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### Characterization of an Epoxy-Anhydride Ablative System Using Computer Treatment of Analytical Results

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# Characterization of an Epoxy-Anhydride Ablative System Using Computer Treatment of Analytical Results

C. GENE TAYLOR and ELMER L. PENDLETON

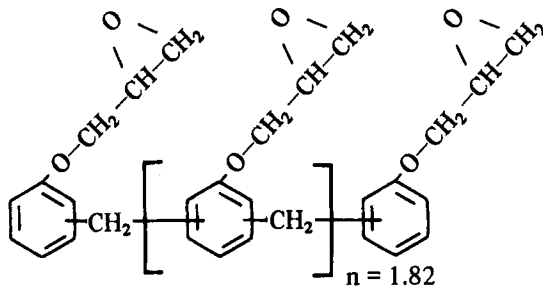
*The Dow Chemical Company, Texas Division  
Freeport, Texas*

## SUMMARY

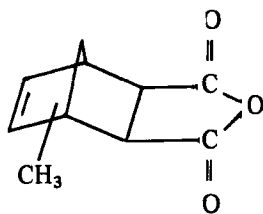
A method has been developed which permits a complete molecular structure description of a polymeric material. Very good molecular descriptions have been achieved for certain epoxy-novolac resin-alicyclic anhydride polymers, which were catalyzed by tertiary amine, by using refined analytical techniques and computer correlation of the analytical data. The method and results are described. The chemical compositions of cured polymers containing various ratios of epoxy-novolac to anhydride are illustrated. The information generated by this work (Contract NAS 7-344) was one element of the NASA-Ames Research Center program to improve char-forming heat shield polymers.

## INTRODUCTION

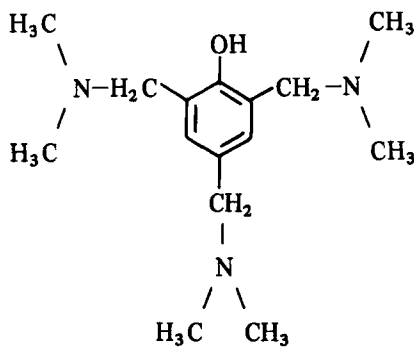
A complete structural characterization of anhydride-cured epoxy-novolac resins has never been reported in the literature, although the determination of certain functional groups present in anhydride-cured resins has been previously reported by Fisch and Hofmann [1]. The results of analyses of this type have not been correlated so that the complete polymer structure could be established.



D.E.N.† 438



Nadic‡ methyl anhydride



DMP§-30

This paper describes the method used in elucidation of the molecular structure of D.E.N.† 438 epoxy-novolac resin cured with various equivalent ratios of Nadic‡ methyl anhydride and catalyzed with DMP§-30 tertiary amine. The characterizations were assisted by the use of a computer program which correlated the data from the functional groups and elemental analyses of each of the formulations.

## EXPERIMENTAL

### Sample Preparation

Samples containing 0.0, 0.25, 0.65, 0.85, and 1.05 equivalents of Nadic methyl anhydride (NMA) per equivalent of D.E.N. 438 (epoxide equiv wt = 178) were prepared for this characterization study, using a 1.5 phr DMP-30 cure accelerator. The samples were cured for 4 hr at 100°C and post-cured for 16 hr at 200°C. After curing was complete, the samples were pulverized and screened through a No. 325 U.S. Standard sieve.

### Instrumental Analysis

Infrared determinations of unreacted epoxide and anhydride concentrations in the cured resins were made on weighed KBr pellets using a Beckman IR 9 double-beam grating spectrometer.

Elemental analyses for carbon, hydrogen, and oxygen were made by standard combustion techniques using a Coleman Model 33 carbon-hydrogen analyzer and a Coleman Model 36 oxygen analyzer. The accuracy accepted for these instruments is  $\pm 0.20\%$  by weight.

Total elemental chlorine in the D.E.N. 438 was determined by burning the sample in a Schöniger oxygen flask and potentiometrically titrating the resulting solution with silver nitrate. Hydrolyzable chloride in D.E.N. 438 was hydrolyzed in alcoholic caustic and potentiometrically titrated with silver nitrate.

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†Trademark of The Dow Chemical Company.

‡Trademark of Allied Chemical Corporation, National Aniline Division.

§Trademark of Rohm and Haas Chemical Company.

### Functional Group Analysis

It is well known that cured epoxy resins, being thermoset polymers, are insoluble in common organic solvents, thereby making analysis by conventional analytical techniques impossible. However, analytical procedures for determining certain functional groups in anhydride-cured epoxy resins have been reported [1]. Using these procedures, or modifications [2] of them, it was possible to determine residual anhydride and monoester contents of five replicates of each formulation. Diester concentration was determined by difference. If the deviation of any one observation was greater than four times the average deviation of the remaining observations, the single observation was legitimately discarded.

Unreacted anhydride was extracted from the powdered polymer sample using acetone, the solution was diluted to volume, and titrations were made on aliquots of this solution. In the first titration, which was done in an anhydrous, alcoholic medium, one equivalent of sodium methoxide reacted with each equivalent of monoester and with each equivalent of anhydride which was present. In the second titration, which was done in an aqueous, alcohol-free medium, one equivalent of sodium hydroxide reacted with each equivalent of monoester, but two equivalents of sodium hydroxide were necessary for each equivalent of hydrolyzed anhydride which was present. Since the monoester group reacted with one equivalent of base in each of the titrations, the difference in equivalents in the two titrations was due to anhydride.

The unreacted anhydride concentration was confirmed by infrared spectroscopy by comparing the absorptivities of the strong NMA bands near 1860 and 1780  $\text{cm}^{-1}$  with the absorptivities of a sample of known anhydride concentration. Infrared was also used to verify complete removal of the anhydride during the acetone extraction process.

To determine the concentration of monoester linked to the polymer, the powdered resin was transesterified with anhydrous methanol in the presence of sodium methoxide and a swelling agent such as toluene or benzene. The anhydride and monoester reacted with sodium methoxide to form the sodium salt of the monomethyl ester of Nadic methyl acid, whereas the diester groups transesterified to the dimethyl ester. The equivalents of base which were used corresponded to the equivalents of anhydride and monoester which were present. The previously determined equivalents of anhydride were subtracted from the total to give the monoester equivalents.

To determine the concentration of diester linked into the polymer, it was assumed that all NMA related concentrations were known with the exception of diester, and it could be determined by difference.

The unreacted epoxide concentration was determined by infrared, using the familiar epoxide band which occurs near  $915\text{ cm}^{-1}$ . The epoxide band in the cured formulation was compared with the same band in raw D.E.N. 438 epoxy-novolac. In the anhydride-cured polymers, unreacted NMA first had to be removed by acetone extraction to avoid band interference.

### Computer Treatment of the Data

Comparison of the analytical data in a computer program allowed solution of the general structure of these polymers. The computer program is a general routine particularly adaptable to this type of problem.

The program that was used is quite simple in principle. It compares the proposed structure of a chemical material to its analyses to determine whether a legitimate "fit" occurs. If all the analyses are properly matched by the proposed structure, then that structure is accepted as a solution. For example, if the proposed structure of a material was methane ( $\text{CH}_4$ ) and the analyses were  $74.9 \pm 0.2\%$  carbon and  $25.1 \pm 0.2\%$  hydrogen, the computer would return the answer that methane is a correct solution to the analyses. If the proposed structure was benzene, this would *not* give a correct solution to the analyses. However, if the structure of the material was proposed to be a mixture of benzene and hydrogen, the computer routine would find as a correct solution to the above analyses: 81.15 wt % benzene, 18.85 wt % hydrogen. This illustration makes the point that the results can be no better than the judgment and capability of the user. A quick check by the researcher in this case could be made to determine the presence or absence of aromatic.

The program used does not return a correct solution unless all its analyses are satisfied. For example, if the proposed structure were methane and the analyses were as follows, *no* correct solution would be found:  $74.8 \pm 0.2\%$  carbon,  $25.1 \pm 0.2\%$  hydrogen,  $0.1 \pm 0.02\%$  nitrogen. Obviously, if the proposed structures were methane *and* nitrogen, then a solution would be found.

Further, the computer program is able to test the amount of substructures and functional groups present against the analyzed concentrations. Examples of functional groups would be hydroxyl, carbonyl, oxirane, active hydrogen, amine, etc. Examples of substructures might be a phenyl ring with four hydrogens or a paraffinic chain eight carbons long, etc.

When an analysis for some functional group (OH, COOH,  $\text{NH}_2$ , etc.) is available, it is good practice to include the analysis as another constraint on the validity of an assumed chemical structure. The advantage of this

capability becomes evident when a situation like the following is encountered. Suppose the analyses are  $62.0 \pm 0.2\%$  carbon,  $10.4 \pm 0.2\%$  hydrogen,  $27.5 \pm 0.2\%$  oxygen,  $18.1 \pm 0.5\%$  hydroxyl as OH,  $18.3 \pm 0.5\%$  carbonyl as C=O. If the compound is assumed to be either allyl alcohol or propionaldehyde with no constraints on OH or C=O, a correct solution would result in each case. However, given these additional constraints, neither one will fit alone. Only a mixture containing 62% allyl alcohol and 38% propionaldehyde will fit.

Notice that in each example the analytical information is specified with limits on the accuracy (i.e.,  $62.0 \pm 0.2\%$  carbon). This is necessary because the computer program does not seek the "best near miss." It only allows results which fall within the specified limits of error. Given an exact analysis (no error limits), the probability that a structure, even the correct one, will properly match to seven significant figures is extremely low. On the other hand, given even a small error range, a proper match is readily achieved.

The limits of accuracy for any analysis depend upon the analytical method used and the type of sample being tested. Sometimes analytical limits can be very tight or narrow. Conversely, some methods are only indicators of a general range of concentration ( $\pm 10\%$ , for example).

An additional feature of the computer program is that it permits the user to prespecify the limits of weight concentration within which any proposed trial material in a mixture may occur. If, for example, the allowed concentration of allyl alcohol had been 0-50% in the allyl alcohol + propionaldehyde mixture, there would have been no solution to the problem as stated. Allowing 60-70% allyl alcohol or any other range which would span the actual situation would result in a valid solution. The value of this feature is that it permits the user to fix the concentration limits of materials that are known to be present. If it is known that some structure cannot exist at greater than or less than certain weight percentile limits, then these would be chosen. This then leads to less chance that a set of assumed structures will produce an impossible combination of material weights.

The user may prespecify a particular trial material to be present at an exact concentration (e.g.,  $15.15 \pm 0\%$ ) if desired. In many cases this is good practice if the material was known to have been added in an exact amount. Again, good judgement is required to assure that the material was not subsequently changed to something else during the mixing or reactions which followed.

The final additional feature in this program system is the ability to

increment across the range of given concentrations of each proposed structure in as fine graduations as is desired. For example, if we use the case with allyl alcohol and propionaldehyde, the quantity of allyl alcohol present might be permitted to range from 60-70% by weight in increments of 0.005% by weight. This would then give at least one valid result at 62% allyl alcohol and 38% propionaldehyde. Choosing very small increments causes more hits or valid combinations to be printed, but it becomes somewhat cumbersome for the user to read through all the printed results. Conversely, if the increments chosen are too large, it is possible not to hit any valid answer even though a valid range of answers lies within the chosen limits.

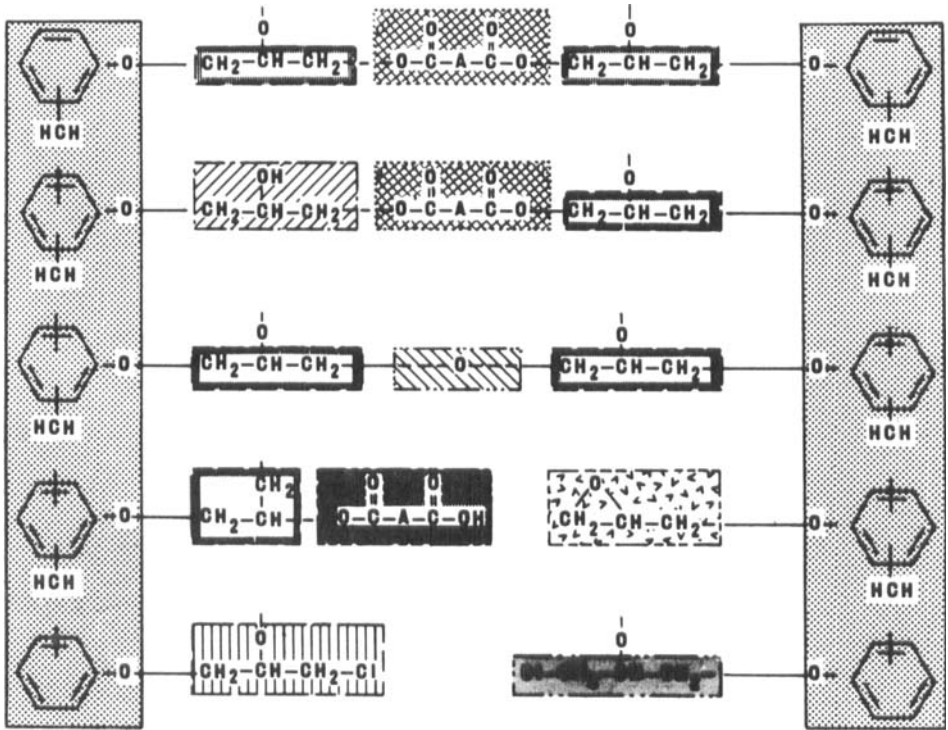
To use this computer system in the characterization of the epoxy-anhydride polymers, it was necessary to first measure all the elements and functional group concentrations in each polymer being studied. Next, since it was known that certain materials were present because they had been put into the polymer formulation, they were fixed as knowns. After we reasoned out the presumed reaction products of the polymer, certain structural parts (links from the polymer chain) were chosen as trial substructures. These were then assigned limits of permissible concentration (based on the formulation reactants). When one of these proposed structural parts could be present over a range of possible concentrations, an increment level was chosen to control how many places to attempt solution for this structure. Each of the assumed structures was then fully defined to the computer program to show how many of each element and how many of each functional group and/or substructure were present.

The program can now be operated. It will print all the valid combinations of the assumed structures which are found to fit within every analytical limitation specified.

## RESULTS AND DISCUSSION

For this program to provide valid results, it was necessary to account for all of the probable substructures which might result when Nadic methyl anhydride, D.E.N. 438, and DMP-30 were mixed in the various ratios (including a mixture containing no anhydride). These several substructures were based on our knowledge of epoxy-anhydride and neat epoxy polymers which are catalyzed by tertiary amines. An effort was made to include all of the major substructures which might result when these ingredients were mixed and cured together. A hypothetical polymer structure of D.E.N. 438 epoxy-novolac which was cured to 200°C with





Where:

**Substructure**

**Nevelac nucleus**

**1, 2, 3 - Propanetriyl**

**Diester of NMA**

**2 - Hydroxy - 1, 3 - Propanediyl**

**Monoester of NMA**

**Ether**

**Unreacted 2, 3 - epoxy propyl**

**3 - Chloro - 2 - oxypropyl**

**3 - Chloro - 1, 2 - propanediyl**

**Enclosed By**

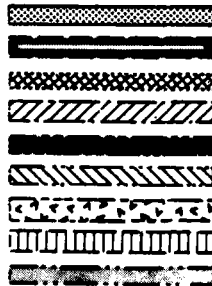


Fig. 1. Possible substructures of polymers using D.E.N. 438 cured with NMA.

NMA is given in Fig. 1. Two substructures, unreacted NMA and DMP-30 catalyst, were not shown because of space limitations in the figure. This structure is not meant to show what a cured epoxy-novolac resin looks like. It is merely a convenient way of presenting all of the substructures in a reacted form.

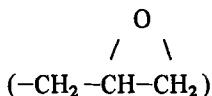
After the cured polymer structure was divided into substructures which we felt accounted for all of the major linkages of atoms, it was then necessary to establish concentration ranges for these substructures. As mentioned earlier, unreacted anhydride, monoester† of NMA, and unreacted epoxide were determined by functional group analysis. Diester† of NMA was determined by difference using the following equation (concentrations in equivalents):

$$\text{diester} = [(\text{original} - \text{unreacted})\text{anhydride}] - [\text{monoester}]$$

Since this equation was based on the fact that no anhydride was lost during cure, a check of the weight loss was made by weighing a batch of formulation before and after cure. The weight loss was < 0.3%.

In addition to the groups whose concentration ranges were determined by functional group analysis, there were other substructures present in these resins. The concentration ranges of these substructures were estimated by calculations based on the amounts of reactants formulated into the polymers in combination with functional group analyses. In certain instances, since known amounts of these substructures were present, they could be represented by single values of weight percentile concentration. How some of the substructures were derived and their limits determined is given in the following:

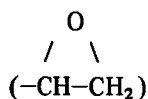
**Unreacted 2,3-epoxy propyl.** The concentration of the unreacted 2,3-epoxy propyl substructure



was determined by measuring the unreacted epoxide

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†Monoester and diester of Nadic methyl acid.



and prorating the results to include a methylene group ( $-\text{CH}_2-$ ).

**1,2,3-Propanetriyl.** The 1,2,3-propanetriyl substructure came from the glycidyl ether portion of the D.E.N. 438 epoxy-novolac molecule. Since the percent epoxide in D.E.N. 438 and the percent D.E.N. 438 in the cured formulations were known, it was possible to calculate the original amounts of 1,2,3-propanetriyl in the polymers. The amounts of this substructure that were tied up in unreacted 2,3-epoxy propyl and in 2-hydroxy-1,3-propanediyl were subtracted from the total 1,2,3-propanetriyl contents to determine the amounts of 1,2,3-propanetriyl in the cured formulations.

**Ether.** To determine dialkyl ether concentration in the catalytically cured polymer using D.E.N. 438 epoxy-novolac, an equation was devised which accounted for all of the original epoxide in the formulation. In this polymer, original epoxy may remain unreacted. It may also react with active  $\text{H}^+$ -containing structures such as water and phenolic OH. The resulting products, however, are glycols and phenyl alkyl ethers, respectively, and not dialkyl ether. The only other possibility is for the epoxy groups to undergo homopolymerization, and this results in dialkyl ether formation. The equation for determining dialkyl ether concentration in catalytically cured resins is as follows (concentrations in equivalents):

$$\begin{aligned} \text{ether} = & [(\text{original} - \text{unreacted})\text{epoxy}] \\ & - [\text{active } \text{H}^+ \text{ from } \text{H}_2\text{O} \text{ and } \text{C}_6\text{H}_5\text{-OH}] \end{aligned}$$

It is felt that this equation more accurately accounts for original epoxide concentration than does the one previously reported [2].

An equation was also devised for calculating dialkyl ether concentration in anhydride-cured epoxy-novolac polymers. Again, an effort was made to account for the possible reactions which the epoxide might undergo. As in the catalytically cured polymer, some of the epoxide may remain unreacted or it may homopolymerize to form ethers. Also, since NMA is present in these formulations, the epoxide may react with anhydride to form either mono- or diesters. In addition, the epoxide may react with

active  $H^+$ -containing structures to form 2-hydroxy-1,3-propanediyl. The extent of this reaction is measured by the increase in concentration of this substructure in the cured polymer over that in D.E.N. 438 epoxy-novolac. It was assumed that the difference in total OH and phenolic OH concentrations in D.E.N. 438 was aliphatic OH, and that it was in the form of 2-hydroxy-1,3-propanediyl. The equation for determining dialkyl ether concentration in anhydride-cured epoxy resins is given below (concentrations in equivalents):

$$\text{ether} = [(\text{original} - \text{unreacted})\text{epoxy}] - [\text{diester}] - [\text{monoester}] \\ - [(\text{final} - \text{original})2\text{-hydroxy-1,3-propanediyl}]$$

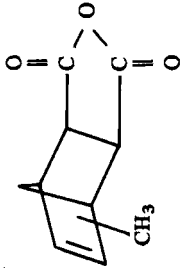
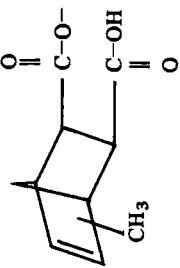
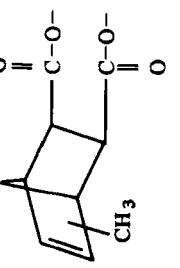
For the formulations characterized in this study the expression for active  $H^+$  reacting with epoxides was equal to zero since a great majority of the active  $H^+$  went to monoester formation. In cases where the initial aliphatic hydroxyl concentration in the resin is considerably lower than that found in our lot of resin (0.91%), it might be possible to form more aliphatic hydroxyls than were initially present. Even if this were true, the expression would probably be negligible. This equation is slightly different from those reported previously [2, 3]. Overall results would be affected so little, however, that no new ones were calculated.

**2-Hydroxy-1,3-propanediyl.** The 2-hydroxy-1,3-propanediyl and monoester of NMA concentrations were dependent upon the equivalents of active hydrogen present in the starting materials. The equivalents of active hydrogen necessary to account for the monoester present in the cured polymer were subtracted from the total active hydrogen. The remaining active hydrogen, if any, went to form 2-hydroxy-1,3-propanediyl.

**Novolac Nucleus.** It was assumed that the backbone of the D.E.N. 438 was composed entirely of novolac chains, excluding the attached 2,3-epoxy propyl groups. This assumption is not entirely correct because there are small amounts of aliphatic and phenolic hydroxyls and aliphatic and hydrolyzable chlorides present.

**3-Chloro-1,2-propanediyl and 3-chloro-2-oxypropyl.** The concentrations of these two substructures were determined by using the analyses for hydrolyzable and total chlorides in D.E.N. 438. It was proposed that any chlorohydrin which was present reacted with Nadic methyl anhydride,

Table 1. Concentration Limits of Substructures in Polymers Using D.E.N. 438 Cured with NMA

Substructure name	Structural formula	Limits, %, in cured polymer formulation				
		0.0 eq NMA	0.25 eq NMA	0.65 eq NMA	0.85 eq NMA	1.05 eq NMA
Unreacted NMA		- (-) <sup>a</sup>	0.00 (0.00)	0.00-0.14 (0.07)	1.16-1.33 (1.24)	4.09-4.42 (4.42)
Monocster of NMA		- (-)	5.31-6.84 (6.34)	6.84-8.25 (7.31)	6.65-8.54 (7.60)	9.20-10.28 (9.56)
Diester of NMA		- (-)	14.83-16.32 (15.97)	34.30-35.69 (35.34)	39.72-41.80 (40.76)	40.40-41.81 (40.75)

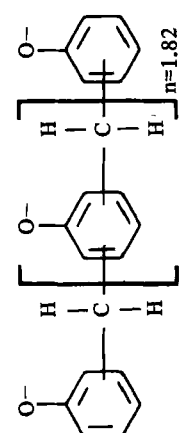
Unreacted 2,3-epoxy propyl	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ -\text{CH}_2-\text{CH}-\text{CH}_2 \end{array}$	1.06-2.00 (1.53)	0.66-1.99 (1.55)	4.58-7.16 (5.87)	3.18-5.30 (3.89)	3.18-4.50 (3.84)
1,2,3-Propane- triyyl	$\begin{array}{c}   \\ -\text{CH}_2-\text{CH}-\text{CH}_2- \end{array}$	21.00-22.28 (21.11)	17.68-19.67 (17.68)	10.11-12.21 (10.20)	9.86-11.56 (10.09)	9.26-10.21 (9.28)
Ether	$-\text{O}-$	7.89-9.00 (7.89)	4.43-5.60 (5.60)	0.10-1.04 (1.04)	0.45-1.46 (0.70)	0 (0)
2-Hydroxy-1,3- propanediyl	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_2- \\   \\ \text{OH} \end{array}$	3.40-4.20 (4.04)	0.38-1.83 (0.38)	0.00-0.40 (0.20)	0.00-0.26 (0.13)	0 (0)
Novolac nucleus		63.15 (63.15)	50.67 (50.67)	38.60 (38.60)	34.37 (34.37)	31.05 (31.05)
3-Chloro-1,2- propanediyl	$\begin{array}{c}   \\ -\text{CH}_2-\text{CH}-\text{CH}_2-\text{Cl} \end{array}$	- (-)	0.10 (0.10)	0.08 (0.08)	0.07 (0.07)	0.06 (0.06)

Table 1. (Continued)

Substructure name	Structural formula	Limits, %, in cured polymer formulation				
		0.0 eq NMA	0.25 eq NMA	0.65 eq NMA	0.85 eq NMA	1.05 eq NMA
3-Chloro-2-oxopropyl	$\begin{array}{c}   \\ \text{O} \\   \\ -\text{CH}_2-\text{CH}-\text{CH}_2-\text{Cl} \end{array}$	0.80 (0.80)	0.52 (0.52)	0.39 (0.39)	0.35 (0.35)	0.32 (0.32)
DMP-30		1.48 (1.48)	1.19 (1.19)	0.90 (0.90)	0.80 (0.80)	0.72 (0.72)
TOTAL %		98.78-102.91 (100.00)	92.33-108.00 (100.00)	95.90-104.86 (100.00)	96.61-105.84 (100.00)	98.28-103.37 (100.00)

<sup>a</sup>Values for "Best Polymer Compositions" are given in parentheses.

forming 3-chloro-1,2-propanediyl. It was assumed that the difference in total and hydrolyzable chlorides was aliphatic chloride and was tied up in a substructure such as 3-chloro-2-oxypropyl.

The substructure names, their formulas, and their concentration ranges in the various polymers prepared for this study are given in Table 1.

During the initial attempts at computer correlation it was necessary to broaden the analytical limits so that an inspection of the calculated output could be made. With the analytical limits broadened, each formulation had many combinations of substructures which met the constraints of the program. This allowed us to choose formulations with analyses close to those that had been measured. Two of the formulations, the catalytically cured D.E.N. 438 polymer and the polymer cured with 0.25 anhydride equivalent per epoxide equivalent, did not fall completely inside every measured analysis (see carbon analyses in Table 2). However, they are very close and it is felt that further refinement of minute substructure components would bring them into range. The formulations cured with 0.65, 0.85, and 1.05 anhydride equivalents per epoxide equivalent met every constraint.

The single "best polymer composition" for each of the cured formulations was chosen on the basis of its respective functional group analyses for unreacted anhydride, unreacted epoxide, and monoester, in the polymers containing NMA, and for unreacted epoxide in the catalytically cured polymer (no anhydride). A composition was "best" if its theoretical values for unreacted anhydride, unreacted epoxide, etc., all fell very close to the average concentration values of the respective functional groups, as determined by analysis. Since the above analyses were determined chemically, it was decided that the selection of the final polymer structure should be influenced to a greater degree by these substructures than by the substructures based only on calculations. In the case of the three formulations which met all constraints, the composition chosen had to have theoretical elemental analyses within the elemental limits established by analysis. For the other two formulations the theoretical elemental analyses and functional group analyses fell as closely as possible to the experimental values. The substructure values of the "best polymer composition" for each of the formulations are given in Table 1 in parentheses directly below the corresponding analytical range for the substructure.

### The Chemical Structure of Cured Polymers

By observing the "best polymer compositions" in Table 1, one can see that unreacted NMA concentration increases as the anhydride to epoxide



Table 2. Comparison of Elemental Analyses of Cured Formulations and Best Polymer Compositions

Element, wt %	Anhydride-epoxide equivalent ratio				
	0.0 eq NMA	0.25 eq NMA	0.65 eq NMA	0.85 eq NMA	1.05 eq NMA
Carbon					
Calculated <sup>a</sup>	73.43	71.78	70.62	70.10	69.92
Found <sup>b</sup>	73.00-73.40	71.32-71.72	70.24-70.64	69.80-70.20	69.53-69.93
Hydrogen					
Calculated	6.46	6.20	6.07	6.02	6.02
Found	6.41-6.81	6.10-6.50	5.94-6.34	5.73-6.13	5.82-6.22
Oxygen					
Calculated	19.57	21.59	22.98	23.59	23.80
Found	19.45-19.85	21.55-21.95	22.89-23.29	23.58-23.98	23.79-24.19
Nitrogen <sup>c</sup>					
Calculated	0.24	0.19	0.14	0.13	0.11
Chlorine <sup>c</sup>					
Calculated	0.30	0.24	0.19	0.16	0.15

<sup>a</sup>The calculated values are the theoretical elemental values for the best polymer compositions.

<sup>b</sup>The found values are the elemental limits established by analysis. These values have been prorated so that the compositions total 100%.

<sup>c</sup>Theoretical values were used for the nitrogen and chlorine compositions.

equivalent ratio increases. Unreacted anhydride is present in significant amounts only in the polymers at 0.85 and 1.05 anhydride equivalent per epoxide equivalent. Essentially all of the anhydride added above 0.85 equivalent per epoxide remains unreacted in the polymer. The monoester content remains fairly constant at the 0.25, 0.65, and 0.85 equivalent levels of anhydride. There is a slight increase in monoester at the 1.05 anhydride equivalent level. The diester content increases and then levels off at approximately 41 wt % in the polymer. This indicates that additional anhydride will not appreciably increase the diester level above that noted at the 0.85 equivalent level. The residual 2,3-epoxy propyl concentration increases, shows a maximum at an anhydride level of 0.65 equivalent, and then falls off slightly. The concentration of the 1,2,3-propanetriyl group decreases, as would be expected since the concentration of D.E.N. 438 also falls off. Ether content decreases from approximately 8% in the polymer containing no anhydride to 0% in the polymer containing 1.05 anhydride equivalents per epoxide equivalent. In the polymer containing no anhydride, epoxy-epoxy polymerization is predominant, resulting in ether formation. In the polymer containing 1.05 anhydride equivalents per equivalent of epoxide, the major reaction is diester formation. In this same formulation, the 2-hydroxy-1,3-propanediyl concentration also decreases to 0%. In the polymers containing anhydride, the majority of the equivalents of active hydrogen react to form monoester groups, and not much is left to form the 2-hydroxy-1,3-propanediyl substructure. The concentration of novolac nucleus also decreases as the concentration of D.E.N. 438 in the formulation decreases. The concentrations of the two chlorine-containing compounds and DMP-30 were kept constant in the characterization and are of minor significance in the cured structure.

The good agreement between the theoretical elemental analyses of the "best polymer compositions," as determined by the computer, and the elemental analyses of the actual formulations, as determined by analyses, can be seen in Table 2. For the formulations cured with 0.65, 0.85, and 1.05 anhydride equivalents per epoxide equivalent, all of the "Calculated" values determined by the computer for carbon, hydrogen, and oxygen fell within the ranges of "Found" values determined by analysis for these same elements. Of the 15 comparisons made for C, H, and O in the five formulations, there were, however, two instances in which the "Calculated" values fell outside the ranges of the "Found" values. The catalytically cured resin (no anhydride) had a theoretical carbon analysis which fell slightly outside the concentration limits which were established by analysis. The carbon analysis of the "best polymer composition" was 73.43%,

whereas the concentration limits established by analysis for the cured formulation were 73.00-73.40%. In the polymer cured with 0.25 anhydride equivalent per epoxide equivalent, the theoretical carbon analysis (71.78%) was also outside of the analytical limits (71.32-71.72%) which were established by analysis. In the above cases the discrepancies are slight and perhaps meaningless. An explanation of the theoretical analyses falling outside of the experimental limits is that in these two formulations there is a very high percentage of D.E.N. 438 present, and the slightest amount of error in the substructures present in trace amounts in D.E.N. 438 may result in an error large enough to force any resulting computer analyses outside the experimental limits.

In summary, complete structural characterizations were achieved on a catalytically cured polymer of D.E.N. 438 and on a series of Nadic methyl anhydride-cured polymers of D.E.N. 438 catalyzed with a tertiary amine. These characterizations were made with the help of a computer program which correlated the concentrations of all substructures required of proposed polymeric configurations with the elemental analyses of the cured formulations.

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