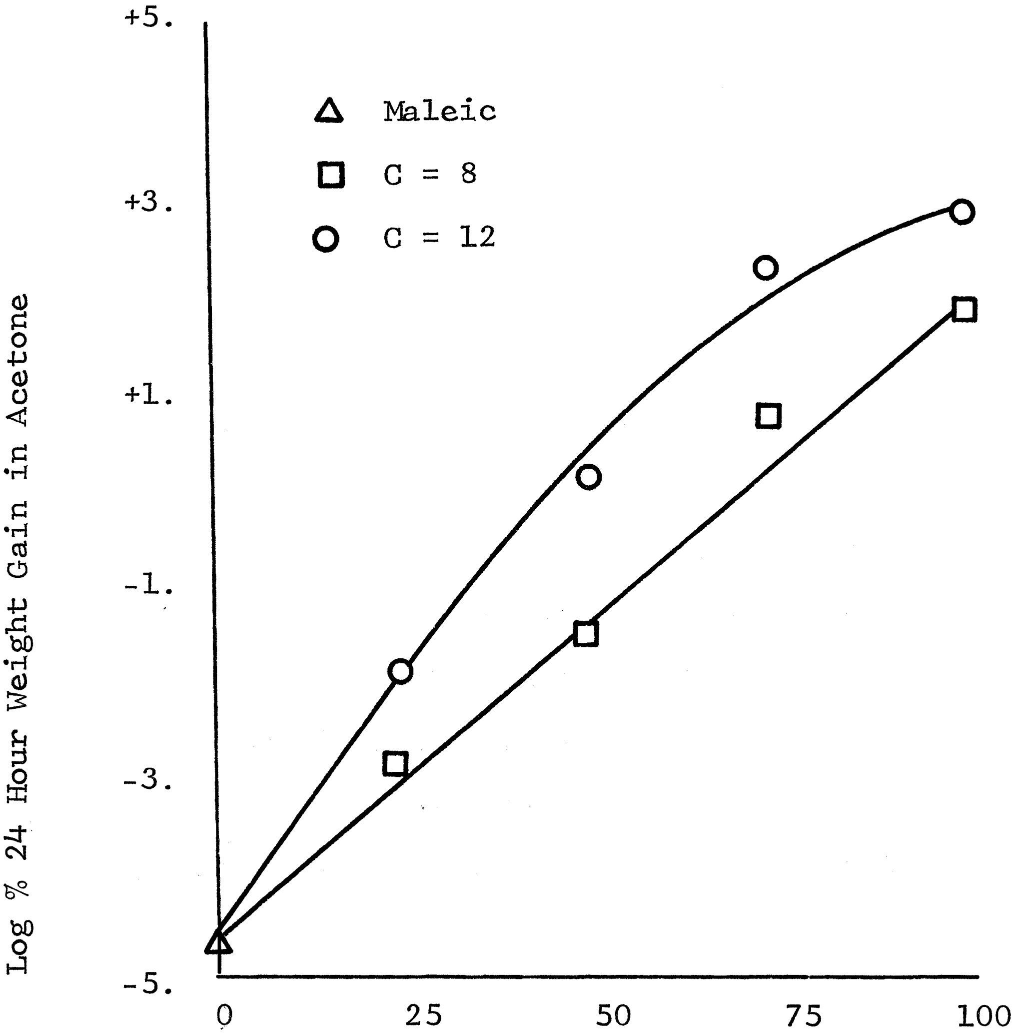


FIGURE VII EFFECT OF BRANCHED DODECENYL SUCCINIC ANHYDRIDE ON THE HEAT DISTORTION TEMPERATURE OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC



Mole percent branched alkenyl succinic anhydride substituted for maleic anhydride

FIGURE VIII EFFECT OF BRANCHED ALKENYL SUCCINIC ANHYDRIDES ON THE SOLVENT SENSITIVITY OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC strain and flexural strength fall off significantly. Toughness values behave synergistically for reasons discussed earlier for the MA/HHPA system. Positive deviations from linearity occur only after yielding begins. Figure V illustrates both the actual toughness curves, as well as the curve neglecting toughness gained from post yielding. In the latter case one can see the approach to linearity. Heat distortion values, obviously influenced by both the effect of the branched alkenyl on the double bond reaction and the significant drop in densities, are linear for the octenyl case, but have a negative deviation for the dodecenyl case. Branched octenyl and branched dodecenyl succinic anhydrides are both unsaturated anhydrides, for which (for reasons discussed later) we can consider the double bond to be at least partially reacted. If the double bond in the branched alkenyl case were highly reactive, however, then we could expect the unsaturated binary system to be analogous to a saturated binary system. For either system a theoretical value, which we will call cross-links per mole of reactants, would remain constant as one anhydride was replaced with another. The heat distortion temperature, therefore, if considered primarily a function of cross-links per unit volume, would exhibit the same variation as moles per unit volume, which in turn is a function of the molecular weight of the reactants and the physical density. If the double bond were considered, therefore, equally reactive as maleic, we would expect an even greater synergistic behavior for the heat distortion temperatures of both branched octenyl and branched dodecenyl succinic anhydrides as exhibited by their physical densities. On the other hand, if we consider the double bond in the branched alkenyl to be non-reactive, a greater negative deviation from linearity would be expected as both the cross-links per mole and moles per unit volume would be decreasing synergistically. This is complicated, however, as in the MA/HHPA system by the presence of excess maleic anhydride which bridges between the unsaturated sites as long as the distance between sites is relatively small. This effect, as shown earlier, tends to shift the binary heat distortion curve in the positive direction. For the MA/HHPA system the normally linear curve has a positive deviation. In the branched alkenyl case, the reactivity of the double bond on the alkenyl chain must be considered much lower than the double bond in the maleic anhydride, such that there is a tendency to shift the normally negative synergistic curve in the positive direction. Amount of shift depends on the ability of excess maleic anhydride to bridge between unsaturated sites, which decreases with the length of the aliphatic chain in the branched alkenyl. The net result of the above effects, as evidenced by Figures VI and VII, is that the heat distortion curve for the MA/OSA system becomes essentially linear, while in the MA/DDSA system a certain amount of negative deviation is retained.

The modulus values for both branched alkenyl anhydrides appear as approximately linear functions of branched alkenyl substituted for maleic. In the DDSA case, however, the modulus should be expected to exhibit a negative deviation from linearity, as the modulus values up to now have consistently supported the heat distortion values when observing the effects of relative degrees of cross-linking. Branched DDSA, as will be discussed later, is one of the formulations which is adversely affected by creep and the flexural strength and modulus are lower relative to the more rigid materials than could be expected at a much faster strain rate. It is interesting to note in this case that a moderate increase in modulus for the branched DDSA material to 3.8×10^5 psi, as indicated by the dotted line in Figure IV, would cause the modulus curve to have the same degree of negative deviation from linearity as the heat distortion curve.

Inspection of the aged heat distortion values in Table XV reveals some instances in which heat distortion values have decreased on aging due to thermal degradation. The degradation of the DDSA system is evidenced both by the 16°C drop in heat distortion temperature, as well as by the increase in weight loss over the MA/DDSA, 1/3, formulation. Some crazing was also present on this formulation as well as on the branched octenyl material. The branched octenyl was so severely crazed, in fact, that careful handling was required not to cause breakage. The 25°C rise in heat distortion temperature for branched octenyl, in spite of the severe crazing, is significant and reflects the reaction of the alkenyl double bond.

Solvent sensitivities of the alkenyl/maleic systems, as shown in Table XV and Figure VIII, are to be expected on the basis of the decrease in density shown in Figure II. The low weight loss on aging of branched OSA and DDSA in Table XV is due to both the high epoxide reactivity for these anhydrides in the as-cured state, as well as a weight gain on heat aging caused by oxidation of the unreacted double bonds in the anhydride structure.

The effects of adding vinyl monomers to the unsaturated anhydride structures are shown in Tables XVI through XX and Figure IX. The general effects of vinyl toluene additions to the unsaturated formulations were to decrease all the as-cured properties, except for the solvent sensitivity which increased due to the decrease in density. A notable exception to this generalization was the maleic anhydride formulation, where the vinyl toluene

TABLE XVI

EFFECT OF VINYL TOLUENE ADDITIONS ON ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT °C		WEIGHT GAIN ** %	
	gms/cm^3	psi	10^5 psi	10^3 psi	200°*	250°	acetone	ethylene dichloride
HHPA	1.242	25,900	5.02	1.5	136	134	.63	.82
HHPA w/VT	1.214	23,550	4.75	1.1	125	130	1.2	5.8
cis-4-THPA	1.264	25,750	5.12	1.1	126	136	.19	.51
THPA w/VT	1.242	23,850	5.07	.91	119	130	.24	.82
MA	1.304	22,700	4.63	.90	156	243	.11	.20
MA w/VT	1.270	21,450	5.39	.56	190	250	.36	.21
MTHPA	1.244	25,500	5.42	.93	121	123	.14	.70
MTHPA w/VT	1.214	25,150	5.26	.93	112	116	.61	3.2
MEMTHPA	1.250	24,650	5.23	.79	145	211	.29	.38
MEMTHPA w/VT	1.226	25,350	5.32	.74	134	200	1.1	2.6

* post cure temperature
** unpolished samples

TABLE XVII

EFFECT OF VINYL TOLUENE CONCENTRATION ON PROPERTIES OF METHYL TETRAHYDROPHTHALIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

MOLES VINYL TOLUENE per EPOXY EQUIVALENT	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT	WEIGHT GAIN * %	
	gms/cm^3	psi	10^5 psi	10^3 psi	°C	acetone	edc
0	1.244	25,500	5.42	.93	121	.14	.70
.25	1.230	26,300	5.29	1.1	114	.21	2.4
.5	1.214	25,150	5.26	.93	112	.61	3.2
1	1.201	24,600	5.15	.92	108	1.4	11.

* unpolished samples; edc = ethylene dichloride

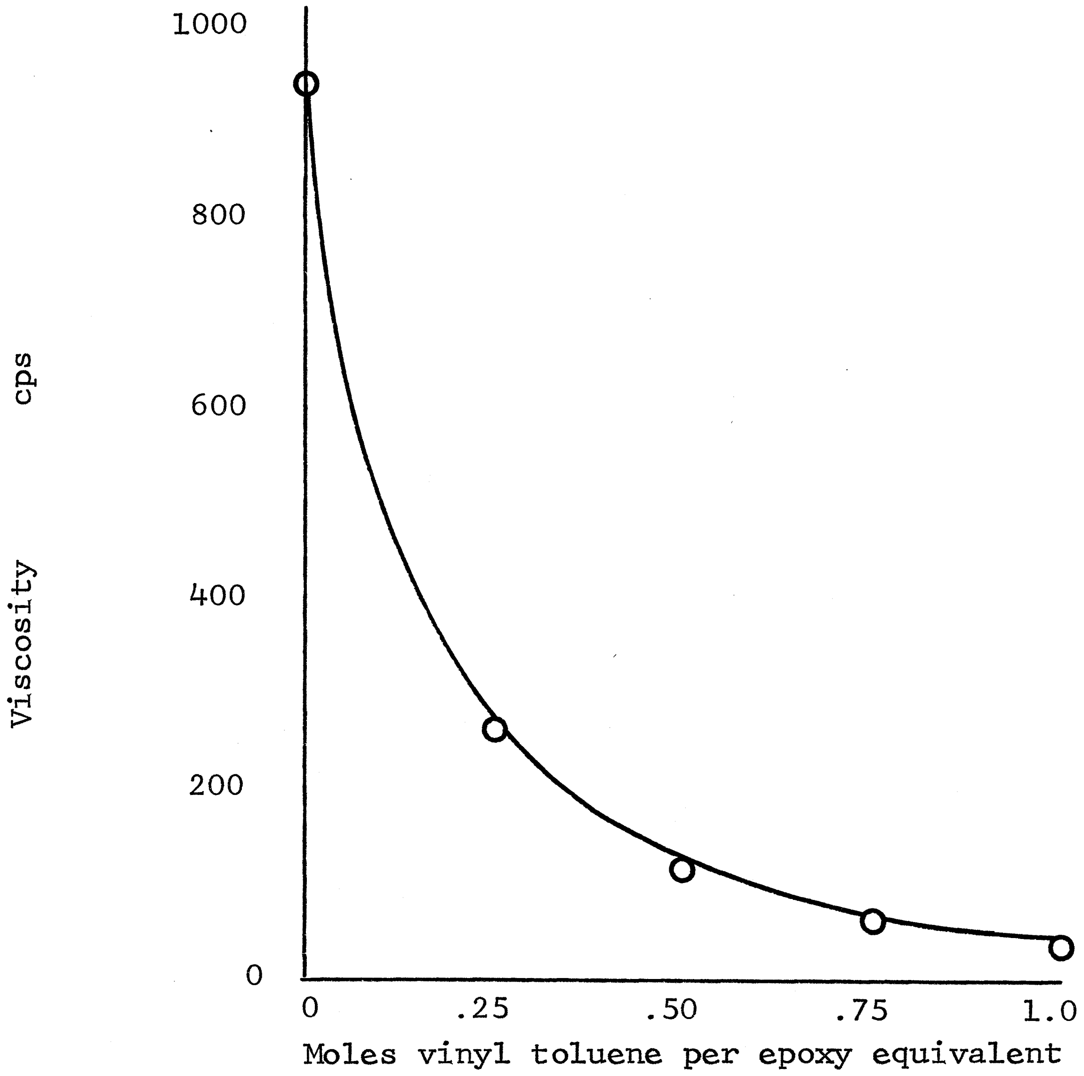


FIGURE IX EFFECT OF VINYL TOLUENE CONCENTRATION ON VISCOSITY OF METHYL TETRAHYDROPHTHALIC ANHYDRIDE/ EPOXIDIZED NOVOLAC MIXTURE

TABLE XVIII

EFFECT OF VINYL TOLUENE ADDITIONS ON THE AGING CHARACTERISTICS OF ALICYCLIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY	FLEXURAL STRENGTH RETENTION	FLEXURAL MODULUS	TOUGHNESS	HDT	WEIGHT LOSS @ 250°C
	gms/cm^3	%	10^5 psi	T_a/T_i	°C	%
HHPA	-.002	38.1	+.26	.06	+4	12.0
HHPA w/VT	-.001	40.7	+.48	.07	+9	11.3
cis-4-THPA	-.011	34.2	+.60	.05	+122	10.0
THPA w/VT	-.015	40.2	+.36	.09	+105	9.4
MA	-.034	38.8	+1.05	.07	+129	19.5
MA w/VT	-.024	41.4	+.35	.11	+76	15.1
MTHPA	-.014	38.2	+.70	.08	+46	14.8
MTHPA w/VT	-.010	38.9	+.72	.09	+30	12.6
MEMTHPA *	-.009	14.4	-.37	.02	+121	8.4
MEMTHPA w/VT*	-.005	28.3	-.24	.06	+122	8.6

* crazed

TABLE XIX

COMPARISON OF MONOCHLOROSTYRENE AND VINYL TOLUENE ADDITIONS IN MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

MOLES MONOMER per EPOXY EQUIVALENT	DENSITY	FLEXURAL STRENGTH	FLEXURAL MODULUS	TOUGHNESS	HDT °C			WEIGHT GAIN** %	
	gms/cm^3	psi	10^5 psi	10^3 psi	200*	250	aged	ace.	edc
0	1.304	22,700	4.63	.90	156	243	285	.11	.20
VINYL TOLUENE									
.3	1.284	22,950	5.04	.76	176	240	272	.29	.15
.5	1.270	21,450	5.39	.56	190	250	266	.36	.21
MONOCHLOROSTYRENE									
.3	1.302	23,000	5.29	.74	178	240	266	.39	.17
.5	1.295	22,650	5.52	.59	182	210	254	.38	.24

* post cure temperature (°C)
** unpolished samples; ace. = acetone, edc = ethylene dichloride

TABLE XX

EFFECT OF VINYL TOLUENE ON A MALEIC/HEXAHYDROPHTHALIC BINARY ANHYDRIDE CURED EPOXIDIZED NOVOLAC

PROPERTIES	HHPA:MA 1:1	w/VT 75°C gel	w/VT * 50°C gel
DENSITY gms/cm^3	1.268	1.242	1.234
FLEXURAL STRENGTH psi	22,950	22,750	23,850
FLEXURAL MODULUS 10^5 psi	4.72	5.00	5.04
TOUGHNESS 10^3 psi	.95	.62	.82
HDT °C	141	142	131
WEIGHT GAIN % **			
acetone	.33	.87	1.8
ethylene dichloride	.35	.84	.77
EFFECT OF AGING			
DENSITY gms/cm^3	-.012	-.012	-.009
FLEXURAL STRENGTH RETENTION %	39.6	43.2	42.7
FLEXURAL MODULUS 10^5 psi	+.84	+.34	+.28
TOUGHNESS T_a/T_i	.07	.13	.10
HDT °C	+70	+33	+29
WEIGHT LOSS %	12.8	10.4	11.2

* lauroyl peroxide catalyst; two layered composite
** unpolished samples

undoubtedly copolymerized with the maleic anhydride under the action of the tertiary butyl perbenzoate. For this formulation significant increases occurred in both modulus and heat distortion temperatures, reflecting the greater degree of cross-linking through unsaturation. In the other anhydride systems, vinyl toluene has apparently polymerized with itself fairly early in the overall reaction and is present in the polymer structure as long aliphatic chains. The presence of long polymer chains rather than unreacted vinyl toluene trapped in the polymer system is evident both by the relatively minor effect on cross-linking density as indicated by heat distortion temperature, as well as reduction in weight loss on aging even for the saturated hexahydrophthalic system where no reaction can be occurring between the vinyl toluene and the anhydride. The effect of these polyvinyl toluene chains is similar to the effect of the long aliphatic chain in the branched DDSA on maleic anhydride cured material, as the net result in both cases is weakening of the resin matrix. It is significant that in this case, at least, although it may not be true for DDSA, the weakening occurs not only for the brittle materials, but for the materials with considerable post yielding as well.

Table XVII and Figure IX show the effects of variable vinyl toluene concentrations on a MTHPA cured system. Properties in general continue to decrease with increasing vinyl toluene concentration. For the formulation with a .25/1 monomer to anhydride ratio, however, a slight increase was noted in flexural strength and toughness, thus indicating that there may be some improvement in toughness when the polyvinyl toluene chains are fairly short or the concentration is fairly low. The solvent sensitivities again increase with decreasing density caused by the presence of polyvinyl toluene chains. The importance of solvent sensitivity dependance on density, especially for ethylene dichloride, can be emphasized by the fact that if we arrange the formulations in Table XVI in order of decreasing density, we also arrange them in order of increasing weight gain in ethylene dichloride. A relatively minor exception is the lower weight gain for MEMTHPA than for cis-4-THPA, possibly due to the greater ethylenic reaction in the former case. Apparently the only advantage in adding vinyl toluene in high concentrations to an anhydride system (maleic excepted) is to lower the viscosity as illustrated in Figure IX.

The vinyl toluene additions apparently slightly inhibit the epoxide-anhydride reaction. This effect is indicated by the greater rise in both modulus and heat distortion temperature on aging for the hexahydrophthalic formulation containing the monomer addition as compared to the hexahydrophthalic formulation itself.

The effect of the vinyl monomers on the maleic system was of the greatest interest because of the apparent copolymerization of the vinyl monomer with maleic anhydride. Table XIX shows the effect of both vinyl toluene and monochlorostyrene on the maleic system at variable concentrations. Very high cross-link densities are reached in relatively short cure times, when compared to the MA cured system itself. Toughness, on the other hand, is markedly reduced, falling to about 2/3 of that for the MA formulation. The presence of tertiary butyl perbenzoate and the unsaturated monomers has caused many more unsaturated sites in the maleate structure to react at 200°C. Increasing the post cure temperature, however, reacts these sites in the absence of either vinyl toluene or tertiary butyl perbenzoate. Eventually at the higher temperature the heat distortion values of the modulus values rise higher for the MA system itself, than for any of the systems containing vinyl monomers. For the vinyl toluene at .5/1 mole monomer/mole anhydride concentration, for instance, the modulus before aging is 66,000 psi higher than that for MA, after aging it is 4,000 psi lower; the heat distortion temperature is 34°C higher before aging, and 19°C lower after aging. The polymer structure after aging evidently bears a similarity with the other formulations containing vinyl toluene, i.e., long polymer chains (in this case vinyl toluene - maleic anhydride copolymer chains) entrapped in the cross-linked network system caused by the maleic anhydride epoxidized novolac reaction. These chains then eventually cause, as in each of the other anhydride systems, a reduction in modulus and heat distortion temperature.

A closer comparison of Table XIX reveals that monochlorostyrene is more effective in increasing the modulus than vinyl toluene, while less effective in increasing heat distortion temperatures. The effect on density is only slight due to the high density of monochlorostyrene itself. Toughness values and solvent sensitivities appear equivalent for both monomers. The chlorine atom in monochlorostyrene, because of its size and electronegativity, (increased resistance to conformational inter-rotation and increased polar bonding) can be expected to cause a greater increase in modulus than the methyl group in vinyl toluene, which is indeed the case. The reason for lower heat distortion values than vinyl toluene at 250°C and after aging is less apparent, but could very well be related to the relative size of the copolymer chains in the two systems. The many competing reactions in such formulations as these, necessarily form very complex structures. Such systems are accordingly worthy of further study in another research program where the structure of the monomer can be varied further and the various monomer reactivity ratios with maleic anhydride can be taken into account.

Attempts to add vinyl toluene to the maleic/hexahydrophthalic binary system produced some very interesting effects. Vinyl toluene at a monomer/anhydride mole ratio of .5/1 is apparently slightly above the solubility limit of the vinyl toluene in the binary system at 75°C, and weight loss of monomer during cure was accordingly high as the excess monomer migrated to the surface and volatilized. The casting temperature was lowered therefore to 50°C and a highly reactive lauroyl peroxide catalyst was utilized in an attempt to decrease the volatility loss. The excess monomer, however, still migrated to the surface, where instead of volatilizing (weight loss during gel was less than 1%), it polymerized forming a clear .006 inch film on the sheet surface. After gelation this film could easily be separated from the surface. Properties of this formulation are shown in Table XX for both the 75°C and 50°C gel. Properties of both are similar with the few differences reflecting the lower monomer content of the formulation gelled at 75°C due to the increased volatility loss during gelation. Flexural tests on the two phase material were run with the film placed in tension. Some improvement in flexural strength and toughness is noted over the material gelled at the higher temperature, but improvement is certainly not significant. In the as-cured state the effect of vinyl toluene on the binary system is similar to the effect of vinyl toluene on maleic anhydride, although to a lesser extent. Heat distortion values are comparable and modulus values are increased. Upon aging, however, both heat distortion temperature and modulus markedly increase for the binary system, leaving the formulations containing vinyl toluene far behind.

The above results complete the work done on the anhydride structures suitable for high temperature applications, as the anhydrides which now come under investigation produce considerably softer, lower strength epoxy resins, suitable for applications far below the aging temperature encountered by the earlier materials. These anhydrides, however, continue to illustrate the marked effect of anhydride structure on properties and provide some clues which aid analysis of the results on the former anhydride formulations. All tests, therefore, run on the softer materials were also run on the succinic and methyl succinic formulations to improve cross correlation between the two sets of data.

Two homologous series of substituted succinic anhydrides are available commercially, the alkenyl and the alkyl succinic anhydrides. The former of these is available both with linear and methyl branched chains. Flexural properties for the more rigid of these anhydrides

TABLE XXI

FLEXURAL PROPERTIES OF EPOXIDIZED NOVOLAC CURED WITH EIGHT CARBON CHAIN SUBSTITUTED SUCCINIC ANHYDRIDES

ANHYDRIDE	FLEXURAL STRENGTH psi	FLEXURAL MODULUS 10^5 psi
branched octenyl	17,200	3.98
linear octenyl	12,450	3.05
linear octyl	11,750	2.79

TABLE XXII

FLEXURAL PROPERTIES OF EPOXIDIZED NOVOLAC CURED WITH BRANCHED ALKENYL SUCCINIC ANHYDRIDES

ANHYDRIDE	CARBON ATOMS ON CHAIN	FLEXURAL STRENGTH psi	FLEXURAL MODULUS 10^5 psi	TOUGHNESS 10^3 psi
branched octenyl	8	17,200	3.98	.63
branched noneyl	9	16,900	3.93	.74
branched dodecenyl	12	16,050	3.63	.81

are shown in Tables XXI and XXII. For the softer materials flexural properties could not be determined due to excessive slippage between supports. Many of the longer chained anhydrides had heat distortion temperatures below room temperature; flexural strain was accordingly high, allowing samples to be pulled through the supports without fracture. The tensile test was used, therefore, in lieu of the flexural test for evaluating the properties of epoxy formulations cured with these long chain anhydrides.

The flexural properties of the formulations were found to depend on strain rate (Figure X through XIV and Table XXIII). The linear octenyl formulations was tested at variable deflection rates ranging from .02 inch/minute to 2 inches/minute and the flexural modulus and yield strength were both found to be linear functions of the log of the strain rate over the entire strain rate region tested. Figure XII shows the set of stress-strain curves for linear octenyl succinic anhydride and illustrates the same linear behavior for both the yield point and proportional limit. Figure XIII and Table XXIII show the properties of other formulations as a function of strain rate. It is apparent from Figure XIII that the flexural properties of the softer materials become shifted downward at slower strain rates due to the increased importance of creep and subsequent slippage between supports.

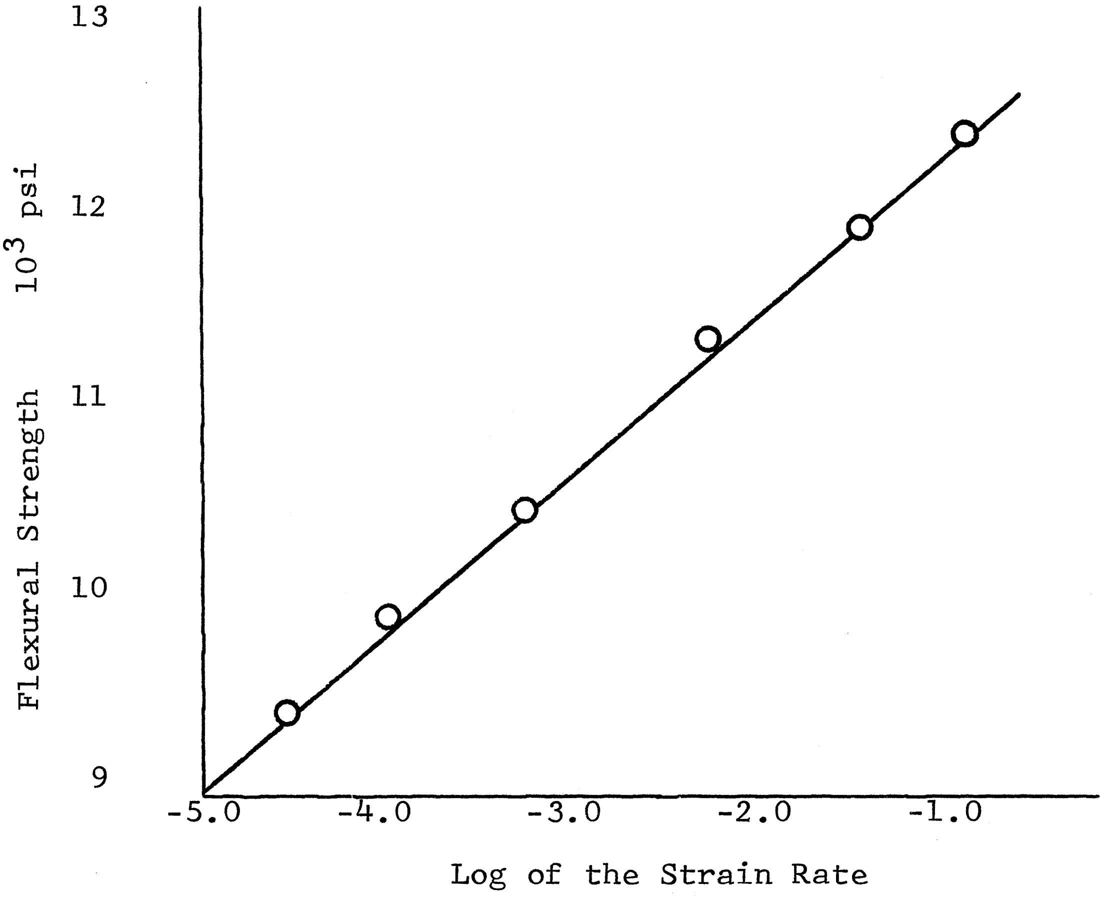


FIGURE X EFFECT OF STRAIN RATE ON FLEXURAL STRENGTH OF n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

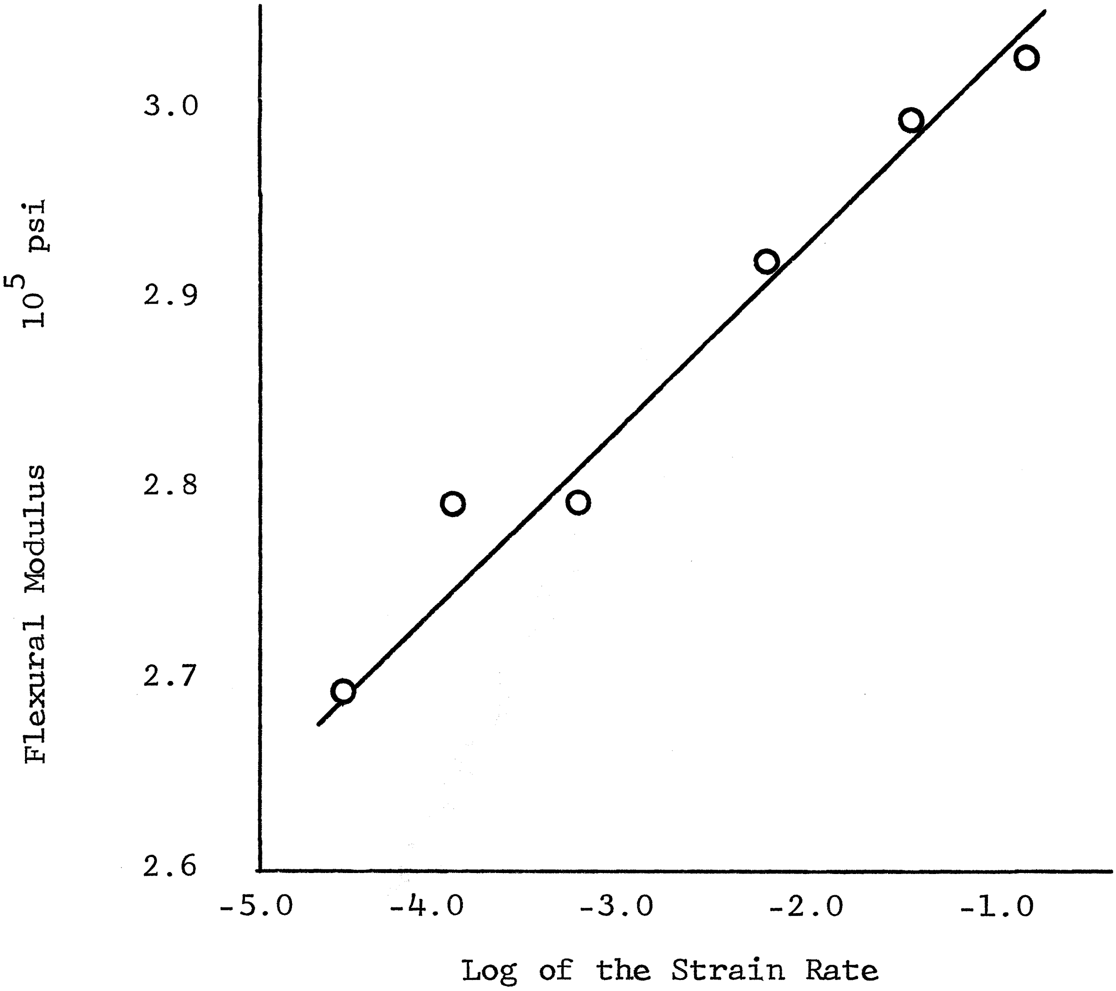


FIGURE XI EFFECT OF STRAIN RATE ON FLEXURAL MODULUS OF n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

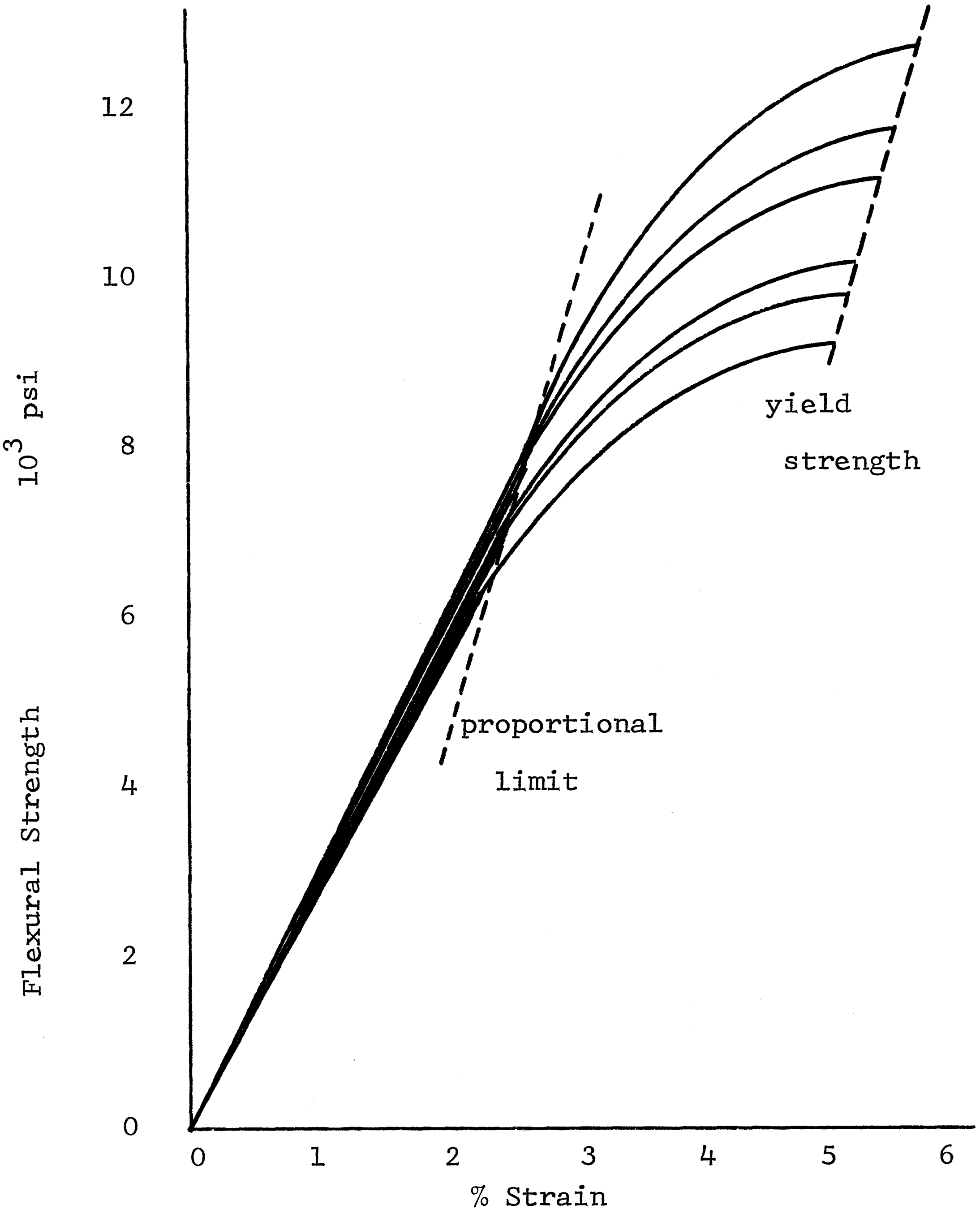


FIGURE XII STRESS-STRAIN CURVES FOR n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC AT VARIABLE STRAIN RATES

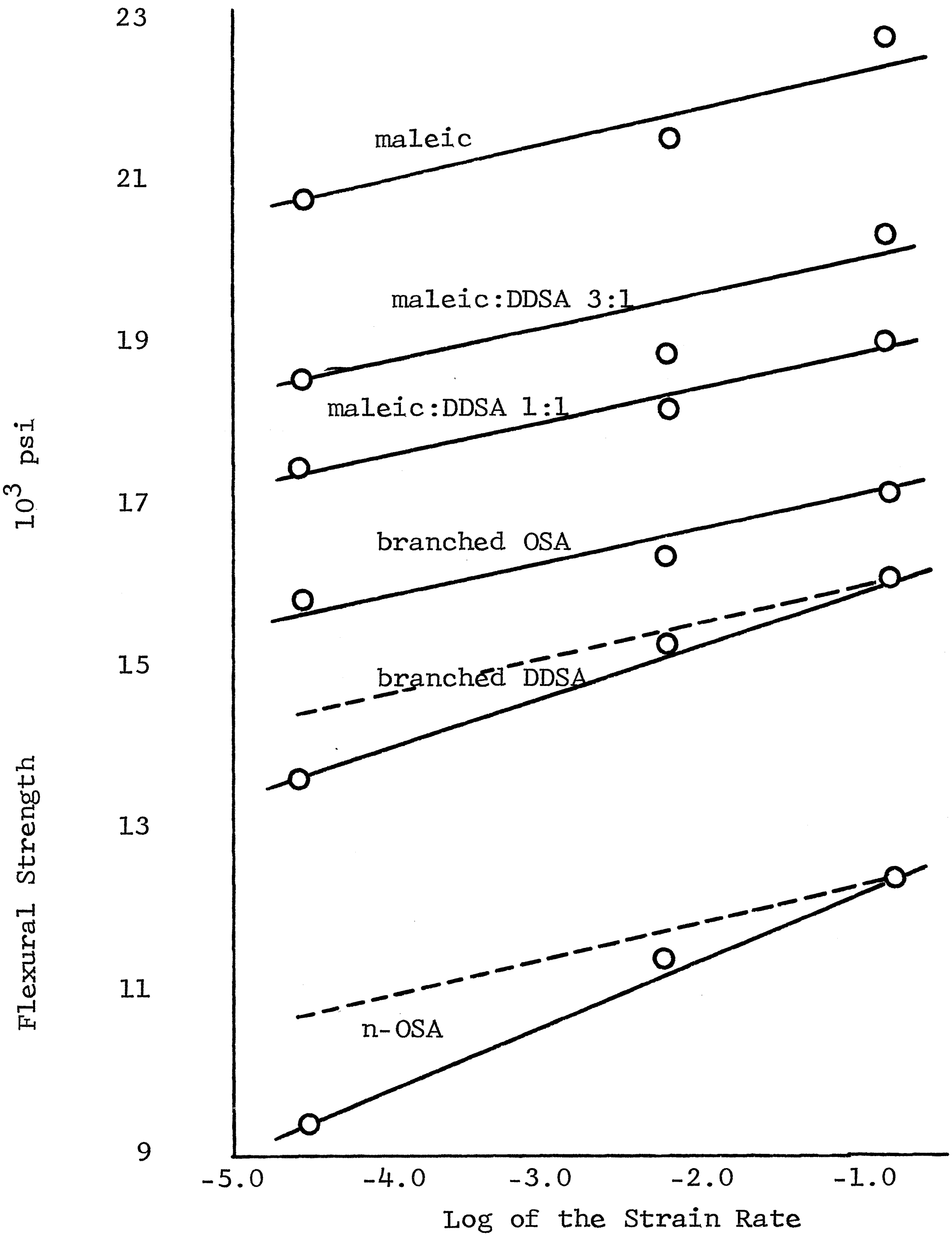


FIGURE XIII EFFECT OF STRAIN RATE ON FLEXURAL STRENGTH

TABLE XXIII

DEPENDENCE OF FLEXURAL MODULUS ON STRAIN RATE

ANHYDRIDE	FLEXURAL MODULUS 10^5 psi 2"/min.*	.5"/min.	.05"/min.
MA	4.63	4.44	4.17
DDSA:MA 3:1	3.95	3.77	3.79
DDSA:MA 1:1	4.14	3.99	3.97
DDSA:MA 1:3	4.34	4.18	4.10
branched OSA	3.98	3.75	3.74
branched NSA	3.93	3.79	3.82
branched DDSA	3.63	3.55	3.41
octyl	2.79	2.75	2.62
n-OSA	3.05	2.92	2.69

* deflection rate

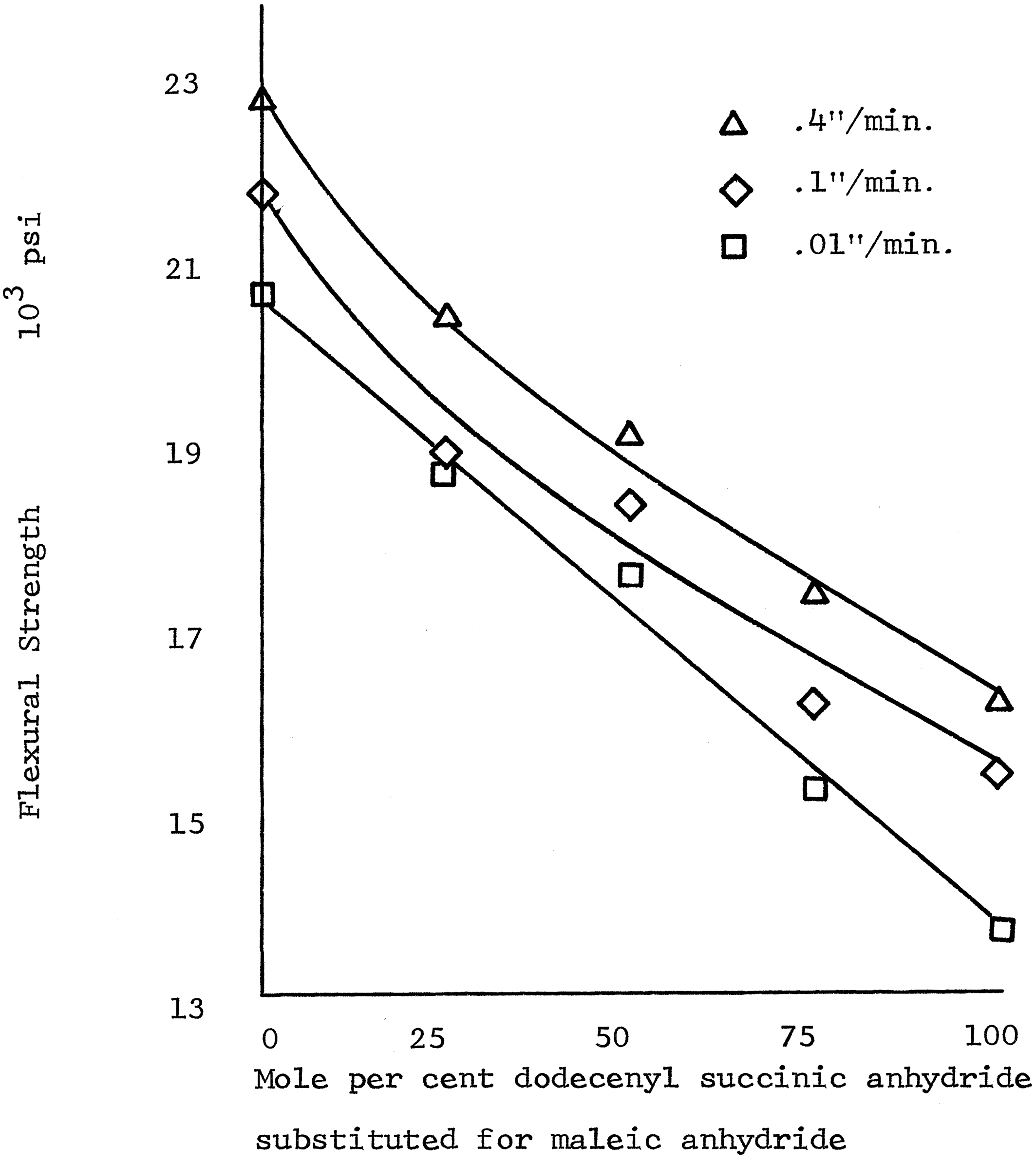


FIGURE XIV FLEXURAL STRENGTH vs MOLE PERCENT BRANCHED DDSA SUBSTITUTED FOR MALEIC AT VARIOUS STRAIN RATES

The strain rate chosen for flexural testing was, therefore, the fastest available rate on the Instron testing machine in order to minimize this problem. For the rigid materials of higher modulus the variations with log of the strain rate were all parallel and the same relative flexural strengths could be expected regardless of the strain rate chosen for testing within the limits of the Instron testing machine. For the softer materials, however, this is not the case and reported results can be a function of deflection rate as shown in Figure XIV. In this case the values for DDSA are shifted downward at slower deflection rates and the curve appears progressively more linear. Modulus values could also be expected to exhibit the strain rate dependance. As can be seen in Table XXIII, however, the changes in moduli are relatively small and the accuracy of modulus determination is not great enough to discern the relative trends as for the flexural yield strength data illustrated in Figure XIII. A further discussion of the time dependance of modulus will be discussed for the stress relaxation data. Suffice it here to say that the flexural properties are a function of strain rate, and that for materials of low modulus and heat distortion temperature (indicates a low glass transition temperature) the relative flexural properties may also become a function of strain rate.

TABLE XXIV

EFFECT OF POLISH ON FLEXURAL STRENGTH OF MALEIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

GRIT	FLEXURAL STRENGTH psi	STANDARD DEVIATION psi	FLEXURAL MODULUS 10^5 psi
500	22,700	350	4.63
320	20,920	1220	4.52
100	19,610	1860	4.45

Another important factor which was found to affect the flexural strength, at least for brittle, flaw sensitive materials, was the final polish on the tensile surface. Table XXIV illustrates this effect for maleic anhydride. Coarser polishes on the tensile surface decreased the measured flexural strength while increasing scatter between values. Standard deviations increase from well below 5 percent to almost 10 percent of the mean value. This indicates that, for the more brittle materials, fracture originates at surface flaws. For the materials that reach a yield stress, however, surface polish was found to be relatively unimportant although it did affect, rather erratically, the amount of strain in the post yielding region of the stress strain curve. The modulus variance in Table XXIV is interpreted merely as the difficulty in determining an accurate cross-sectional area for the coarser polishes.

The flexural properties for the 8 carbon chain substituted succinic materials illustrated in Table XXI, reveal a marked similarity between octyl succinic anhydride and linear octenyl succinic anhydride, indicating that the double bond in the alkenyl structure is essentially nonreactive. The greatest difference in properties lies between the branched and linear alkenyls rather than between the alkenyls and the alkyl. This is supported by the tensile strength data in Table XV. Attempts to prove

TABLE XXV

PROPERTIES OF SUCCINIC AND SUBSTITUTED SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

ANHYDRIDE	DENSITY	TENSILE STRENGTH	TENSILE MODULUS	TENSILE ELONGATION	HDT	TOUGHNESS	WEIGHT GAIN % *	
	gms/cm^3	psi	10^6 psi	%	°C	10^3 psi	ace.	edc
succinic	1.295	12,300	.44	6.6	106	.56	.07	.20
methyl succinic	1.258	11,700	.46	8.0	98	.71	.24	.89
n-OSA	1.157	6,030	.30	7.1	45	.23	14.	26.
n-DDSA	1.111	2,160	.09	14.	L.T.40	.23	28.	61.
n-HDSA	1.081	900	.05	4.2	L.T.40	.02	28.	71.
branched OSA	1.143	9,620	.37	5.0	79	.34	7.0	10.
branched NSA	1.136	9,380	.36	5.1	74	.32	10.	16.
branched DDSA	1.110	8,810	.35	6.3	68	.41	16.	38.
octyl	1.141	5,630	.26	15.	41	.57	CR**	CR
dodecyl	1.100	2,270	.10	20.	L.T.40	.37	15.	CR
hexadecyl	1.072	1,430	.05	18.	L.T.40	.21	20.	68.

* 24 hours total immersion; unpolished samples
** CR = cracked

the double bond reactive in the branched case by reaction with vinyl toluene through the addition of tertiary butyl perbenzoate, proved unsuccessful. The branched octenyl formulation both foamed at 100°C and had evidence of immiscibility. The branched dodecenyl formulation had a layered structure indicative of immiscibility, as well as a total loss in transparency, indicative of a non-homogenous system. The alkenyl double bond must be somewhat reactive, however, to account for higher flexural strengths,tensile strengths, moduli, and heat distortion temperatures than the linear case. Solvent sensitivities are also greater for the linear material in spite of a higher physical density (see Table XV). Another possibility for the difference between properties in the branched and linear case is a marked difference in epoxide-anhydride reactivity, as in the case of the maleic-succinic comparison. The results, however, do not appear to support this conclusion. Percent weight gains in boiling water for the three 8 carbon chain substituted succinic anhydride cured materials revealed no substantial difference in the amount of excess anhydride present (linear octenyl, .7%; branched octenyl, 1.0%; and linear octyl, 1.0%). Evidence is, moreover, indisputable that some double bond reaction is occurring in the branched alkenyl case. Increasing the post cure temperature for the branched octenyl cured formulation increases the heat distortion temperature 6°C; aging further increases the heat distortion temperature to 104°C. The degree of reaction of this double bond, however, must remain relatively low as indicated by the discussion of the MA/OSA and MA/DDSA binary systems, for which the effect of the branched alkenyl addition to the maleic system has the effect of a saturated anhydride rather than that of an unsaturated anhydride in which the double bond could be considered mutually reactive with maleic. The initial low reactivity of the double bond is further indicated by the severe crazing which occurs on aging both the linear and branched octenyl formulations. This crazing evidently results from oxidation of the double bond at high temperatures which can both increase cross-linking density by bridging between two unsaturated sites or degrade the alkenyl chain by a mechanism comparable to the cleavage of a alkene in ozonolysis. The linear octenyl material was crazed so severely as to cause fracture upon handling. The branched octenyl formulation was also severely crazed. In spite of this crazing which tends to decrease the measured heat distortion temperature, a 25°C rise in heat distortion temperature was recorded after aging. A closer look at the structure of the branched alkenyl anhydrides can explain both the initial reaction of some of the double bonds, as well as the relative stability of the remainder. Branched dodecenyl succinic anhydride, for instance, is prepared from a thermally activated reaction between maleic anhydride and 4,6,8 trimethyl-1-nonene (propylene tetramer). During this reaction isomerization of the alkene occurs by migration of the double bond down the chain; the most stable isomer being 2,4,6, trimethyl-2-nonene. After reaction with maleic anhydride, therefore, branched dodecenyl succinic anhydride is a mixture of isomers with the double bond in variable positions on the alkenyl chain. The reactivity of these double bonds will vary depending on the presence of adjacent electron withdrawing methyl groups. In the linear dodecenyl succinic anhydride all the double bond positions would be relatively equivalent and relatively non-reactive, as there can be no electron withdrawing methyl groups adjacent to the double bond. This accordingly explains why the double bond reaction is more significant in the case of branched dodecenyl succinic anhydride than in linear dodecenyl succinic anhydride. The degree of reactivity would depend on the relative proportions of the branched dodecenyl succinic isomers which have double bonds in positions with adjacent methyl groups. Even neglecting this, however, the degree of reaction would be expected to be low due to the low concentration of unsaturated sites in the cured system. The concentration of unsaturated sites per gram in a maleic anhydride cured epoxidized novolac system is 1.6 times higher than in a branched dodecenyl succinic anhydride cured system. The density is also 1.110 grams/cm^3 for the branched DDSA system compared to 1.304 grams/cm^3 for the maleic system. Accordingly few unsaturated sites in the branched DDSA case have an opportunity to react due to the low volumetric concentration of unsaturated sites. For branched octenyl succinic anhydride the aliphatic chain is shorter and the density is higher, accordingly the double bond reaction can more readily occur. This, as discussed earlier, is why the heat distortion values for the MA/OSA system are linear, while for the MA/DDSA system they are negatively synergistic with increasing mole percents of branched alkenyl substituted for maleic.

The presence of the methyl branches on the alkenyl chain can be expected to contribute to the increase in modulus for the branched alkenyls over the linear alkenyls. The modulus is also higher due to the increase in cross-linking caused by the reacted double bonds. The methyl branches also cause a decrease in density for the branched alkenyls over their linear counterparts. In this case, however, the density decrease is not accompanied by a corresponding increase in solvent sensitivities, as its adverse effects are cancelled out by the increase in cross-linking due to the reaction through unsaturation.

The differences in moduli noted between linear octenyl succinic anhydride and octyl succinic anhydride is due to the inhibited conformational rotation caused by the presence of the double bond. This double bond and the subsequent higher density are also responsible for the higher tensile yield strength, as well as the lower tensile elongation. Verifying a comparison made earlier between the toughness values determined from the flexural test for hexahydrophthalic and cis-4-tetrahydrophthalic, the double bond reduces the amount of strain which occurs in the post yielding region before fracture. The toughness values determined from the tensile test, as well as the tensile elongation, are notably higher for octyl succinic anhydride than for linear octenyl succinic anhydride. The slight differences in solvent sensitivities and heat distortion values could be explained solely on the basis of the slightly lower density for the octyl succinic cured material. The degree of epoxide-anhydride reaction is also slightly lower for the octyl material based on the weight gain in boiling water. The HBr-acetic reagent is valueless in determining the excess epoxide for these low density formulations due to the significance of the diffusion of acetic acid into the materials. The change in heat distortion temperatures on aging for the octyl succinic formulation was 19°C, which would place it somewhere between hexahydrophthalic and methyl succinic in extent of epoxide-anhydride reaction. The change in heat distortion on aging for linear octenyl succinic anhydride could not be determined, as was previously noted, because of the severe crazing.

The effect of chain length on the properties of substituted succinic anhydride cured formulations is evident in Table XXII and Figures XV through XVIII. Density, tensile strength, flexural strength, and moduli all decrease with increasing chain length while tensile elongation increases. Heat distortion temperature also decreases which is illustrated by the data in Table XV. Solvent sensitivities tend to increase due to the decrease in density. Essentially the effect of increasing chain length is to decrease both physical and cross-linking density, and to subsequently affect all the other properties according to their dependence on these two density factors.

Figure XVII shows that in the case of the initial modulus there is an increase for very short chains due to increased resistance to inter-conformational rotation. As chain length increases, however, the decrease in density and importance of carbon-carbon bond rotations along the chain itself become important, and the initial modulus accordingly decreases. In Figures XXVIII and XIX, it should

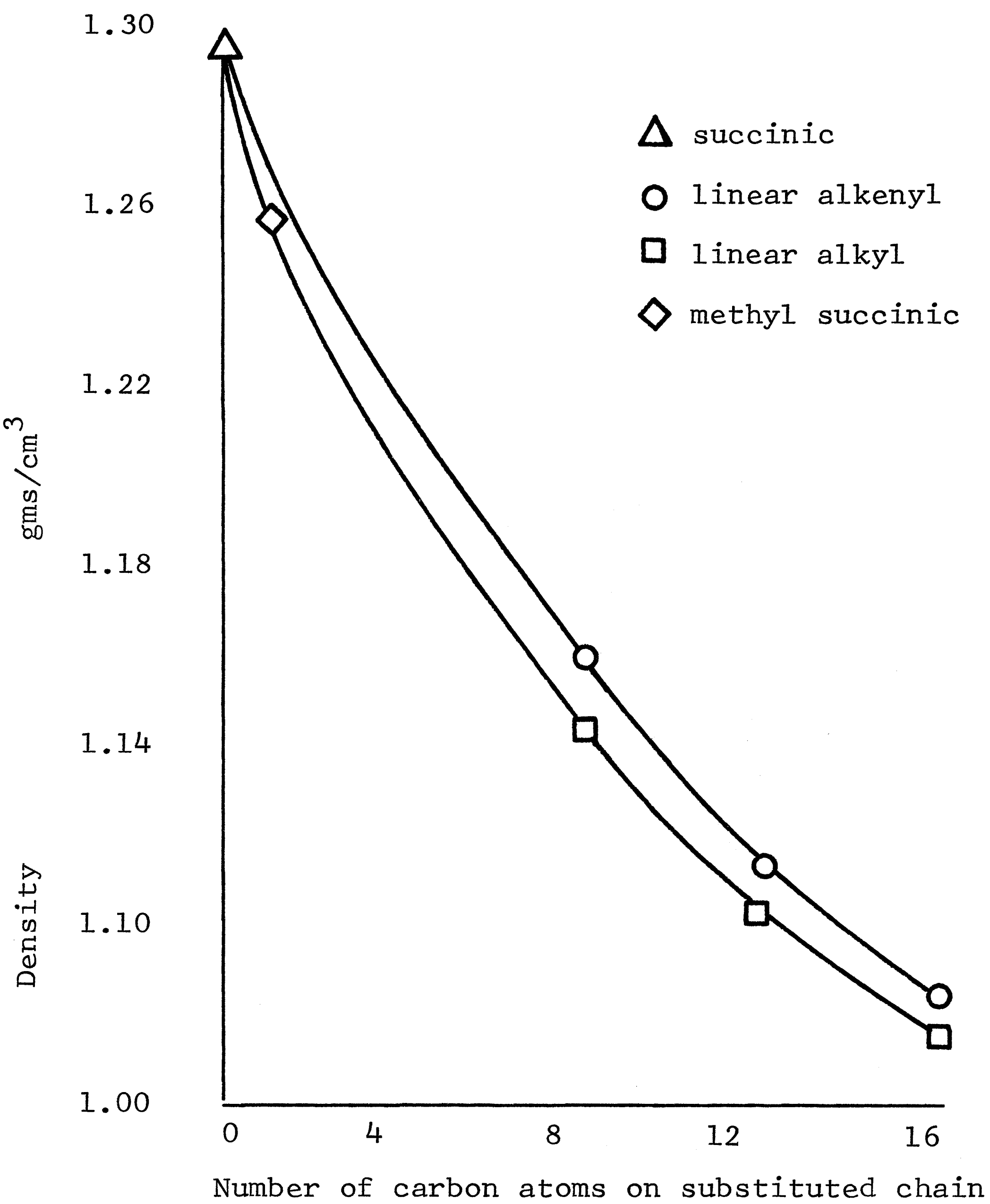


FIGURE XV EFFECT OF SUBSTITUTED CHAIN LENGTH ON DENSITY

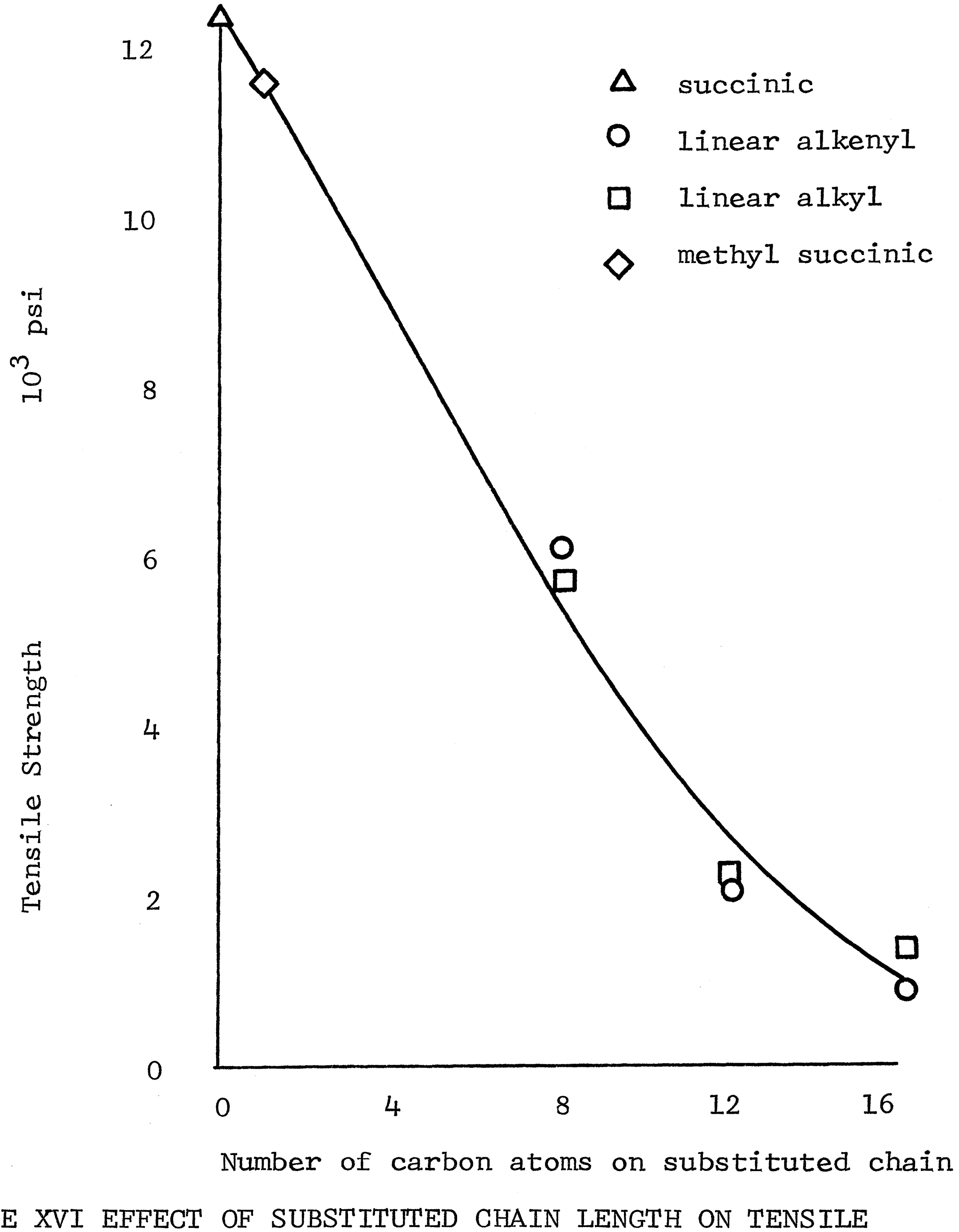


FIGURE XVI EFFECT OF SUBSTITUTED CHAIN LENGTH ON TENSILE STRENGTH

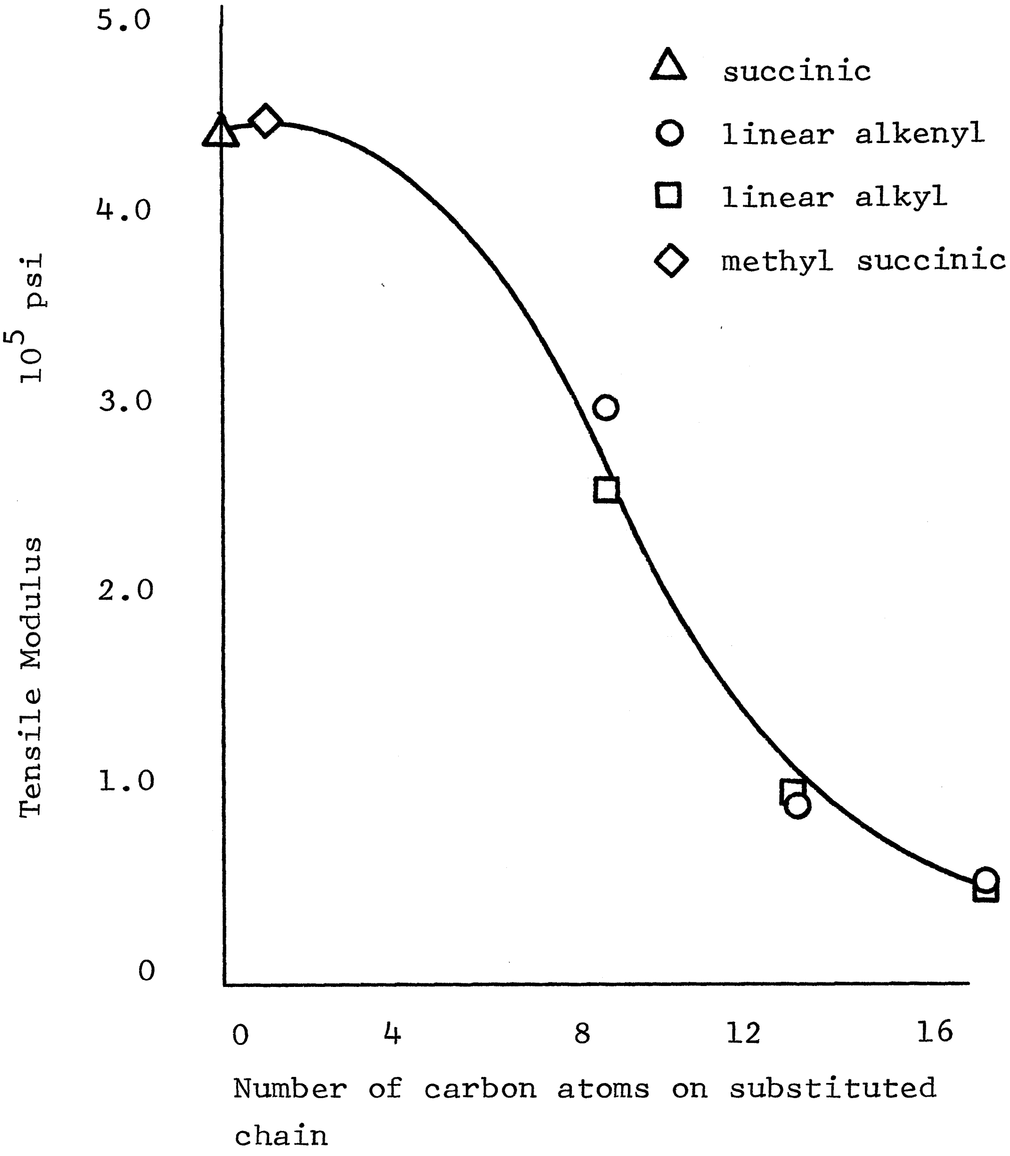


FIGURE XVII EFFECT OF SUBSTITUTED CHAIN LENGTH ON TENSILE MODULUS

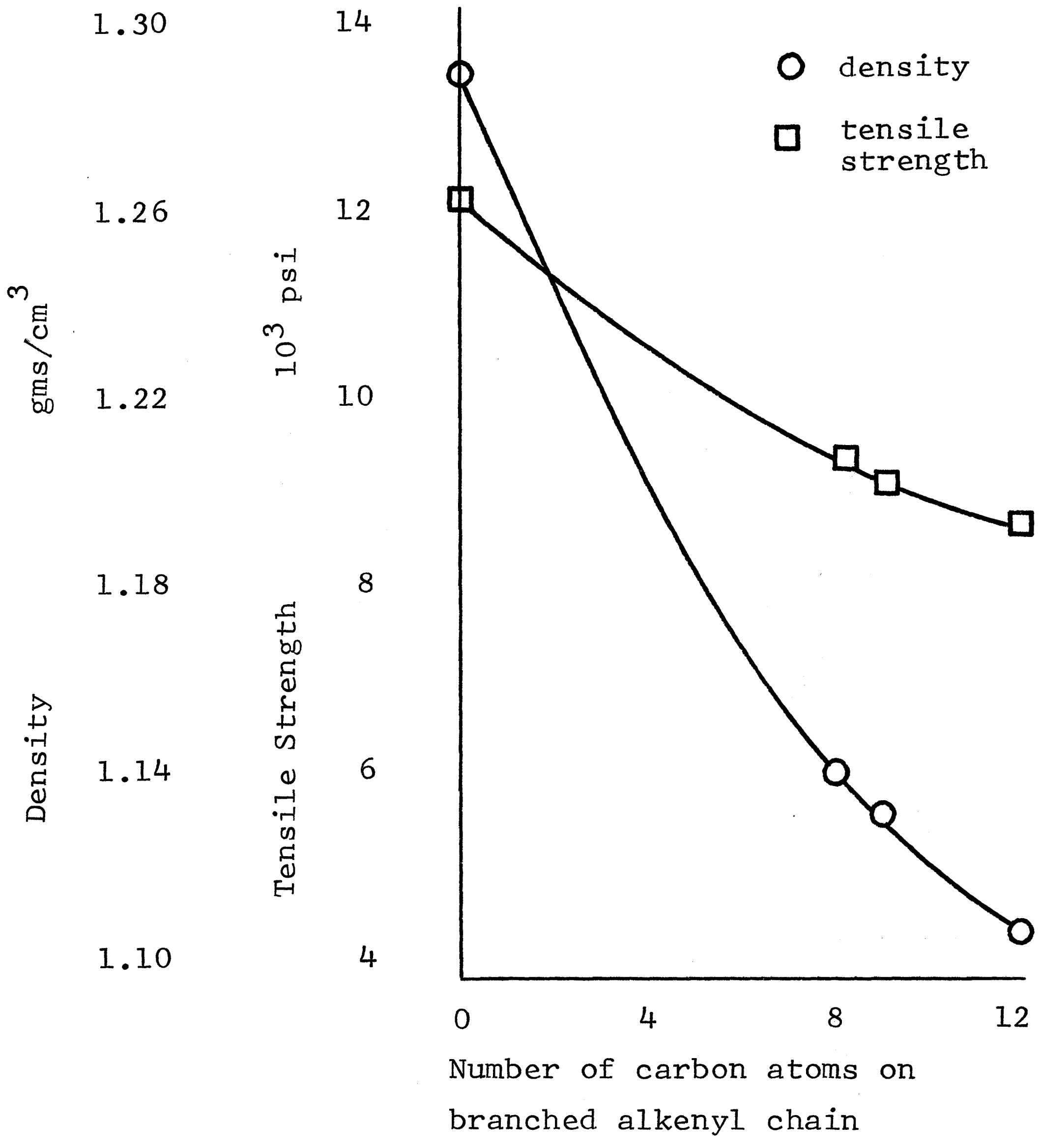


FIGURE XVIII EFFECT OF BRANCHED CHAIN LENGTH ON DENSITY AND TENSILE STRENGTH

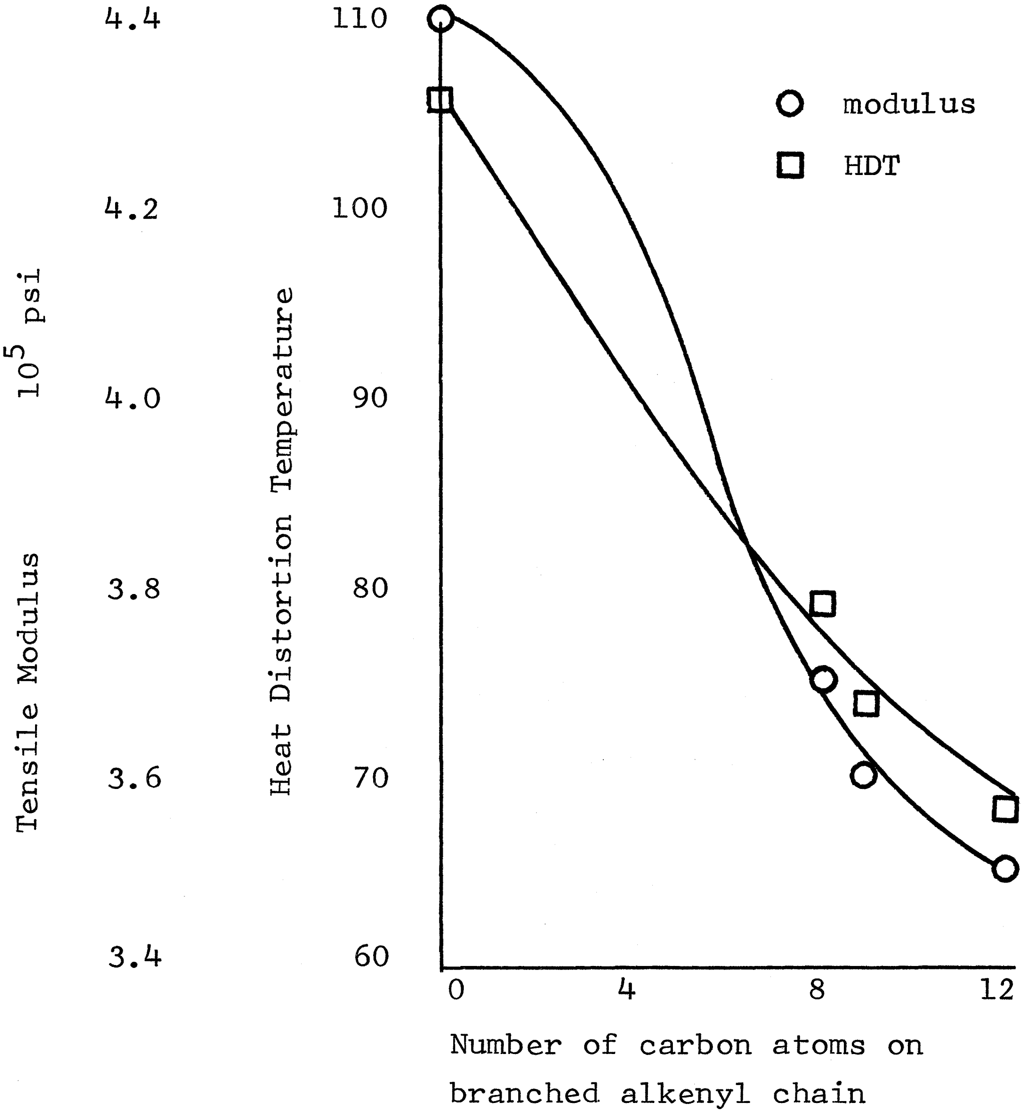


FIGURE XIX EFFECT OF BRANCHED CHAIN LENGTH ON TENSILE MODULUS AND HEAT DISTORTION TEMPERATURE be noted that it is impossible to have a branched chain with less than three carbon atoms; therefore, the property values for chain lengths of less than three are identical to the linear case. This is the basis for drawing the modulus curve as shown in Figure XIX.

A seeming disparity in Table XV is the low elongation for the n-HDSA cured formulation. The failure, however, in this case was by tearing with fracture originating at the surface. Failure in all the other cases was ductile, and failure was associated with necking in the post yield region of the stress strain curve (failure for branched OSA bordered on brittle as failure occurred essentially at the yield point). The double bond, as was concluded earlier, is essentially unreacted in the linear alkenyl materials; however, at high temperatures oxygen will diffuse into the formulations and attack the unreacted unsaturated sites. This surface hardens the material and results in the tear type failure noted for n-HDSA. Further proof of this conclusion is shown in Table XVI. When the oxidized surface was sanded off the post cured n-HDSA material, the elongation increased markedly. This oxygen embrittlement is most severe for n-HDSA because of its very low density which permits a rapid rate of oxygen diffusion into the cured material. Judging from the depth of specimen discoloration, oxygen penetration was at least

TABLE XXVI

EFFECT OF SURFACE OXIDATION ON TENSILE PROPERTIES OF n-HDSA

	TENSILE STRENGTH psi	TENSILE MODULUS 10^5 psi	TENSILE ELONGATION %
as cured n-HDSA *	900	.05	4.2
n-HDSA with oxidized surface removed	1010	.03	35.

* tear failure

.020" for n-HDSA, and less than .010" for n-DDSA and n-OSA. Oxygen penetration in the corresponding linear alkyl cured materials was even greater, due to their lower densities. Eventually one should expect the same type of surface embrittlement to occur on all the linear alkenyl formulations. On aging, for instance, the linear and branched octenyl formulations severely crazed as previously noted, but the octyl formulation was uncrazed. The crazing resulted from the same type of oxygen attack on the double bond as noted for the n-HDSA cured material. It is possible, of course, for this oxygen attack to be either cleavage of the alkenyl chain by an ozonolysis type mechanism, or to be an increase in cross-linking due to oxygen bridging between unsaturated sites. Only the latter effect, however, would account for surface hardening of the n-HDSA formulation. Degradation, on the other hand, also occurs as evidenced by the decrease in heat distortion temperature on aging the branched DDSA formulation. Apparently oxygen at high temperatures will initially increase cross-linking density by bridging between unsaturated sites which are close enough for reaction to occur, and then subsequently at higher temperatures or longer times, decrease the cross-linking density by cleaving the remaining unreacted unsaturated sites. We would expect, therefore, degradation to be more pronounced for the longer chained materials due to the lower concentration of unsaturated sites per unit volume. This explains why the heat distortion temperature for branched OSA increases on aging, while the heat distortion temperature for branched DDSA decreases. The initial surface embrittlement is contributing to the reduced tensile elongations of all the linear alkenyl succinic anhydride cured materials in Table XV as compared to their saturated alkyl counterparts.

The tensile properties in Table XV were found to have the same type of strain rate dependence as the flexural properties. Figure XX shows that the tensile yield strength is a linear function of the log of the strain rate. The tensile strain rate chosen for testing was the A.S.T.M. recommended rate of 2"/inch/minute. Figures XXI and XXII show the effect of log strain rate on tangent modulus and elongation. As in the case of the flexural test, modulus values are relatively unaffected by small changes in strain rate. Elongation values, however, are markedly affected. Elongation, yield strength, and toughness are properties which depend on chain mobility; i.e. side by side chain slippage, etc. These properties are much more time dependent than the elastic modulus, which is heavily dependent on those factors inhibiting free rotation about carbon-carbon bonds. Table XXVII shows that the moduli are equivalent in both the tensile and

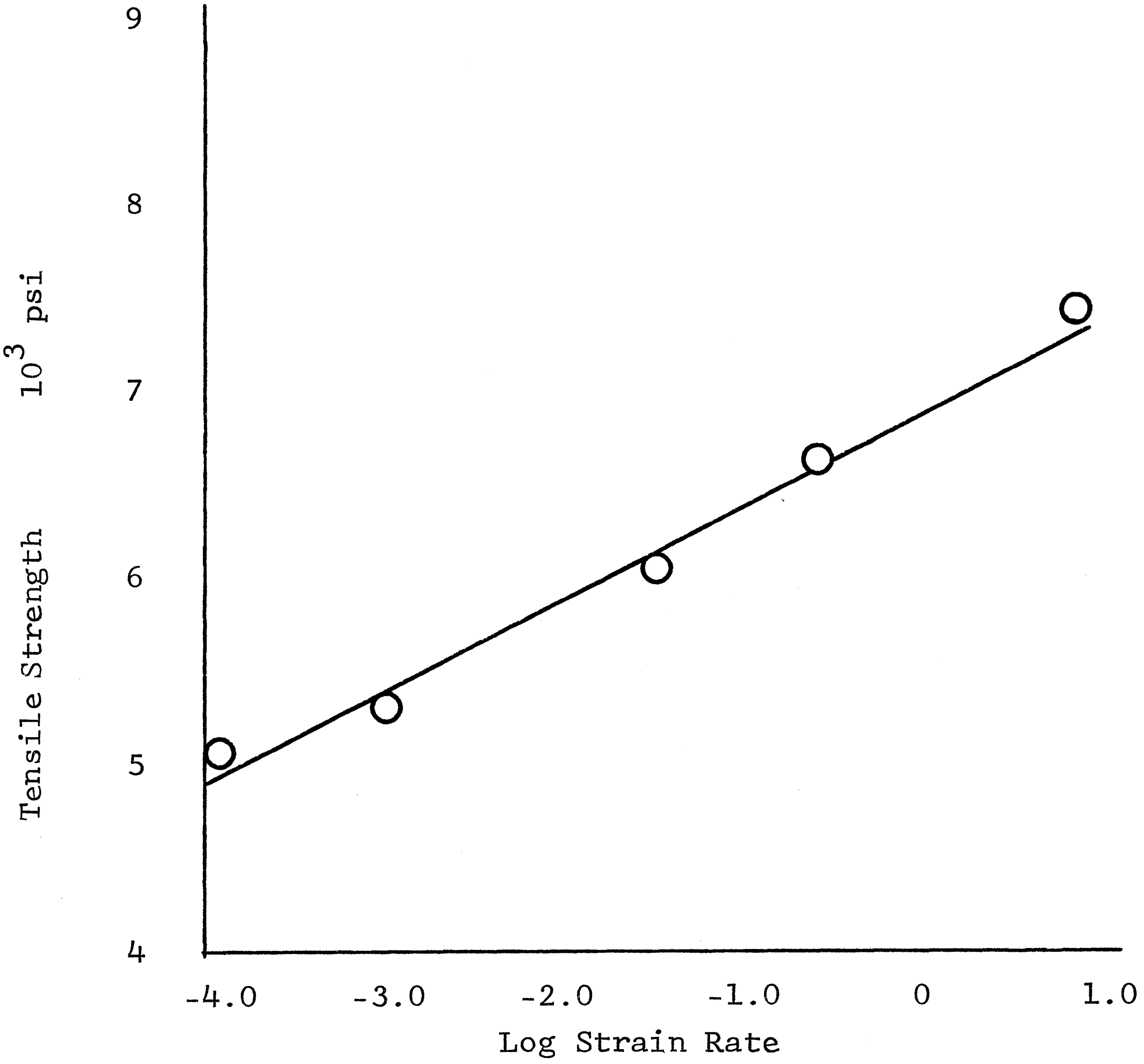


FIGURE XX TENSILE STRENGTH OF n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC AT VARIOUS STRAIN RATES

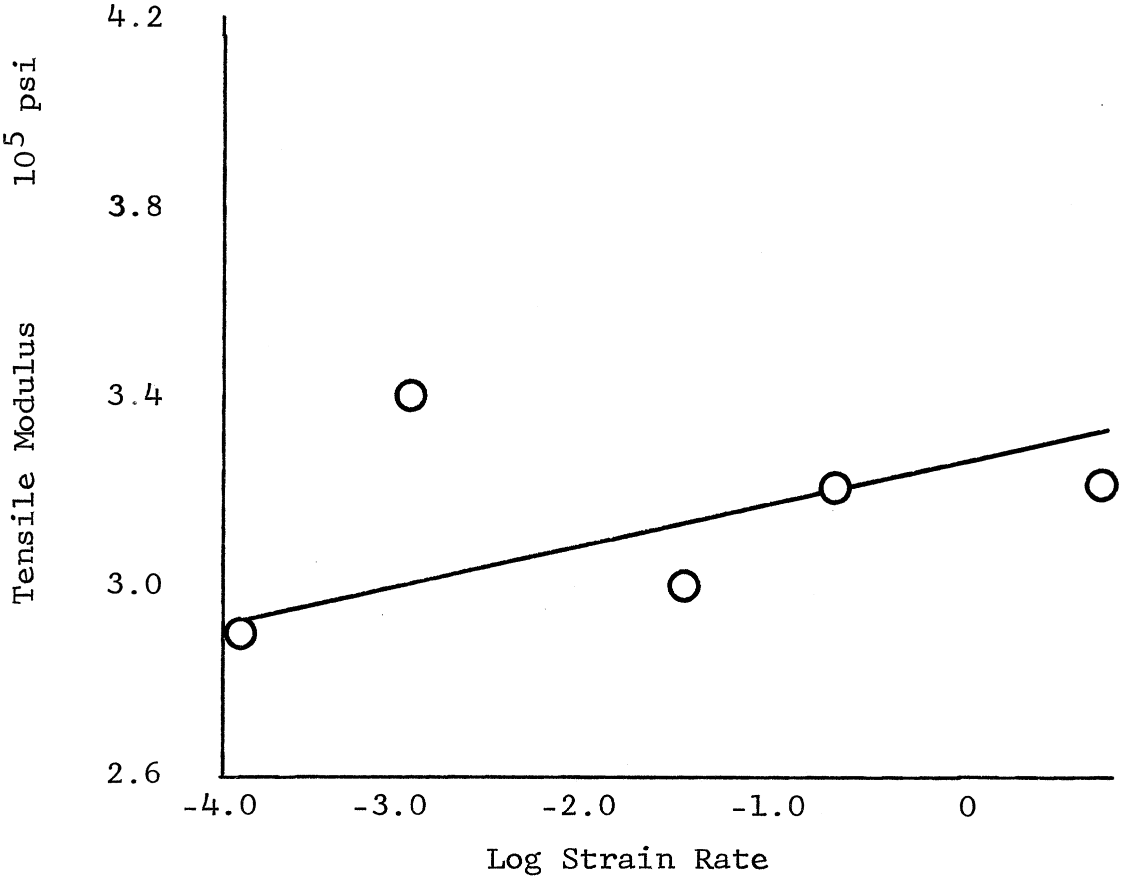


FIGURE XXI <u>TENSILE MODULUS OF n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC AT VARIOUS STRAIN RATES</u>

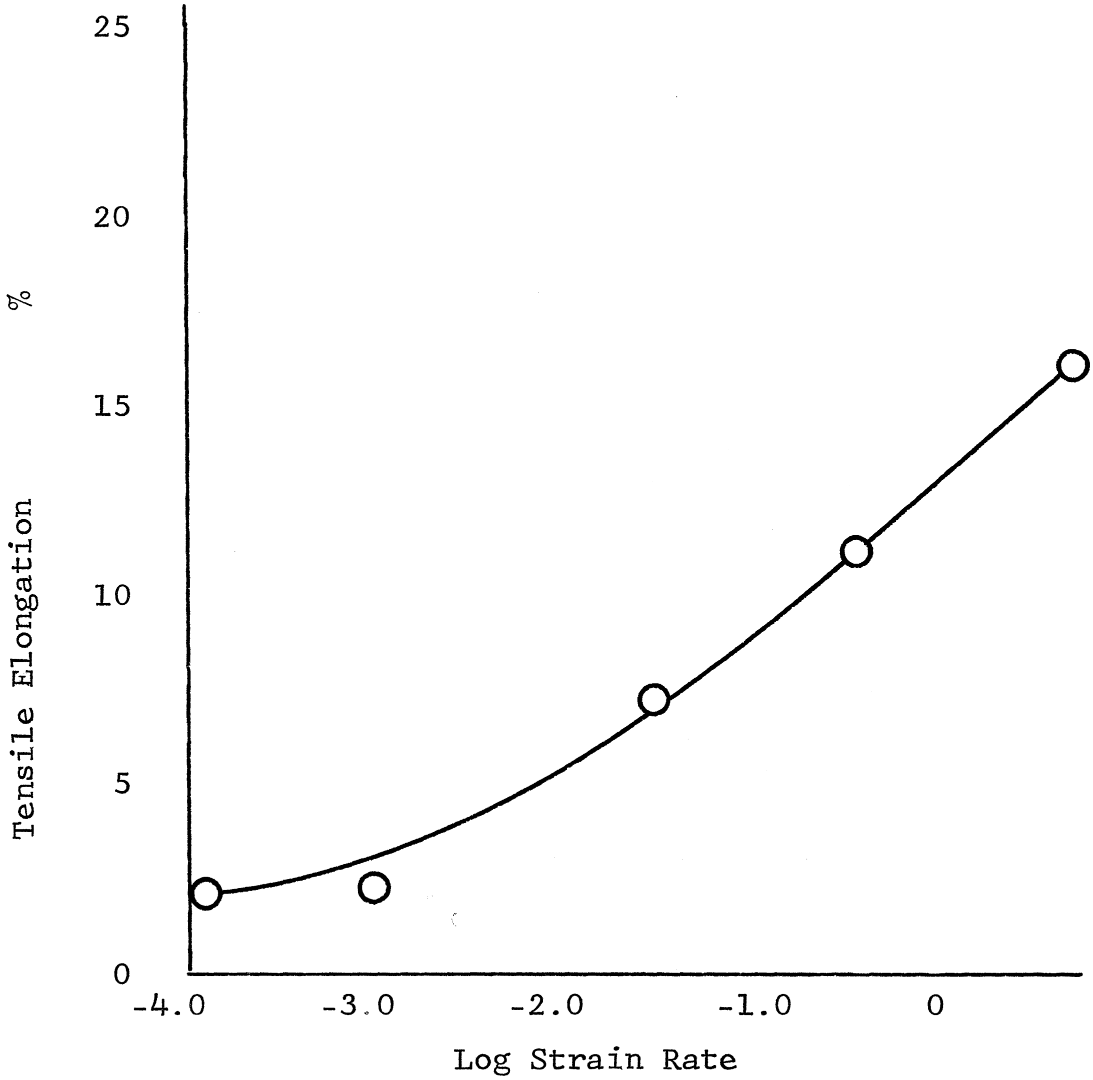


FIGURE XXII TENSILE ELONGATION OF n-OCTENYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC AT VARIOUS STRAIN RATES

TABLE XXVII

COMPARISON OF TENSILE AND FLEXURAL DATA

ANHYDRIDE	TENSILE MODULUS 10^5 psi	FLEXURAL MODULUS* 10^5 psi	S_t/S_f **
succinic	4.4	4.4	.60
methyl succinic	4.6	4.3	.58
n-octenyl	3.0	2.9	.51
branched octenyl	3.7	3.8	.57
branched noneyl	3.6	3.8	.57
branched dodecenyl	3.5	3.6	.56
octyl	2.6	2.7	.50

* Modulus at .2"/minute strain rate (corresponding to 1"/minute deflection rate)

**Ratio tensile yield stress to flexural yield stress at .2"/minute strain rate flexural tests, but that the relative yield strength is lower for the softer materials in the tensile test. The yield strength in tension/yield strength in flexure ratio decreases with decreasing modulus. The yield strength in compression is apparently less time dependent than the yield stress in tension, and this is reflected in the flexural yield strength. This certainly indicates an excellent area for future research work: determination of the tensile/compressive yield strength ratio, λ, as a function of anhydride structure or the material structure in general. It may be, for instance, that λ is primarily a function of cross-linking density and is relatively independent of the other factors which affect interconformational conversion; i.e., substituted groups, cyclic rings, aromatic rings, unsaturated sites, etc.

Materials such as the 12 carbon atom and 16 carbon atom substituted succinic anhydride cured formulations have properties which are highly time and temperature dependent. Accordingly physical data for these materials is more reliable for engineering design purposes if known as a function of time and temperature. Stress relaxation curves of modulus vs time offer a valuable insight into the properties of these formulations; unfortunately, this research was limited in this area by a lack of proper test equipment. A modulus spectrum could be determined from a stress relaxation curve corresponding to a higher temperature, and translated to room temperature by the time-temperature superposition principle. The effect of temperature on viscoelastic properties is to multiply the time scale by a constant factor at each temperature. This shift factor is chosen as unity at the reference temperature, and can be determined as a function of temperature from the amount of shift on the log time axis required to superimpose the modulus values at a particular temperature with the master curve at the reference temperature. Due to the inability to vary temperature (requires Instron environmental chamber or equivalent), complete stress relaxation curves could not be determined for the materials in Table XXV due to the time limitation. A complete stress relaxation curve exhibits a hard elastic region in which the modulus is relatively constant, followed by a viscoelastic transition region in which the modulus values fall off sharply often approaching linearity with log time, and finally a soft elastic region where the modulus approaches a constant value, G_e. This behavior can be expressed mathematically as:

$$G(t) = G_e + \int H(\ln r)\, e^{-t/r} d\ln r$$

An approximate solution to this equation at t = r (r = relaxation time) reveals that:

$$H(\ln r) = dG(r)/d\ln t$$

TABLE XXVIII

EQUILIBRIUM MODULUS VALUES FOR FORMULATIONS ABOVE THEIR GLASS TRANSITION TEMPERATURES AT ROOM TEMPERATURE

ANHYDRIDE	EQUILIBRIUM MODULUS 10^6 psi
n-dodecenyl	.018
n-hexadecenyl	.004
n-dodecyl	.017
n-hexadecyl	.004

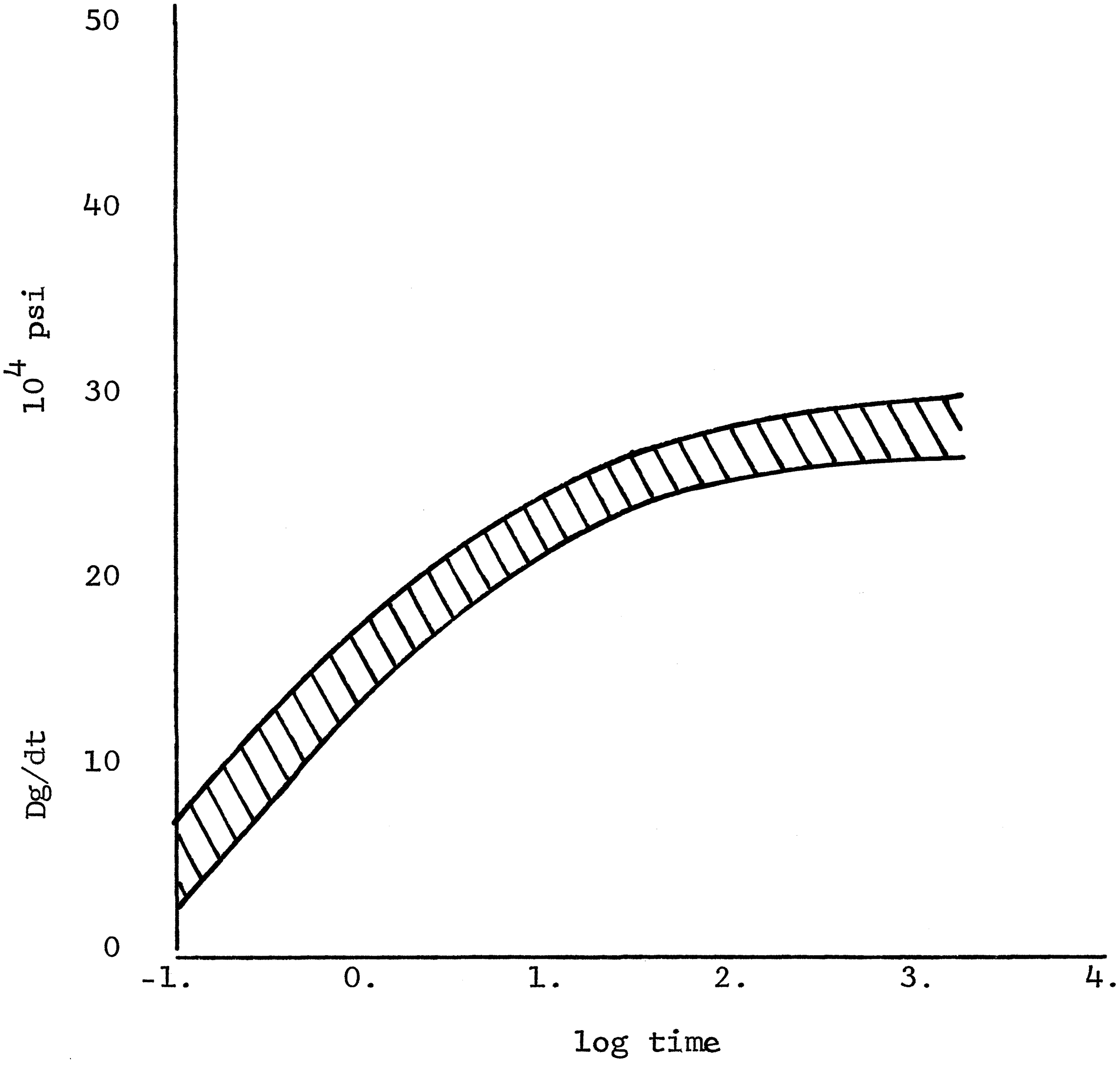


FIGURE XXIII RELAXATION SPECTRUMS OF FORMULATIONS BELOW THEIR GLASS TRANSITION TEMPERATURES AT ROOM TEMPERATURE

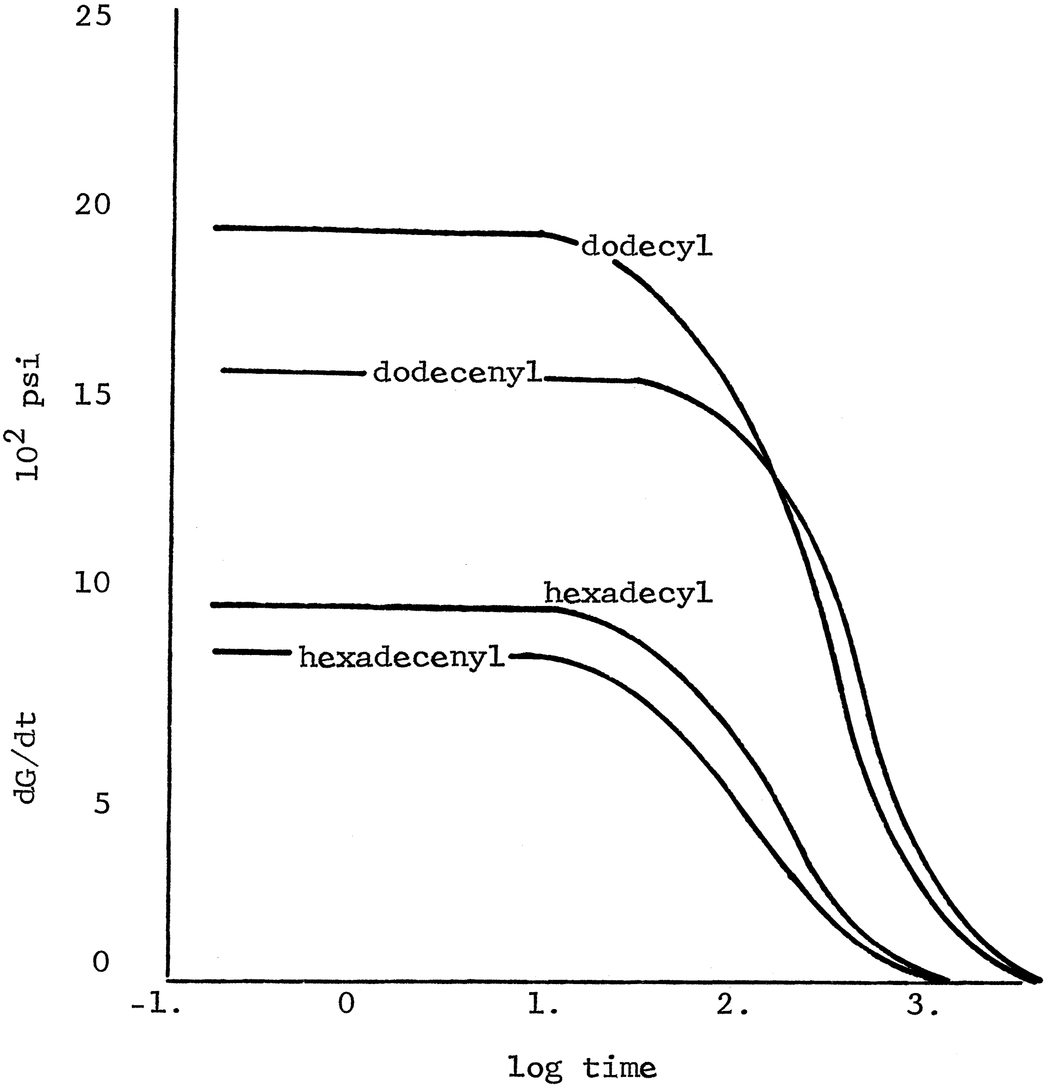


FIGURE XXIV RELAXATION SPECTRUMS OF FORMULATIONS ABOVE THEIR GLASS TRANSITION TEMPERATURES AT ROOM TEMPERATURE

A subsequent plot of H(ln r) vs log t shows that H(ln r) goes through a relatively constant maximum region corresponding to the linear viscoelastic transition region on the stress relaxation curve. One can accordingly determine three values from a stress relaxation curve which can be considered functions of a given material and which are temperature independent in the linear viscoelastic region. These values are G_o (modulus at t = 0), G_e (modulus at t = infinity), and $H(\ln r)_{max.}$ (slope of viscoelastic transition region).

H(ln r) vs log t curves are illustrated in Figure XXIV for the soft materials above their glass transition temperatures. Equilibrium modulus values were calculated and are tabulated in Table XXVII. The equilibrium modulus is primarily a function of cross-linking density and is, accordingly, equivalent for the linear alkenyl anhydrides and the linear alkyl anhydrides of a given chain length. The restrictions placed on inter-conformational rotation are relatively unimportant as compared to the restrictions placed on chain mobility due to cross-linking. The H(ln r) vs log t curves in Figure XXIII for the rigid materials below their glass transition temperatures, are surprisingly similar, and appear to be approaching similar $H(\ln r)_{max.}$ values; accounting no doubt for the parallel behavior with log strain rate illustrated in Figure XIII. All the relaxation spectrums for the rigid materials fell within the shaded region depicted in Figure XXIII. It was indeed unfortunate that adequate equipment was not available so that G_e values could have been determined on all the materials, and the time-temperature superposition principle utilized to determine the complete stress relaxation curve at room temperature.

The results of this investigation have elucidated many facets of the alicyclic dicarboxylic anhydrides which should enable a formulator to better select a given anhydride for a given application. There are, of course, as in any research which covers such a wide variety of materials, many areas left for further investigation. The differences in the epoxide-anhydride reactivities, for instance, are certainly a function of the catalyst, which in this case was held constant both in type and concentration. A more reactive tertiary amine could narrow the reactivity gap found between succinic and hexahydrophthalic anhydrides, and it could reduce the amount of etherification which occurred in the maleic anhydride cured composition. The very significant crazing found in the MEMTHPA cured systems also warrants further research. This anhydride is widely used for high temperature applications and is considered a premium material. The crazing which occurred at the 250°C age may or may not occur at lower temperature ages. Since this crazing has apparently eluded earlier researchers, it very well may be confined to the 250°C region corresponding to the onset of the reverse Diels-Adler reaction. If, however, this crazing is found at temperatures as low as 200°C it could be of considerable commercial significance. For many applications which require retention of tensile strength, flexural strength, or toughness after elevated temperature exposure, other less expensive anhydrides may prove to be superior to MEMTHPA and represent a significant cost savings to the formulator.

The flexibilization of brittle materials by the addition of branched alkenyl succinic anhydrides is also of considerable commercial significance. These results have certainly shown that flexibilization does not occur at high cross-linking densities unless one defines flexibilization as a reduction in modulus. Since the properties of anhydride binary systems have been found to be principably either additive or, especially for the branched alkenyls, negatively synergistic, one should not expect these anhydrides to improve the toughness, elongation, or flexural strength of any anhydride system, beyond the properties of the branched alkenyl cured systems themselves. Although certainly not brittle materials their flexural strengths, toughness, and tensile elongations are inferior to many of the other anhydrides tested in this research. Hexahydrophthalic, succinic, and methyl succinic should all prove to be superior flexibilizing agents compared to the branched alkenyls for the purpose of improving toughness and elongation. In the case of maleic anhydride, for instance, replacement of maleic with hexahydrophthalic to a 1:1 ratio increases toughness from $.90 \times 10^3$ psi to $.95 \times 10^3$ psi, while replacement with DDSA to a 1:1 ratio reduces toughness to $.70 \times 10^3$ psi.

The toughness values determined on all the formulations in this research could provide the basis for continued investigation, themselves. These values are rarely if ever reported, and this is the first time they have been tabulated for the materials included in this research. How useful the toughness values, as determined from the area under the stress-strain curve, may be in predicting behavior in actual conditions, however, remains questionable. The strain rates encountered in impact are, of course, many magnitudes faster than the strain rates encountered in a tensile or flexural test. The toughness values can accordingly be expected to change, and the relative values may also change. A correlation study between the flexural toughness values and a measure of impact strength in flexure (i.e., Izod or falling rod), or the tensile toughness values and a measure of impact in tension (i.e., tensile impact) would be most revealing in determining the value of the former measurements. Even neglecting impact correlations, however, the toughness values can be of significant value to the formulator as they indicate the amount of energy required to fracture the material at non-impact strain rates.

The value of this research lies not only in a better understanding of the anhydrides tested, but in that it provides the information in terms of the effect of anhydride structure on properties which should enable a formulator to predict the final properties of a cured material based on his knowledge of the anhydride. Utilizing results of this research, for instance, one should be able to predict the properties of 4-methyl hexahydrophthalic anhydride, an anhydride which was not included in this investigation. The presence of the methyl group can be expected to increase resistance to inter-conformational rotations when compared to hexahydrophthalic anhydride cured epoxidized novolac. The elastic modulus should, therefore, be greater than that for the hexahydrophthalic anhydride cured system, and the increase, as evidenced by the increase in elastic modulus when the methyl group was added to tetrahydrophthalic anhydride, is approximately $.30 \times 10^5$ psi. One should assume this change to be a maximum, since the addition of the methyl group in the presence of the double bond may have a greater effect than the addition of the methyl group itself due to the effect of the methyl group on the double bond reactivity. The predicted elastic modulus is accordingly 5.2 x 10^5 psi. The flexural yield strength should be equivalent to those of the other multi-ring anhydride cured materials which all gave roughly equivalent as-cured flexural yield strengths (approximately 25,000 psi). The physical density of the 4-methyl HHPA cured system would be lower than for the HHPA system and the decrease should be roughly equivalent to the .020 gm/cm^3 decrease exhibited by MTHPA compared to THPA; thus, the predicted density is 1.222 gms/cm^3. The methyl group in the 4 position on the cyclohexane ring is too far from the carboxyl group in the anhydride ring to have much effect of reactivity, therefore, one would expect a high extent of epoxide-anhydride reaction for this system as for the HHPA system. The presence of the methyl group would still lower cross-linking density, however, due to its effect on physical density. The heat distortion temperature, therefore, should be lower than for the HHPA cured system. The extent of this decrease can be expected to be less than that for methyl succinic compared to succinic at a high extent of reaction, where the difference is approximately 35°C. For the saturated anhydrides the change in heat distortion temperature due to the presence of a methyl group should be roughly proportional to the change in physical density. For the MSA/SA case a .030 gm/cm^3 change in density corresponds to a 35°C change in the HDT; for the HHPA/MHHPA case, therefore, one could expect roughly a 21 - 23°C change in HDT since a .020 gm/cm^3 change is expected in density. Thus, the expected HDT range is 115 - 125°C. The toughness values for the MHHPA cured system should be slightly lower than for the HHPA case again due to the presence of the methyl group, and the predicted toughness range becomes 1.1 - 1.3 x 10^3 psi. On aging, one could predict that the flexural strength retention would be similar to HHPA (roughly 38%); the elastic modulus should remain higher than the HHPA system (5.5 - 5.6 x 10^5 psi); the weight loss should also be higher than for the HHPA system, (10 - 11%), due to the lower cross-linking density; while the HDT and physical density should remain relatively unchanged, as characteristic of saturated systems which are highly reacted in the as-cured condition. In both the aged and as-cured conditions, the MHHPA cured system should be more solvent sensitive than the HHPA cured system due to the lower density.

After this research was essentially completed, MHHPA was ordered from Aldrich Chemical Company (catalog # 14, 993-4), and several property determinations were made

TABLE XXVIX

COMPARISON OF PREDICTED PROPERTIES OF 4-METHYL HHPA CURED EPOXIDIZED NOVOLAC WITH ACTUAL PROPERTIES

PROPERTY	PREDICTED	ACTUAL
Flexural Strength psi	25,000	25,000
Flexural Modulus 10^5 psi	5.2	5.0
Toughness 10^3 psi	1.2	1.1
Density gms/cm^3	1.222	1.218
HDT °C	120	128

and compared to the predicted values. This comparison is shown in Table XXVIX. These values are, of course, for epoxidized novolac with an equivalent cure cycle to that utilized in this research. Relative values, however, could be predicted regardless of cure cycle, epoxide resin structure, catalyst concentration, etc. Changing these variables may affect relative properties to the extent that they affect the anhydride-epoxide reaction. It is highly likely, for instance, that the reactivity gap between succinic and hexahydrophthalic anhydrides could be narrowed by a change in catalyst concentration or reactivity. Water absorption may also affect the relative properties, as its effect would depend on the solubility limit of the acid in the anhydride, as well as the reactivity of the acid itself. The presence of acid above a few percent generally lowers the degree of cure either by the relative non-reactivity of the acid compared to the anhydride (causes non-reacted epoxide and acid in cured structure), or by the promotion of etherification (causes non-reacted anhydride in cured structure). These effects should accordingly be taken into account when using the data from this thesis for predicting the properties of other anhydrides.

CONCLUSIONS

The structure of alicyclic dicarboxylic anhydrides was found to have a significant effect on the final physical and chemical properties of a cured epoxidized novolac resin, and with certain limitations, one can predict the final properties of a cured system with reasonable accuracy from the theoretical structure; therefore, a formulator can better select an anhydride curing agent for a given application based on his knowledge of its structure. Addition of vinyl monomers to anhydride cured systems do not produce any advantages except viscosity reduction, an exception being the maleic anhydride cured system where the cross-linking rate was significantly increased. A number of conclusions have also been reached regarding the specific dependence of properties on structure, the strain rate dependence of properties, and the testing methods in general. Specific conclusions are as follows:

Anhydride Structure

1. The multi-ring anhydride cured epoxies have higher yield strengths and elastic moduli,

but lower densities than their single ring anhydride cured counterparts.

2. The saturated anhydride cured epoxies have higher toughness, but lower densities and elastic moduli than their unsaturated anhydride cured counterparts.

3. The presence of a methyl group on the anhydride structure increases elastic moduli and solvent sensitivity, but decreases density, toughness, and heat distortion temperatures.

4. Methyl groups, cyclic rings, and unsaturated sites on the anhydride structure all tend to increase the elastic modulus.

5. Based on heat distortion temperatures, only the maleic anhydride and methyl endomethylene tetrahydrophthalic anhydride cured formulations exhibited significant increases in cross-linking due to the double bond reaction before aging.

6. The double bond in all the unsaturated anhydrides reacts upon aging, resulting in high heat distortion temperatures, high moduli, and significant decreases in physical density and weight losses when compared to their saturated anhydride cured counterparts.

7. Upon aging all the formulations embrittle such that toughness is only a fraction (.02-.12) of its

as-cured value.

8. Saturated single ring anhydride cured epoxies exhibit the best retention of properties on aging, retaining over 50% of their as-cured flexural strength.

9. Formulations containing methyl endomethylene tetrahydrophthalic anhydride craze on aging, resulting in exceptionally low retention of flexural strength and toughness; formulation changes which reduce heat distortion temperatures (cross-linking density), also reduce crazing.

10. The methyl endomethylene tetrahydrophthalic cured DGEBA formulation exhibited higher as-cured toughness and better retention of flexural properties on aging, but lower heat distortion temperatures and poorer solvent resistance when compared to methyl endomethylene tetrahydrophthalic anhydride cured epoxidized novolac.

11. Isomerization of unsaturated multi-ring anhydrides decreases double bond reactivity as compared to the cis-4-isomer; therefore, the isomeric mixture as a curing agent results in lower heat distortion temperatures and higher weight losses on aging.

12. The decrease in contraction coefficient, which

causes lower densities at higher post cure temperatures, is much more significant for the unsaturated anhydride cured formulations than for the saturated anhydride cured formulations.

13. The extent of the anhydride-epoxide reaction for the various anhydrides has the same relative order as their acid dissociation constants in water.

14. Maleic anhydride readily absorbs moisture during melting and mixing, and this moisture converts the anhydride to the acid which promotes etherification.

15. Hexahydrophthalic anhydride is an excellent hardener for combining high toughness with moderate heat distortion temperatures and good solvent resistance; properties are aided by a high extent of epoxide-anhydride reaction.

16. When the double bond reaction becomes significant, properties of a saturated/unsaturated binary system become negatively synergistic, unless a bridging agent such as excess unsaturated anhydride is present; in the latter case, the property versus mole percent saturated anhydride substituted for unsaturated anhydride curve is shifted in the positive direction.

17. Toughness values of a binary system are negatively synergistic if there is a brittle-ductile failure transition as one anhydride is replaced by the other.

18. Addition of branched alkenyl succinic anhydrides to flaw sensitive maleic anhydride cured formulations weakens the material and reduces toughness, flexural strength, and ultimate flexural strain.

19. Properties of linear alkenyl succinic anhydride cured systems, including equilibrium modulus, closely parallel those of linear alkyl succinic anhydride cured systems, indicating that the double bond in the linear alkenyl succinic anhydrides is unreacted.

20. Linear octenyl succinic cured epoxidized novolac exhibits slightly higher density, heat distortion temperature, and tangent modulus as compared to linear octyl succinic anhydride cured epoxidized novolac due to the presence of the unsaturated site.

21. Properties of branched alkenyl succinic anhydride cured systems differ substantially from the linear alkenyl succinic cured materials with higher tangent moduli, flexural yield strength,

and heat distortion temperatures. Solvent sensitivities are improved in spite of a lower physical density. Differences are attributed to methyl groups on substituted chain and some double bond reaction.

22. Effect of increasing substituent chain length in substituted succinic anhydride cured systems is to decrease density, tensile yield strength, flexural yield strength, tangent modulus, and heat distortion temperature while increasing tensile elongation.

23. Based on relaxation spectrums and heat distortion temperatures, linear alkyl and alkenyl succinic anhydrides, with 12 or more carbon atoms in the substituted chain, produce cured materials with glass transition temperatures below room temperature.

24. Oxygen attack on the unsaturated sites of alkenyl succinic anhydrides at high temperatures results in surface embrittlement and eventual crazing.

<u>Vinyl monomer additions</u>

1. Addition of vinyl monomers to anhydride/epoxy mixtures markedly reduce formulation viscosity.

2. Effect of vinyl toluene additions to anhydride

cured formulations (except for maleic anhydride) was to decrease all the as-cured properties, except for solvent sensitivity which increased due to the decrease in density. Properties were also found to decrease further with increasing vinyl toluene content.

3. Vinyl toluene was present in the cured structure as polyvinyl toluene chains rather than individual vinyl toluene molecules, resulting in lower weight losses on aging and a relatively minor effect on the extent of cross-linking.

4. Addition of vinyl toluene or monochlorostyrene to the maleic anhydride cured formulation resulted in significant as-cured increases in elastic moduli and heat distortion temperatures; however, on aging, the elastic modulus and heat distortion temperature of the maleic anhydride cured formulation increased beyond those for the maleic/vinyl monomer formulations.

5. Monochlorostyrene is more effective than vinyl toluene in increasing modulus, but less effective in increasing heat distortion temperature for the as-cured maleic anhydride cured system.

Test methods

1. Flexural properties are a function of strain

rate and for materials of low modulus and heat distortion temperature (indicates low glass transition temperature), the relative flexural properties may also become a function of strain rate.

2. The flexural test up to 2"/minute deflection rates is not a good test for low moduli materials, when determining ultimate properties, because of the tendency to achieve high flexural strains before fracture, allowing substantial slippage between supports.
3. Polish on the tensile surface affects measured flexural properties. Flexural strength of flaw sensitive maleic anhydride cured epoxidized novolac decreased with coarser polishes, while the scatter between values increased.
4. Tensile properties are a function of strain rate.
5. The tangent modulus determined in flexure and tension is the same.
6. The tensile yield strength/flexural yield strength ratio decreases with decreasing initial modulus, indicating a greater time dependence of yield strength for the tensile test.
7. A 24 hour water boil is a good method for indicating excess anhydride, but a 24 hour

immersion in a HBr-acetic reagent is a poor method for indicating excess epoxide due to complicating side effects.

8. The oxidized surface layer formed on aging may act as a protective barrier against chemical attack.

BIBLIOGRAPHY

1. Andrews, R. D., "Correlation of Dynamic and Static Measurements on Rubberlike Materials," *Industrial and Engineering Chemistry*, vol. 44, pp.707-710,1952.

2. Anonymous, *Aliphatic Chemicals*, technical data sheet, Humphrey Chemical Company.

3. _______, *Anhydride Hardners for Epoxy Resins*, Technical booklet, Allied Chemical Corporation, 1966.

4. _______, *Ciba, EPN 1139*, technical bulletin, Ciba Products Company, 1970.

5. _______, *D.E.N. Epoxy Novolac Resins*, technical booklet, Dow Chemical Corporation, 1967.

6. _______, *Nadic 200 Acid Anhydride*, technical bulletin TA 46-441, Allied Chemical Corporation, 1969.

7. _______, *Technical Service Notes 96*, Ciba Products Company.

8. _______, Vanderide Liquid Anhydrides, technical data sheet, R. T. Vanderbilt Company, 1970.

9. Bavley, A., C. Knuth and F. Michelotti, "Resin Compositions," U. S. 2,938,014, (May 24, 1960).

10. Belanger, W. J., D. D. Hicks and J. E. Masters, "Epoxide Resin Compositions," U.S. 2,934,521,(April 26, 1960).

11. Belanger, W. J., D. D. Hicks and J. E. Masters, "Modified Epoxide Resins," U.S.2,947,717, (August 2, 1960).

12. Belanger, W. J. and J. E. Masters, "Epoxide Resin Compositions," U.S. 2,947,717, (August 2, 1960).

13. Benningen, W. F., "Compositions Comprising Epoxy Compounds and Hydroxyl Terminated Polyester Resins and Process of Making the Same," U. S. 2,830,031, (April 8, 1958).

14. Bokon, A., "Optimum Curing Conditions for Solid Epoxy Resins Determined by Statistical Evaluation," technical paper, A.C.S. Symposium, New York City, 1960.

15. Bruins, P., Epoxy Resin Technology, John Wiley, New York, 1968.

16. Canaan, N., G. H. Hicks and T. J. Suen, "Diepoxy Resinour Compositions," U.S. 2,801,232, (July 30, 1957).

17. Castan, P., "Process of Preparing Synthetic Resins," U. S. 2,324,483, (July 20, 1943).

18. Christie, S. H., "Anhydride Blends as Curing Agents for Epoxy Resins," S.P.E. Tech. Papers, vol. 12, Session 5, pp. 1-5, 1966.

19. Christie, S. H., "Effects of Resin Parameters on Properties of Cured Epoxy Resins," Modern Plastics, pp. 134-142, (August, 1965).

20. Cuthrell, R. E., "Epoxy Polymers III," Journal of Applied Polymer Science, vol. 11, pp. 955-967.

21. Cuthrell, R. E. "Macrostructure and Environment Influenced Surface Layer in Epoxy Polymers," Journal of Applied Polymer Science, vol. 10, pp. 949-952.

22. Dearborn, E. C., R. M. Fuoss, A. K. MacKenzie and R.G. Shepherd, "Epoxy Resins from Bis-, Tris-, and Tetrakis-Glycidyl Ethers," Industrial and Engineering, Chemistry, vol. 45, pp. 2715-2721.

23. Dearborn, E. C., R. M. Fuoss and A. F. White, "Acid Acceleration of Epoxy Condensations," Journal of Polymer Science, vol. 16, 1955, pp. 201-208.

24. Delmonte, J., "Selecting Epoxy Resins," Chemical Engineering Progress, vol. 58, pp. 51-54, 1962.

25. Delmonte, J., "Semi-Rigid Epoxy Resin Compositions and Method," U. S. 3,188,362, (June 8, 1965).

26. Ehlers, G., "A Modified Vicat Type Apparatus for Measuring Softening Points of Thermosetting Plastics and Laminates," A.S.T.M. bulletin, (Feb., 1959).

27. Ehlers, G., "Correlation between Structure and Thermal Stability of Epoxy Resins," Polymer, vol. 1, pp. 304-314, (Sept., 1960).

28. Eirich, F. R., "Copolymerized and Cross-linked Epoxide Resins," U. S. 2,848,433, (Aug. 19, 1958).

29. Feltzin, J., M. K. Barsh, E. J. Peer and I. Petker, "Kinetics of Epoxy Polymerization," *Preprints of Papers*, vol. 24, ACS Symposium, Chicago, Sept. 1964, p. 282.

30. Fisch, W. and W. Hofmann, "Reaction Mechanisms, Chemical Structures and Changes in Properties during the Cure of Epoxy Resins," *Plastics Technology*, pp. 28-32, (Aug. 1961).

31. Fisch, W., W. Hofmann and J. Koskikallio, "The Curing Mechanism of Epoxy Resins," *Journal of Applied Chemistry*, vol. 6, p. 429, 1956.

32. Fisch, W., W. Hofmann and R. Schmid, "Chemistry of Epoxide Resins XVII," *Journal of Applied Polymer Science*, vol. 13, pp. 295-308, 1969.

33. Fischer, R. "Polyesters from Epoxides and Anhydrides," *Industrial and Engineering Chemistry*, pp. 321-322, (April, 1960).

34. Fleming, G. J., "Mechanisms for Initiating Thermal Degradation of Certain Anhydride Cured Epoxides," *Journal of Applied Polymer Science*, vol. 10, pp. 1813-1830, 1966.

35. Fleming, G. J., "Thermal Properties of an Epoxide Cured with Bicyclo Diels-Alder Anhydride Adducts," *Journal of Applied Polymer Science*, vol. 13, pp. 989-997, 1969.

36. Harry, L. D. and R. F. Helmreich, "Two Flexible Epoxy Resins," *S.P.E. Journal*, vol. 17, pp. 583-586, 1961.

37. Hodgman, C. D., editor, *Handbook of Chemistry and Physics*, The Chemical Rubber Pub. Co., Cleveland, 1962.

38. Ishai, O., "Delayed Yielding of Epoxy Resin," *Journal of Applied Polymer Science*, vol. 11, pp. 1863-1879, 1967.

39. Ishai, O., "Delayed Yielding of Epoxy Resin Under Tension Compression and Flexure I," *Journal of Applied Polymer Science*, vol. 11, pp. 963-981, 1967.

40. Lee, H. and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967.

41. Levitan, T., "The Use of a Statistically Designed Experiment for Studying Resin Parameters," technical paper, R.I.P. division of S.P.I., Chicago, (Feb., 1965).

42. Mack, A.C., "Formulation and Cure Cycle Study for an Anhydride Cured Epoxy Novolac System," Industrial and Engineering Chemistry Product Research Development, vol. 3, p. 213, 1964.

43. Moehlenpah, A.E., O. Ishai and A. T. Dibenedetto, "The Effect of Time and Temperature in the Mechanical Behavior of a Plasticized Epoxy Resin Under Different Loading Modes," Journal of Applied Polymer Science, vol. 13, pp. 1231-1245, 1969.

44. Morrison, R. T. and R. N. Boyd, Organic Chemistry, Albyn and Bacon, Boston, 1966.

45. Phillips, B., P. S. Starcher, C. W. McGary and C. T. Patrick, "Curable Composition Compressing a Diepoxide, A Polycarboxylic Anhydride and a Polyhydric Compount," U.S. 2,890,196, (June 9, 1959).

46. Schechter, L. and J. Wynstra, "Glycidyl Ether Reactions with Alcohols, Phenols, Carboxylic Acids and Acid Anhydrides," Industrial and Engineering Chemistry, vol. 48, pp. 86-93, 1956.

47. Skeist, I., Epoxy Resins, Reinhold, 1958.

48. Updegraff, I. H., "Polymerizable Compositions Containing Polyglycidyl Esters of Polycarboxylic Acids," U. S. 2,781,333, (Feb. 12, 1957).

49. Warburton, J. A., "Methyl Nadic and Hexahydrophthalic Anhydrides as Curing Agents for Epoxide Novolac Resins," U. S. 3,218,288, 1965.

50. Weinschank, C., "Condensation of Epichlorohydrin with Phthalic Anhydride under Influence of Tertiary Bases," Chemiker Zeitung, p. 1311, 1905.

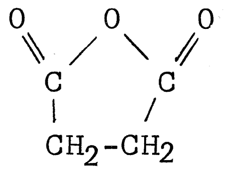
51. Weiss, H. K., "Optimum Conditions for Curing Nadic Methyl Anhydride-Epoxy Casting Resins," Technical paper, S.P.I. Upper Midwest RETEC, Minneapolis, Minn., (Oct. 21, 1958).

52. Wheelock, C. E., "Thermosetting Resins," U.S. 3,028,370, (April 3, 1962).

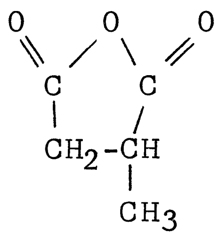
APPENDIX A

The theoretical structures and commercial sources of all the materials utilized in this investigation are compiled in this Appendix. The lot numbers or catalog numbers are also included. The structures were either obtained from the suppliers or from one of the following sources: Aldrich Chemical Catalog 14, Aldrich Chemical Company, 1968, pp. 401-482; H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, 1967, pp. 12.6 - 12.7

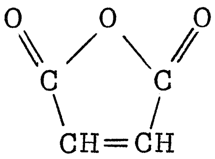
Succinic anhydride: Matheson, Coleman, and Bell; catalog # 2503.



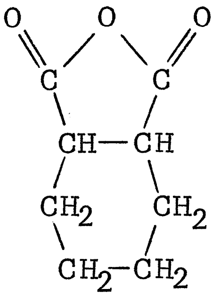
Methyl succinic anhydride: Eastman Organic Chemicals; catalog # P7613.



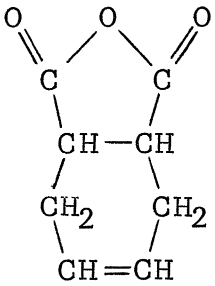
Maleic anhydride: Matheson, Coleman, and Bell; catalog # MX110.



Hexahydrophthalic anhydride: J. T. Baker Company; catalog # F998.



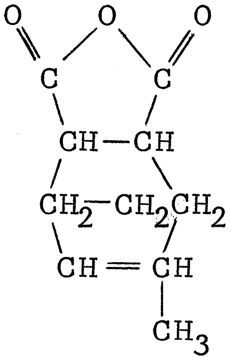
cis-4-Tetrahydrophthalic anhydride: Eastman Organic Chemicals; catalog # P5724.



Tetrahydrophthalic anhydride isomers: Allied Chemical Corporation; Nadic 200, Lot # 1258030.

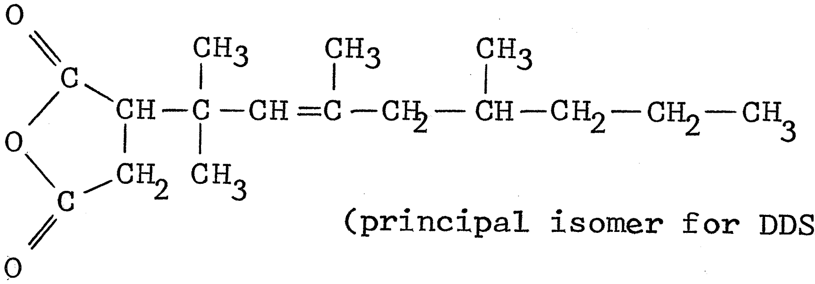
Methyl tetrahydrophthalic anhydride isomers: R. T. Vanderbilt Company; Vanderide 2, Lot # 35.

Methyl endomethylene tetrahydrophthalic anhydride isomers: Allied Chemical Corporation; Nadic methyl anhydride, Lot # 0357421.



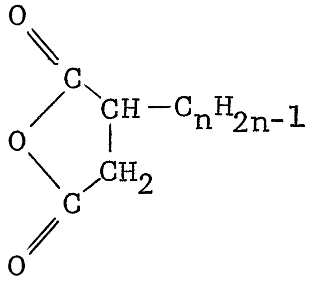
(principal isomer)

Methyl branched alkenyl succinic anhydrides: Humphrey Chemical Company; OSA (lot # 12), diisobutylene substituent; NSA (lot # 131), tripropylene substituent; DDSA (lot # 1050), propylene tetramer substituent.



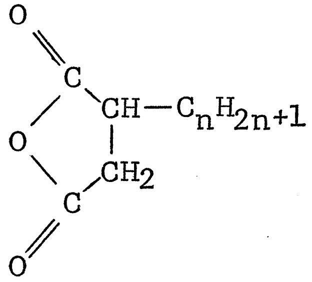
(principal isomer for DDSA)

Linear alkenyl succinic anhydrides: Humphrey Chemical Company; n-OSA (lot # 32, 695), 1-octene substituent; n-DDSA (lot # 22), 1-dodecene substituent; n-HDSA (lot # 338), 1-hexadecene substituent.



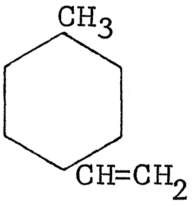
(generalized formula)

Linear alkyl succinic anhydrides: Humphrey Chemical Company; octyl (lot # 24); dodecyl (lot # 34E); hexadecyl (lot # 24).

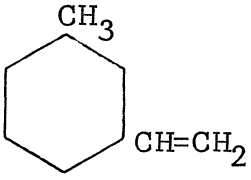


(generalized formula)

Vinyl toluene: Borden Chemical Company; Lot # 184-24; mixture of meta and para isomers (approximately 60% meta).

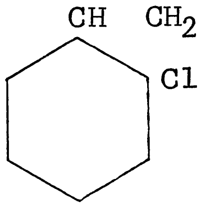


para

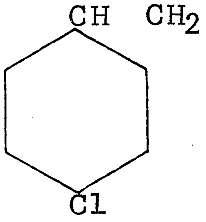


meta

Monochlorostyrene: Dow Chemical Company; Lot # 08170-09; mixture of ortho and para isomers (60% ortho minimum).



ortho

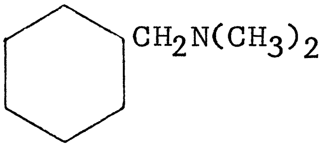


para

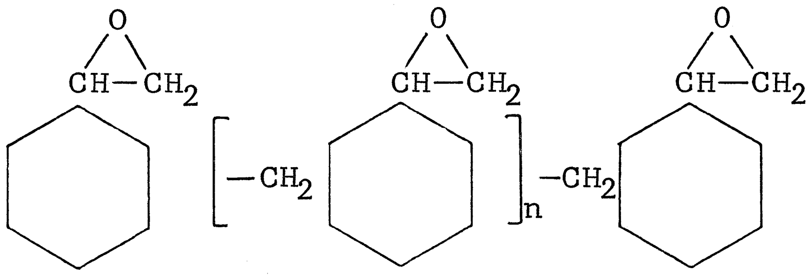
Tertiary butyl perbenzoate: Wallace and Tiernan; Lot # KJ266.

Lauroyl peroxide: Cadet Chemical Corporation; Lot # UV066.

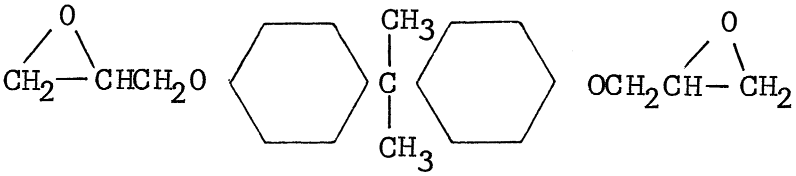
Benzyldimethylamine: Ciba Products Company; accelerator 062, Lot # G107033.



Diglycidyl ether of phenol formaldehyde novolac: Dow Chemical; DEN 431, Lot # 11138, 431601.



<u>Diglycidyl ether of bisphenol A</u>: Ciba Products Company; Ciba 6005, Lot # H460.



APPENDIX B

Sample calculations of all the properties reported in this thesis are given below for succinic anhydride cured epoxidized novolac. Exceptions are the viscosity data which is on the MTHPA/vinyl toluene system, and the stress relaxation data for materials above their glass transition temperature which is on the hexadecyl succinic anhydride cured formulation. Standard deviations are calculated for the yield strength (tensile and flexure), moduli (tensile and flexure), toughness (tensile and flexure), and tensile elongation data, in order to indicate the accuracy of the measurements in each case.

Density:

1. number of specimens per value = 2
2. test temperature = 23-25°C
3. average reported to nearest .001 gm/cm^3
4. formulae:

$$D = \frac{(W_a)\,(D_{WT})}{W_a - W_w}$$

W_a = specimen weight in air

W_w = specimen weight in water

D_{WT} = density of water at temperature T

5. sample calculations:

$$\#1 \quad \frac{(.6433)(.99845)}{.6433 - .1473} = 1.295 \text{ gms/cm}^3$$

$$\#2 \quad \frac{(1.1108)(.99845)}{1.1108 - .2542} = 1.295 \text{ gms/cm}^3$$

average density = 1.295 gms/cm^3

Heat Distortion Temperature:

1. number of specimens per value = 2
2. heating rate = 2°C/minute
3. average reported to nearest 1°C
4. formulae:

$$\text{specimen stress} = \frac{^3P\ L}{2\ d\ w^2} = 264 \pm 5 \text{ psi}$$

p = load

L = span + 4 inches

d = specimen thickness

w = specimen width

5. sample calculations:

$$\#1 \quad \frac{(3)(668/454)(4)}{(2)(.131)(.510)^2} = 259 \text{ psi}$$

$$\#2 \quad \frac{(3)(831/454)(4)}{(2)(.143)(.540)^2} = 264 \text{ psi}$$

#1 HDT (@ 10 mil deflection) = 106.5°C

#2 HDT (@ 10 mil deflection) = 106.5°C

average HDT = 106°C

Tensile Yield Strength: (A.S.T.M. D638-61T)

1. number of specimens per value = 5
2. test temperature = 72 ± 2°F

3. average reported to 3 significant figures

4. formulae:

$$Y.S. = \frac{P}{d\ w}$$

P = load at yield

d = thickness

w = width

5. sample calculations

$$\#1 \quad \frac{(802)}{(.127)(.525)} = 12{,}029 \text{ psi}$$

$$\#2 \quad \frac{(820)}{(.126)(.522)} = 12{,}467 \text{ psi}$$

$$\#3 \quad \frac{(820)}{(.128)(.524)} = 12{,}226 \text{ psi}$$

$$\#4 \quad \frac{(767)}{(.120)(.505)} = 12{,}657 \text{ psi}$$

$$\#5 \quad \frac{(824)}{(.128)(.525)} = 12{,}262 \text{ psi}$$

average yield strength = 12,300

6. standard deviation = 260 psi

Tensile Elongation: (A.S.T.M. D638-61T)

1. number of specimens per value = 5
2. test temperature = 72 ± 2°F
3. average reported to 2 significant figures
4. values determined from Instron 1" extensionmeter:

#1 5.0%

#2 7.2%

#3 5.6%

#4 7.7%

#5 7.3%

average elongation = 6.6%

5. standard deviation = 1.2%

Tensile Modulus: (A.S.T.M. D638-61T)

1. number of specimens per average value = 5
2. test temperature = 72 ± 2°F
3. average reported to signifcant figures
4. formulae:

$$E = \text{modulus} = \frac{S_1 - S_2}{e_1 - e_2} = \text{initial slope}$$

$e_1 - e_2 = .005$ inch/inch

$$S_1 - S_2 = \frac{P_1 - P_2}{d\ w}$$

d = specimen thickness

w = specimen width

P_1 = load @ e_1

P_2 = load @ e_2

5. sample calculations

#1 $$\frac{(145)}{(.127)(.525)(.005)} = 4.3494 \times 10^5 \text{ psi}$$

#2 $$\frac{(150)}{(.126)(.522)(.005)} = 4.5614 \times 10^5 \text{ psi}$$

#3 $\dfrac{(140)}{(.128)(.524)(.005)}$ $= 4.1748 \times 10^5$ psi

#4 $\dfrac{(135)}{(.120)(.505)(.005)}$ $= 4.4554 \times 10^5$ psi

#5 $\dfrac{(150)}{(.128)(.525)(.005)}$ $= 4.4644 \times 10^5$ psi

average modulus = 4.4×10^5 psi

6. standard deviation = $.15 \times 10^5$ psi

<u>Tensile</u> <u>Toughness</u>:

1. number of specimens per average value = 5
2. test temperature = ± 2°F
3. average reported to 2 significant figures
4. formulae:

$$T = (A)(e)\frac{P}{d\ \ w}$$

A = area under stress-strain curve measured by compensating polar planimeter

e = strain corresponding to 1" on horizontal axis

P = load corresponding to 1" on vertical axis

d = specimen thickness

w = specimen width

5. sample calculations

#1 $\dfrac{(9.80)(.025)(100)}{(.127)(.525)}$ $= .3674 \times 10^3$ psi

#2 $\dfrac{(16.99)(.025)(100)}{(.126)(.522)}$ $= .6458 \times 10^3$ psi

#3 $\frac{(12.53.5)(.025)(100)}{(.128)(.524)} = .4672 \times 10^3$ psi

#4 $\frac{(16.97)(.025)(100)}{(.120)(.505)} = .7001 \times 10^3$ psi

#5 $\frac{(17.06)(.025)(100)}{(.128)(.525)} = .6347 \times 10^3$ psi

average toughness = $.56 \times 10^3$ psi

6. standard deviation = $.14 \times 10^3$ psi

Flexural Yield Strength:

1. number of specimens per average value = 5
2. test temperature = 72 ± 2°F
3. average value reported to nearest 50 psi
4. formulae:

$$Y.S. = \frac{3\ P\ L}{2\ w\ d^2}$$

L = span = 2 inches

P = load

w = specimen width

d = specimen depth

5. sample calculations

#1 $\frac{(3)(42.8)}{(.432)(.120)^2} = 20,640$ psi

#2 $\frac{(3)(48.8)}{(.469)(.121)^2} = 21,320$ psi

#3 $\frac{(3)(52)}{(.445)(.129)^2} = 21,065$ psi

#4 $$\frac{(3)(61.9)}{(.470)(.137)^2} = 21{,}051 \text{ psi}$$

#5 $$\frac{(3)(50)}{(.436)(.129)^2} = 20{,}674 \text{ psi}$$

average yield strength = 20,950 psi

6. standard deviation = 290 psi

Flexural Modulus:

1. number of specimens per average value = 5
2. test temperature = 72 ± 2°F
3. average reported to 3 significant figures
4. formulae:

$$E = \frac{3\ L\ (P_1 - P_2)}{2\ w\ d^2\ (e_1 - e_2)} = \text{initial slope}$$

$$e_1 - e_2 = 6\ d\ (D_1 - D_2)\ /\ L^2$$

$$E = \frac{L^3\ (P_1 - P_2)}{4\ w\ d^3\ (D_1 - D_2)}$$

L = 2 inches

$D_1 - D_2$ = .08 inch (D = deflection)

w = specimen width

d = specimen depth

P_1 = load @ D_1

P_2 = load @ D_2

5. sample calculations

#1 $$\frac{(13.4)}{(.432)(.120)^3(.04)} = 4.4875 \times 10^5 \text{ psi}$$

#2 $\frac{(14.7)}{(.469)(.121)^3(.04)} = 4.4225 \times 10^5$ psi

#3 $\frac{(17.3)}{(.445)(.129)^3(.04)} = 4.5275 \times 10^5$ psi

#4 $\frac{(21.8)}{(.410)(.137)^3(.04)} = 4.5100 \times 10^5$ psi

#5 $\frac{(17)}{(.436)(.129)^3(.04)} = 4.5400 \times 10^5$ psi

average modulus = 4.50×10^5 psi

6. standard deviation = $.05 \times 10^5$ psi

<u>Flexural Toughness</u>:

1. number of specimens per average value = 5
2. test temperature = 72 ± 2°F
3. average reported to 2 significant figures
4. formulae:

$$T = A \frac{3\ P\ L}{2\ w\ d^2} \frac{6\ d\ D}{L^2}$$

L = 2 inches

P = 10 lbs.

D = .1 inch

T = A (4.5) / w d

A = area under stress-strain curve measured by compensating polar planimeter

w = specimen width

d = specimen depth

5. sample calculations:

#1 (4.5)(18.455) / (.120)(.432) = 1.602 x 10^3 psi

#2 (4.5)(16.70) / (.121)(.469) = 1.324 x 10^3 psi

#3 (18.05)(4.5)/(.129)(.445) = 1.415 x 10^3 psi

#4 (4.5)(20.635)/(.137)(.470) = 1.442 x 10^3 psi

#5 (4.5)(15.33)/(.129)(.436) = 1.227 x 10^3 psi

average flexural toughness = 1.4 x 10^3 psi

6. standard deviation = .14 x 10^3 psi

Weight Loss on Aging:

1. number of specimens per average value = 2
2. test temperature = 250 ± 2°C
3. average reported to nearest .1%
4. formulae:

weight loss = $(100)(W_i - W_a)/W_i$

W_i = initial weight after post cure

W_a = aged weight

5. sample calculations:

#1 (100)(7.56 - 6.52)/(7.56) = 13.75%

#2 (100)(7.65 - 6.61)/(7.65) = 13.65%

average weightloss = 13.7%

Chemical Resistance:

1. number of specimens per average value = 3
2. test temperature = 23-25°C, unless otherwise noted for specific reagents
3. average reported to 2 significant figures

4. formulae:

   weight gain = $(100)\ (W_c - W_i)/W_i$

   W_i = initial weight after post cure

   W_c = weight after chemical exposure

5. sample calculations:

   #1 (100)(.8730 - .8570)/.8570 = 1.9%

   #2 (100)(.8159 - .8005)/.8005 = 1.9%

   #3 (100)(.7869 - .7721)/.7721 = 1.9%

   average weight gain = 1.9%

Viscosity:

1. number of samples per value = 1
2. test temperature = 23.5°C
3. reported to nearest 5 cps.
4. calculations:

   values taken from a linear plot of viscosity vs Brookfield number @5 rpm (plot determined from 3 standard fluids with known viscosities)

Formulation	Brookfield Number Spindle # 1	Viscosity
MTHPA	57.6	940 cps
MTHPA/VT 4/1	16.7	270 cps
MTHPA/VT 2/1	7.1	115 cps
MTHPA/VT 4/3	3.7	60 cps
MTHPA/VT 1/1	2.2	40 cps

Stress Relaxation:

1. number of specimens per reported value = 1
2. test temperature = 70 - 72^{o}F
3. reported to nearest 100 psi (equilibrium modulus)
4. formulae:

$$G(t) = \frac{P(t)}{d\ w\ e}$$

e = strain = .0094 inch/inch

d = specimen thickness

w = specimen width

P(t) = load at time t

5. calculations:

modulus ploted vs log time (see Figure XXV); all H(log t) vs log t curves are a plot of the slope of the modulus vs log t curve

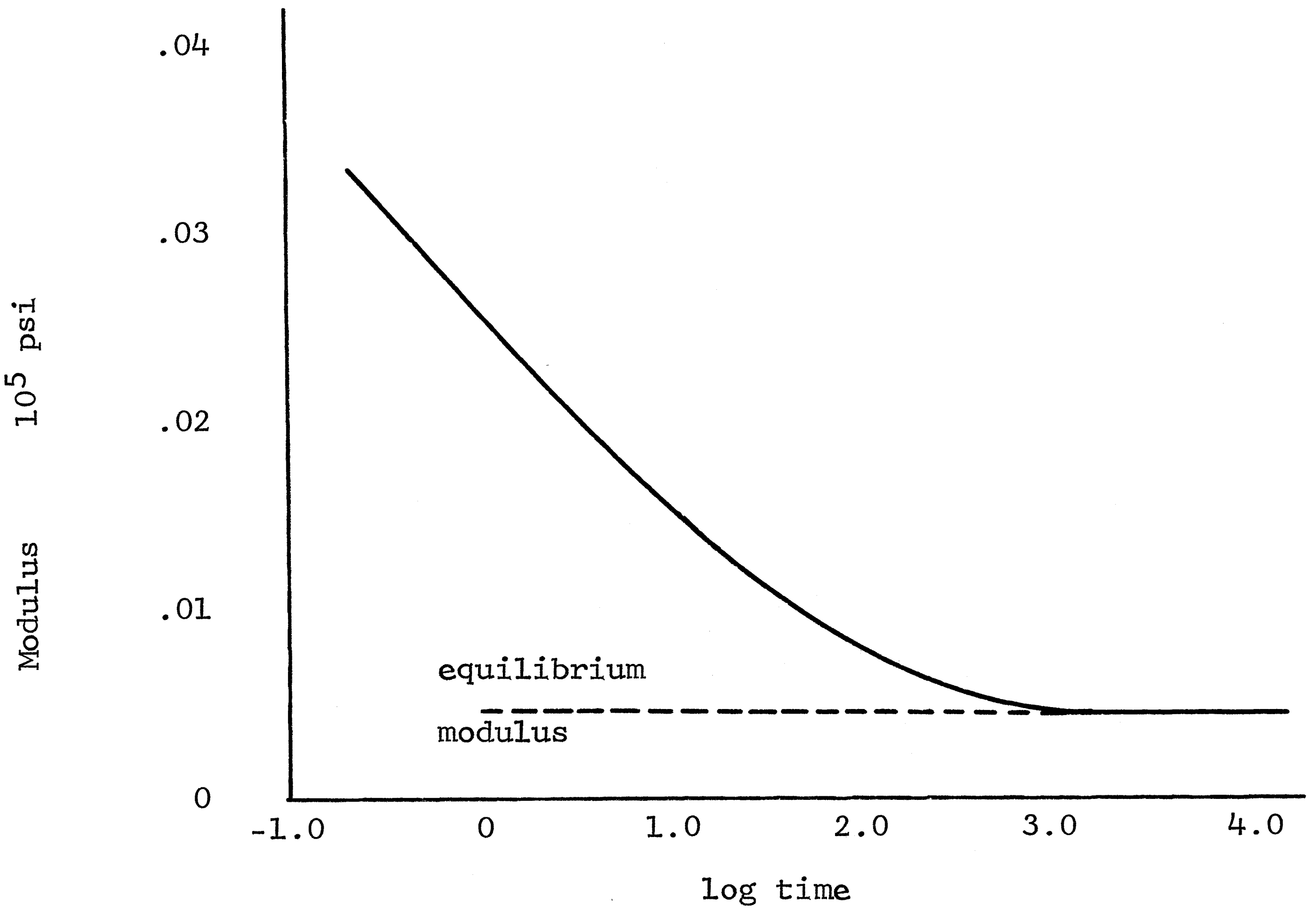


FIGURE XXV MODULUS RELAXATION CURVE FOR HEXADECYL SUCCINIC ANHYDRIDE CURED EPOXIDIZED NOVOLAC

The vita has been removed from
the scanned document

CORRELATION OF PHYSICAL AND CHEMICAL PROPERTIES OF ANHYDRIDE-CURED EPOXY RESINS WITH THEORETICAL STRUCTURE

Ronald E. Johnson

Abstract

The structure of alicyclic dicarboxylic anhydrides was found to have a significant effect on the final physical and chemical properties of a cured epoxidized novolac resin, and the final properties of a cured system can be predicted with reasonable accuracy from the theoretical structure. Properties were related to structure in terms of cyclic rings, unsaturation, substituted groups, etc. Measured properties were flexural strength, tangent modulus, toughness (area under the stress-strain curve), density, heat distortion temperature, and solvent sensitivity, as well as the retention of these properties after 250°C aging. The tensile test was substituted for the flexural test for the softer materials due to excessive slippage between supports.

The anhydride structure was found to influence properties primarily through its effect on physical density, cross-linking density, inter-conformational rotations, and extent of reaction. Overall results revealed hexahydro-

phthalic anhydride as an excellent hardner in the as-cured state for combining high toughness with good heat distortion temperatures and solvent resistance. Succinic anhydride is a close second in toughness although adversely affected in other properties by its low extent of reaction. Aging of the materials reveals the saturated single ring anhydrides to be superior in retention of properties, although all the materials embrittle severely, with methyl endomethylene tetrahydrophthalic anhydride having the lowest property retentions due to crazing.

Vinyl monomers were added to the unsaturated systems in an attempt to enhance properties by promotion of the reaction through unsaturation. These additions were found to produce no advantageous properties except viscosity reduction; an exception being the maleic anhydride cured system where the cross-linking rate was significantly increased.

The branched alkenyl succinic anhydrides were investigated as "flexibilizers" for a maleic anhydride cured system and the flexural strength, tangent modulus, toughness, and heat distortion temperatures were all found to decrease with increasing mole percent branched alkenyl succinic anhydride substituted for maleic anhydride. Properties of the substituted succinic anhydride cured materials, themselves, reveal that density, tensile strength, and moduli all decrease with increasing chain length while tensile elongation and solvent sensitivity increase. Essentially the effect of increasing chain length is to decrease both physical and cross-linking density and to subsequently affect all the other properties according to their dependence on these two density factors. Substituted succinic anhydrides with methyl branched alkenyl chains produced higher strength materials with higher heat distortion temperatures than the corresponding anhydrides with linear chains. The unsaturated substituted succinic anhydrides were found to be sensitive to surface embrittlement at high temperatures resulting in lower tensile elongations and toughness when compared to their saturated counterparts.