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PREPARATION OF A CTBN-MODIFIED EPOXY RESIN

PDO 6989182, Final Report

W. E. Richardson, Project Leader

Project Team:
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O. A. Krueger
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Bendix Kansas City Division

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Prepared by C. H. Smith, D/814, under PDO 6989182

The chemistry of the various types of reactions possible between a carboxyl-terminated butadiene/acrylonitrile (CTBN) liquid copolymer and a diglycidyl ether of bisphenol A (DGEBA) type epoxy resin to prepare a CTBN/DGEBA adduct is discussed. Both a dilution and a non-dilution synthesis technique are described. Several properties of the CTBN precursor and the modified epoxy resin were determined and are presented.

THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

A prime contractor for the
Atomic Energy Commission
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SUMMARY

In order to provide the capability to supply production quantities of a 10-percent carboxyl-terminated butadiene/acrylonitrile copolymer (CTBN)/epoxy resin adduct for electronic assembly manufacture, an investigation of the reaction parameters for preparing the material was performed. Analyses of the CTBN precursor are listed and both a dilution and a non-dilution synthesis technique giving identical end-product properties are described. Scale-up of the product to pilot plant quantities was successful. Characterization of the adduct was performed and the results are given. This work demonstrated the production feasibility of the material.

DISCUSSION

SCOPE AND PURPOSE

This project was undertaken to investigate the synthesis parameters for producing a modified epoxy resin used for the encapsulation of electronic assemblies. The adduct is formed by reaction of a carboxyl-terminated butadiene/acrylonitrile (CTBN) liquid copolymer with epoxy resins of the diglycidyl ether of bisphenol A (DGEBA) type. Studies were performed in laboratory glassware and then scaled up to pilot plant quantities. The material provides a more crack-resistant encapsulating resin than the system currently used in the production. The synthesis procedure developed and described will allow Bendix Kansas City Division to manufacture and supply the 10-percent CTBN/epoxy resin adduct for production use.

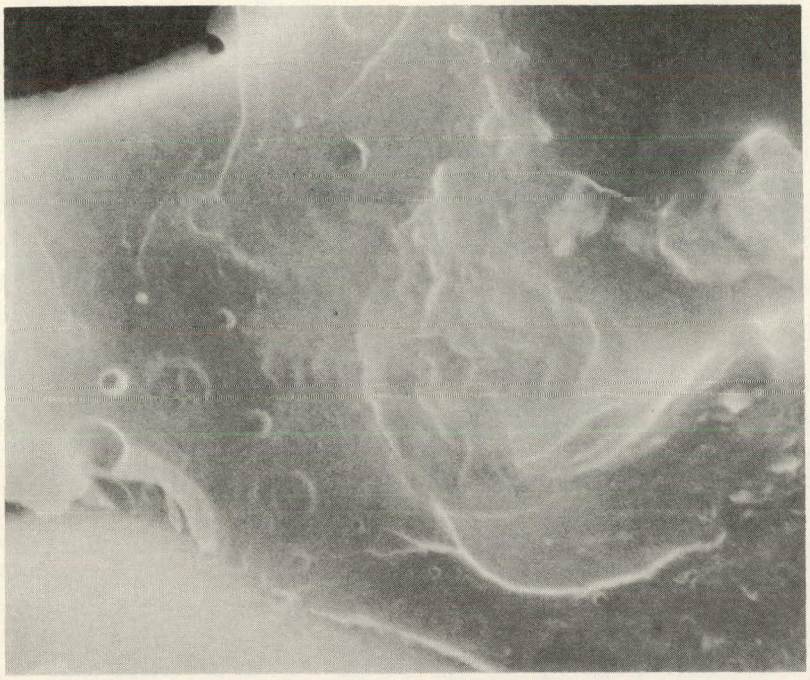
ACTIVITY

CTBN/Epoxy Resin Reactions

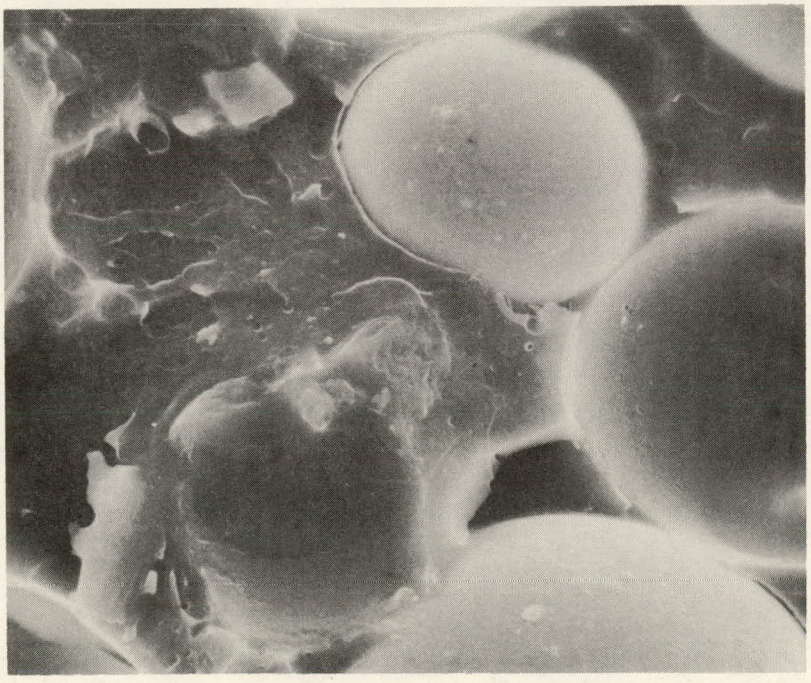
It was discovered by McGarry and his coworkers that by adding a carboxyl-terminated butadiene/acrylonitrile (CTBN) liquid copolymer to a brittle thermosetting material a more crack- and shock-resistant product is obtained.[1-4] The addition of this material to epoxy resins of the diglycidyl ether of bisphenol A (DGEBA) type (e.g., Shell Epon 828) produces a two-phase system which tends to increase impact strength by means of a crazing mechanism. This two-phase system, consisting of a brittle matrix and rubber microgels ranging usually from 0.1 μm to 1.0 μm in size, has the ability to craze as opposed to the catastrophic cracking and failure of the pure matrix material when subjected to high stresses or impact loadings.[5,6] Photomicrographs of these rubber-like microgels at 1000X and 3000X appear in Figure 1.

The use of such a system can be considered in relation to the encapsulation of electronic components. One of the prime contributors to the failure of potted electrical units during thermal cycle testing is stress cracking at vital locations within the matrix. The incorporation of such a "toughening agent" to the potting resin system alleviates such cracking and, consequently, improves the chances for successful encapsulation.

From a chemical viewpoint, this phenomenon appears to exist expecially when there is a possibility for the formation of a chemical bond at the rubber-matrix interface. This bond can be easily facilitated if the liquid rubber possesses reactive terminal sites such as carboxyl groups; the labile carboxyl groups



1000X

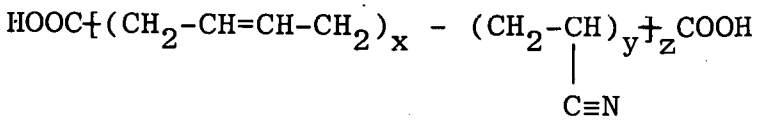


3000X

Figure 1. Photomicrographs of Rubber-Like Microgels Found in Cured 10-Percent CTBN/Epoxy Resin Adduct

are free to react with the functional groups of the epoxy matrix system.

Hycar CTBN-1300X8 was the carboxyl-terminated liquid copolymer of butadiene and acrylonitrile used in this investigation. This material is supplied commercially by B. F. Goodrich Chemical Company, Cleveland, Ohio and may be represented structurally, for most purposes, as shown below:



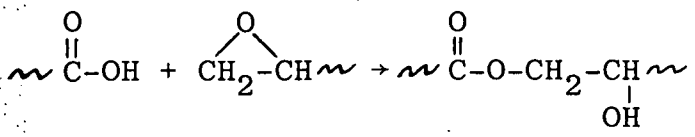
(1)

where, averaged, x=5, y=1, and z=10.

Hycar CTBN may be thought of as a dicarboxylic acid in regard to its reaction chemistry. It follows the crosslinking and chain extension reactions for carboxylic elastomers as compiled and illustrated in Brown's 1963 critical review.[7] Additional information, provided by the Bendix Materials Evaluation Department, which serves to characterize Hycar CTBN is given in Table 1, and a typical gel permeation chromatography curve of the material is shown in Figure 2.

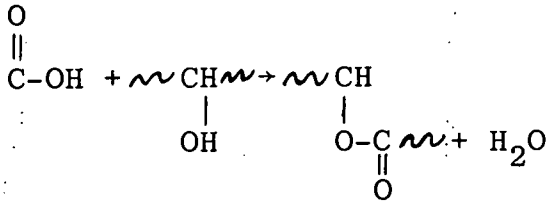
Apparently, the only sites on the CTBN molecule that can react with epoxy resins are the terminal carboxyl groups.[8] However, there are three reactions that can occur between carboxyl-containing polymers and epoxy resins of the DGEBA type. These reactions are given below.

Esterification, epoxy-acid reaction:



(2)

Esterification, acid-aliphatic hydroxyl reaction:



(3)

Table 1. Typical Hycar CTBN-1300X8 Properties

Property	Lot Number						Vendor Data	Specification Limits*
	34-3-B	34-3-L	10-123	34-3-K	10-150	10-141		
Brookfield Viscosity at 27°C (Pa•s)	130.0	126.0	130.0	114.0	120.0	140.0	115.0 ±10.0	120.0 ±25.0
Carboxyl Content (equivalents per hundred grams)	0.055	0.059	0.056	0.059	0.059	0.057	0.053	0.055 ±0.006
Bound Acrylonitrile Content (percent)	15.84	18.06	16.68	18.44	17.99	16.49	18-19	18.2 ±2.0
Volatile Content (percent)	0.055	0.97	0.056	1.06	0.059	0.057	---	2.0 maximum
Dry Ash (percent)	0.16	---	0.08	---	0.19	0.18	---	---

*Per Bendix Material Specification 2140645.

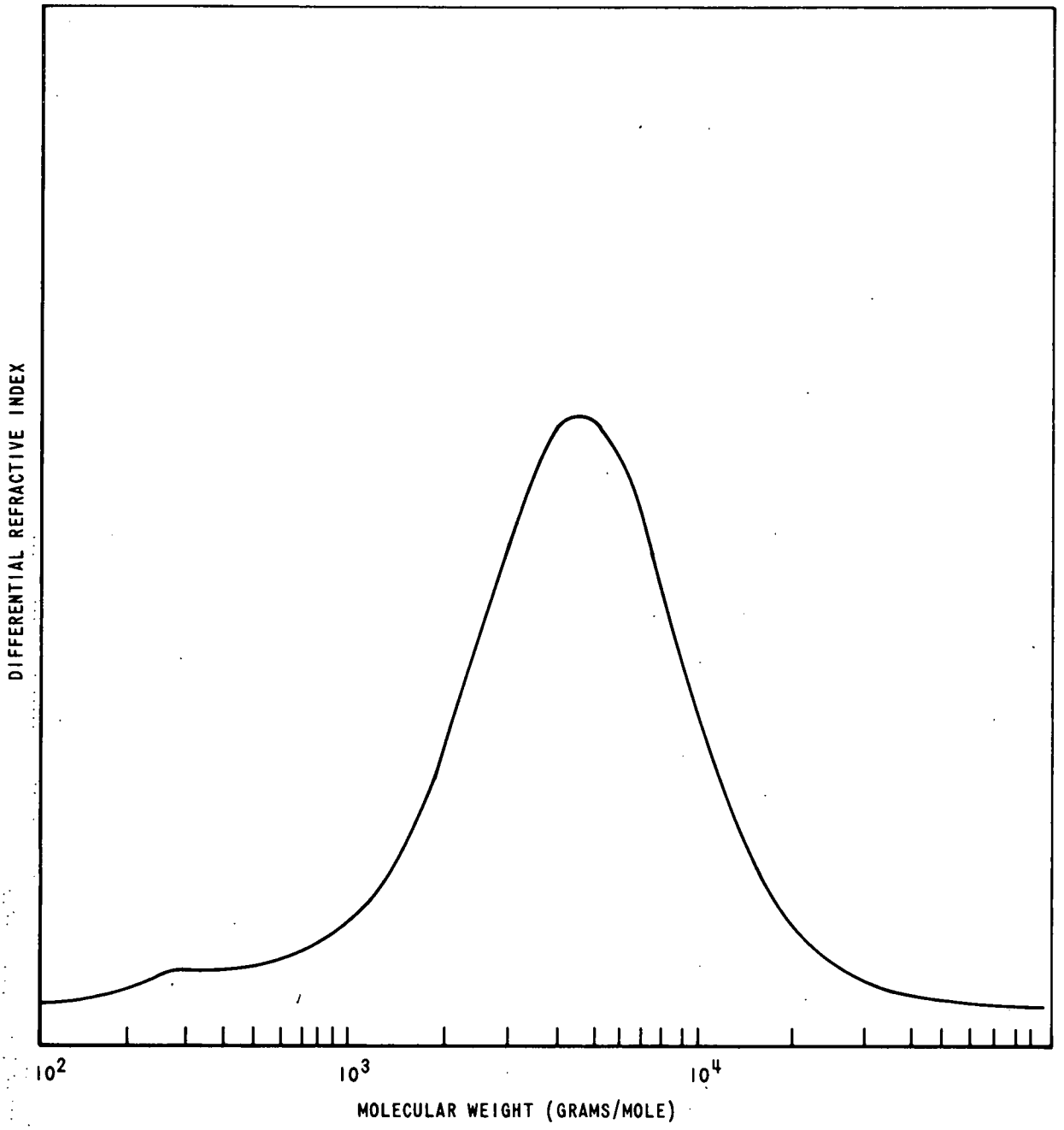
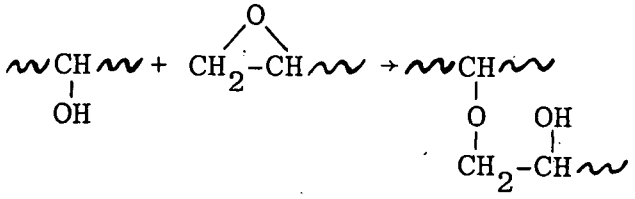


Figure 2. Gel Permeation Chromatograph Curve of Carboxyl-Terminated Butadiene/Acrylonitrile Copolymer (CTBN)

Etherification, epoxy-aliphatic hydroxyl reaction:



(4)

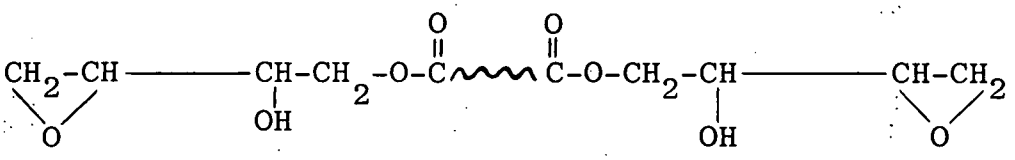
Reaction 2 (esterification) and Reaction 4 (etherification) are the important reactions. Reaction 3 may take place, but it does so to a much lesser extent. When approximately equal molar amounts of carboxyl and epoxy groups are used, Reaction 2 may be looked at as a chain extension reaction (that is, a building up of molecular weight by reaction of the carboxyl and epoxy groups). Shecther and Wynstra[9] and Alvey[10] showed with model compounds that when the reaction is base catalyzed (tertiary amine), Reaction 2 proceeds until all of the acid is consumed.

Reaction 4 may be looked upon as a crosslinking reaction. In this reaction, the remaining epoxy groups react with the pendant hydroxyl groups formed in Reaction 2 to crosslink the chain extended molecules. Reaction 4 is also the basic curing reaction of an epoxy resin with itself.

Higher molecular weight amines such as tributyl amine will promote Reaction 2 but not Reaction 4. Thus, when CTBN is reacted with an approximately equal molar amount of epoxy resin, a high molecular weight, non-crosslinked rubber is obtained.

These reactions deal with a rubber-rich system (i.e., approximately equal molar amounts of carboxyl and epoxy groups). However, the case in point is a resin rich system. In this type of system, there is a large excess of epoxy groups. Using, for example, a reaction condition having about 100 epoxy groups per carboxyl group, it is statistically unlikely that any significant build-up of molecular weight by Reaction 2 (esterification) would occur. What would be formed is probably an epoxy-terminated rubber with the following structure.

Epoxy terminated rubber:



(5)

DGEBA CTBN DGEBA

These reactions tend to indicate that a true solution is formed in the reaction between CTBN and epoxy resin rather than a two-phase system. The question now is how to rationalize chemically the formation of a two-phase system. Apparently, the phase separation is related to some critical structure or molecular weight of the epoxy matrix. In a previous reported study, using an epoxy resin (100 grams), CTBN (10 grams), and piperidine (5 grams) system having a pot-life of approximately two hours, precipitated particles were found after about sixty minutes.[5] This same work indicated phase separation is dependent upon the acrylonitrile content of the CTBN. The lower the acrylonitrile content, the larger the particle size.

The phase separation is, therefore, attributed to the chemical reaction and solubility relationship of the liquid rubber and the epoxy resin prior to gelation. There is no apparent growth of the particles during cure. Study of the composition of the particles by infrared analysis shows them to be very similar in structure to the epoxy-terminated rubber (as shown in Reaction 5); however, some of the material probably remains in solution with the matrix and may have influence on the toughening properties. Certain curing catalysts affect the phase separation, and different catalysts should give different structure to the rubbery phase.

Experimental Work

A method reported in the literature for synthesizing the crack-resistant CTBN/epoxy resin system employed an amine catalyst at the time of initial mixing. This not only ensured complete esterification, but also created the two-phase system for precipitation of the rubber-like microgels.[5]

For this study, it was desirable to have an adduct-type material that could be catalyzed, by an amine curing agent, at a later time. Prior work by Furney indicated that a usable adduct could be prepared by reacting 20 pbw CTBN with 80 pbw Epon 828 for approximately 3-1/2 hours at 150°C.[11] This adduct is then diluted with an additional 100 pwb of Epon 828. The resulting mixture is combined with filler and catalyzed with either diethanolamine or Shell Curing Agent Z. This produces a finished product having impact and shock resistant capabilities very similar to the "one-shot" CTBN/epoxy-resin/amine-catalyst system described in the literature.

Initially, the CTBN/epoxy reaction was carried out in a four liter resin reactor fitted with a thermometer, an air-driven stirrer, a nitrogen inlet tube, and a heating mantle. It was observed that the CTBN was insoluble in the epoxy resin at room temperature and formed a two-phase system with the CTBN on the epoxy surface.

It appeared that homogeneity was not achieved until the mix had attained a temperature of 71°C. To alleviate this condition, the two precursors were both heated to 71°C prior to reaction. Given below is a brief summary of the primary procedure used to prepare laboratory batches of the 10 percent CTBN/epoxy resin adduct.

Dilution Technique for Synthesis of 10-Percent CTBN/Epoxy Resin Adduct

A. Heat 1200 grams of Epon 828 to 71°C.

B. Heat 300 grams of CTBN to 71°C.

C. Blend the two heated materials together and heat the mixture to 150°C ±5°C. Hold the materials at this temperature for 3-1/2 hours with constant stirring and a dry nitrogen purge.

D. Cool the reaction mixture to 71°C and dilute with 1500 grams of Epon 828.

E. Homogenize this blend for one hour at a temperature of 71°C under a dry nitrogen purge.

F. Cool the mixture to room temperature and transfer to a storage container. Store in a sealed container under a dry nitrogen blanket.

Reaction rates for preparation of the 10-percent CTBN-epoxy resin adduct as a function of temperature was assessed by Creed.[12] He measured the disappearance of carboxyl groups at 71, 93, 120, and 150°C using a potentiometric method. Although he found that some reaction did occur at 71°C, it was necessary to maintain temperatures above 120°C in order to complete the process within a reasonable length of time. On that basis, the reaction conditions of 3-1/2 hours at 150°C were selected for this work.

An alternate method for preparing the CTBN/epoxy adduct was also investigated. It consisted of initially mixing the CTBN with the epoxy resin in a 1:9 ratio, thereby eliminating the dilution step as required in the previous method. The procedure used for this method is given below.

Non-Dilution Technique for Synthesis of 10-Percent CTBN/Epoxy Resin Adduct

A. Heat 2700 grams of Epon 828 to 71°C.

B. Heat 300 grams of CTBN to 71°C.

C. Blend the two heated materials together and heat the mixture to 150 ±5°C. Hold the materials at this temperature for 3-1/2 hours with constant stirring under a dry nitrogen purge.

D. Cool the reaction mixture to room temperature and transfer to a storage container. Store in a sealed container under a dry nitrogen blanket.

The above procedure is readily accomplished and certainly more expeditious than the dilution technique. The analytical results comparing the end-products from the dilution and non-dilution techniques exhibit no significant differences in properties as shown in Table 2. In addition, gel permeation chromatograph curves of the product made from both procedures (Figure 3) indicate that the two materials are very similar. Consequently, it was deemed feasible that, to expedite the synthesis of the 10-percent CTBN/epoxy resin adduct, the non-dilution method was appropriate.

Table 2. Analysis of Laboratory Batches of 10-Percent CTBN/Epoxy Resin Adduct

Sample Designation	CTBN Lot Number	Viscosity at 27°C (Pa•s)	Carboxyl Content (percent)	CN Content (percent)
100173 (1)*	10-150	30.1	0	1.69
90473 (1)	34-3-B	26.1	0	1.32
82773 (1)	34-3-B	27.2	0	1.12
82073 (1)	10-150	26.8	0	1.50
92873 (2)	10-150	27.7	0	1.40
92773 (2)	34-3-B	28.0	0	1.13
92673 (2)	10-141	28.5	0	1.25

*1. Dilution technique.
2. Non-dilution technique.

Scale-up of the 10-percent CTBN/epoxy resin adduct procedure to pilot plant quantities (70 kg) was included in the objectives of this investigation. Both the dilution and non-dilution techniques were evaluated and again no differences in end-product properties were observed. Test results for these pilot plant batches are given in Table 3.

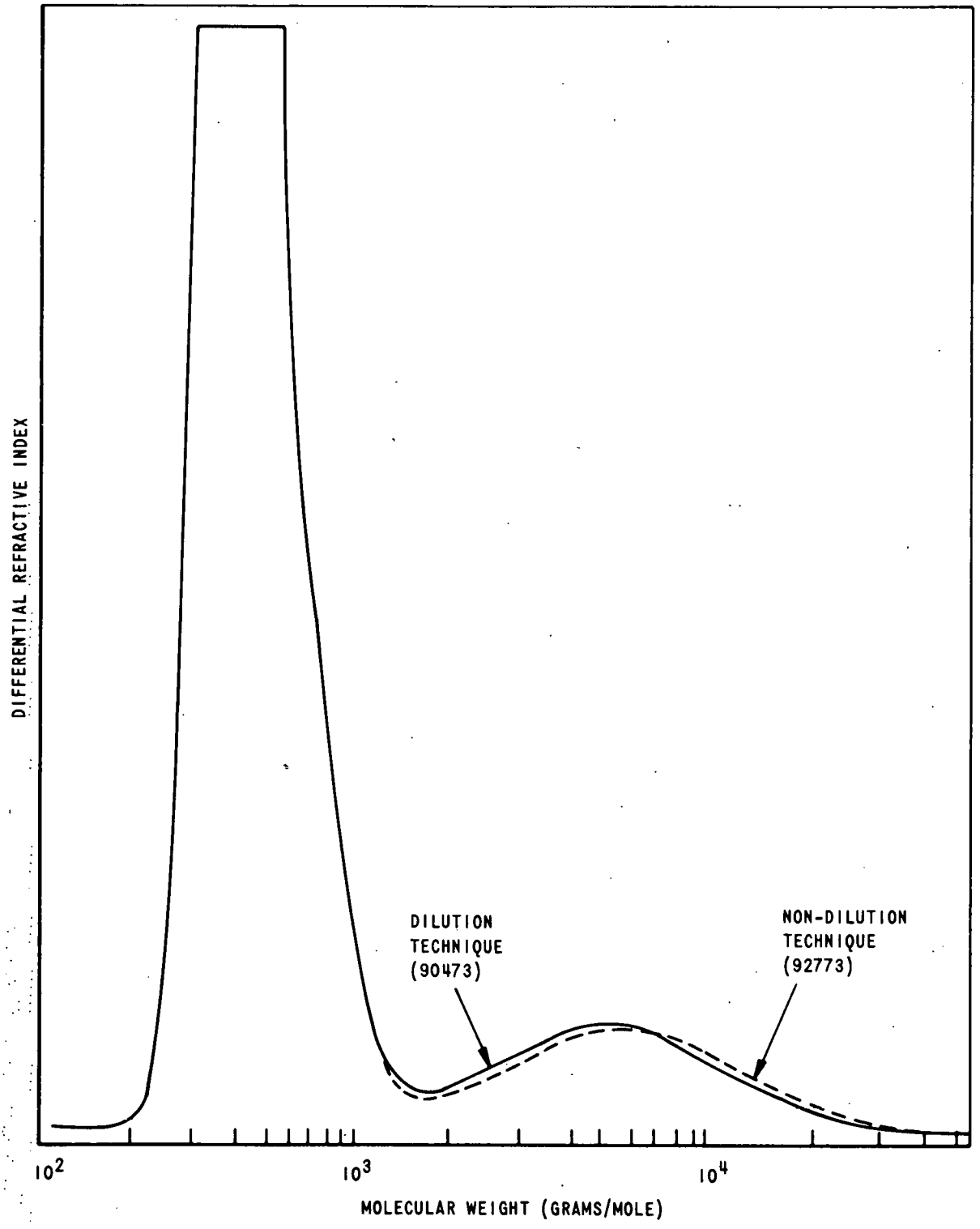


Figure 3. Gel Permeation Chromatograph Curves of 10-Percent CTBN/ Epoxy Resin Adduct

Table 3. Analysis of Pilot Plant Batches of 10-Percent CTBN/Epoxy Resin Adduct

Sample Designation	CTBN Lot Number	Viscosity at 27°C (Pa•s)	Carboxyl Content (percent)	CN Content (percent)
731127 (1)*	34-3-L	25.0	0	1.67
731129 (2)	34-3-L	26.0	0	1.93
731101 (1)	34-3-K	29.0	0	2.03

*1. Dilution technique.
2. Non-dilution technique.

ACCOMPLISHMENTS

It is evident from the literature that the CTBN/epoxy resin reaction is rather complex and that several competing reactions occur simultaneously during the preparation of the adduct. However, under controlled reaction conditions as described in this report, a reproducible end-product can be achieved using both a dilution and non-dilution technique.

It was demonstrated that the reaction could be scaled-up to provide 70-kilogram quantities of the adduct per batch having properties identical to the laboratory product.

FUTURE WORK

Although limited evaluation of the adducts was performed throughout the course of this investigation to assure formation of the phase separation step providing microgels, additional investigation of the adducts prepared for this work in specific casting resin formulations will be conducted on PDO 6984803. Thermal, physical, and electrical data will be obtained on these resin formulations, and, in addition, processing characteristics of the materials will be evaluated.

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[11] Deleted.

[12]K. E. Creed, Laboratory Report Number ME 73-06, General Electric, Neutron Devices Department, St. Petersburg, Florida, June 20, 1973.

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