Crosslinked Epoxies

Crosslinked Epoxies

Proceedings of the
9th Discussion Conference
Prague, Czechoslovakia, July 14 – 17, 1986

Editors
Blahoslav Sedláček · Jaroslav Kahovec

W DE G

Walter de Gruyter · Berlin · New York 1987

Editors
Blahoslav Sedláček, PhD., DSc.
Jaroslav Kahovec, PhD.
Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
Heyrovský sq. 2
CS-162 06 Prague 616
Czechoslovakia

Library of Congress Cataloging in Publication Data

Crosslinked epoxies.
Bibliography: p.
Includes indexes.
1. Epoxy resins--Congresses. I. Sedláček, B. (Blahoslav)
TP1180.E6C76 1987 668.4'226 87-8838
ISBN 0-89925-401-2 (U.S.)

CIP-Kurztitelaufnahme der Deutschen Bibliothek

Crosslinked epoxies : Prague, Czechoslovakia, July 14–17, 1986 / ed. Blahoslav Sedláček. - Berlin ; New York : de Gruyter, 1987. - (Proceedings of the ... discussion conference / Institute of Macromolecular Chemistry ; 9)
ISBN 3-11-010824-0
NE: Sedláček, Blahoslav [Hrsg.]; Ústav Makromolekulární Chemie <Praha>: Proceedings of the ...

 Printing: Gerike GmbH, Berl Binding: Dieter Mikolai, Berlin. - Printed in Germany.

DEDICATED TO PROFESSOR MANFRED GORDON
ON THE OCCASION OF HIS 70TH BIRTHDAY

PREFACE

Crosslinked epoxies are modern epoxy materials (resins and composites), highly suitable for a variety of applications, which are frequently used in extreme conditions. This is a short, insufficient characterization of the materials and processes discussed at the 9th Discussion Conference as part of the 1986 Prague Meetings on Macromolecules. The Conference was organized by the Institute of Macromolecular Chemistry, Prague (V. Kubánek, Director, and P. Čefelín, PMM Chairman) under the sponsorship of IUPAC, the Czechoslovak Academy of Sciences and the Czechoslovak Chemical Society. The scientific programme of the Conference was prepared by K. Dušek (Chairman) and the following members: E.M. Pierce, I. Havlíček, J. Hrouz, M. Ilavský, J. Kolařík, L. Matějka, and M. Raab.

This volume consists of 55 papers based on special lectures and selected posters presented at the Conference. Its scope was delimited by 11 Conference topics, including nearly all the modern aspects of the synthesis, mechanism and kinetics of curing, network formation, chemical and physical properties and their changes, characterization of processes (diffusion, curing, ageing, mobility in resins, etc.), and application of epoxy resins and composites.

All the accepted papers have been divided up into five chapters, the titles of which characterize the scope of each chapter: 1. New Epoxy Resins and Curing Systems; 2. Mechanism and Kinetics of Curing Reactions; 3. Network Build-up in Curing; 4. Structure and Properties of Resins - Curing, Ageing and Phase Separation; 5. Material Properties and Applications of Cured Resins and Composites.

The individual papers vary in conception and aim: Some of them are theoretical, others experimental or applied; there are original papers and survey articles; there are also evaluations of scientific methods, instrumentation and economic aspects in some papers. In spite of the complex character of numerous papers, the division into chapters, used together with the Contents, Author Index and Subject Index, should allow the reader to find easily a required paper.

I would like to express my warm thanks to all the authors who contributed to this volume for their efficient cooperation, permament effort and mutual understanding.

When working together with the de Gruyter Publishers I always appreciate very much their careful and precise work. My sincere thanks.

Prague, January 1987

Blahoslav Sedláček
PMM Editor

Contents

New Epoxy Resins and Curing Systems

Mechanism and Kinetics of Curing Reactions

NETWORK BUILD-UP IN CURING

STRUCTURE AND PROPERTIES OF RESINS - CURING, AGEING AND PHASE SEPARATION

Materials Properties and Applications of Cured Resins and Composites

New Epoxy Resins and Curing Systems

EPOXY/EPISULFIDE RESINS

J. P. Bell and W. H. Ku

Chemical Engineering Department and Polymer Science Program, U-139, University of Connecticut, Storrs, CT 06268, USA

Abstract

Mixtures of epoxy and episulfide resins have been formulated to provide stable liquids at room temperature. When mixed with a polyamide curing agent, these resin mixtures gel rapidly, in 2-10 minutes at room temperature, with a very low amount of heat evolved. The product has two glass transition regions, by dynamic mechanical analysis, lower water absorption, and other attractive properties. The mechanism of reaction was studied via a series of episulfide, epoxide and secondary amine model compounds. The kinetics of the various steps were also examined, and the rate constants determined. The reaction proceeds by 1) the normal epoxy-amine reaction, 2) anionic attack of the rather stable sulfide ion on episulfide groups and epoxide groups. The kinetic data predict two primary structures, consistent with the experimental observations.

Introduction

Episulfide resins appear similar in structure to standard epoxy resins, such as the diglycidyl ether of bisphenol A(DGEBA), but with the oxirane oxygen atoms replaced with sulfur. The change of the epoxy oxygens to sulfur has a number of important consequences: 1) the curing reaction with amines proceeds much more rapidly at relatively low temperature (1), 2) the tendency of the episulfide to crystallize is significantly higher than the corresponding DGEBA resin from which it was synthesized (2,3), 3) the properties of these episulfide resins appear better than or comparable to those of their epoxy analogs (3,4). The episulfide resins have no odor, and physically appear much like their DGEBA cousins except for some improved properties which we shall discuss below.

Although reported in both literature and patents in the 1960's, episulfides have received little attention since that time. This may be attributed, at least in part, to the difficulties in handling a crystalline solid which melts at 92^{o}C, and yet cures in a few minutes at room temperature. Difficulties in synthesizing and purifying the episulfide from the corresponding epoxide were also a deterrent, but a simple, inexpensive synthesis route via thiourea has been demonstrated. This and related synthesis routes are described elsewhere (2, 4-11).

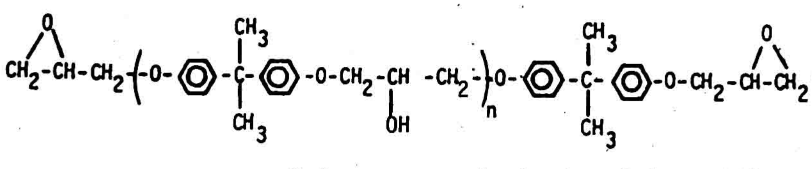
Recently Ku and Bell (1) have described a method of formulating the episulfide into an episulfide/epoxy blend of wider than usual molecular weight distribution. This has the effect of inhibiting crystallization, such that the mixture may be used as a liquid which can be readily mixed with a liquid curing agent. Further improvements in the formulation have been described by Fernandez (4) within the last few months. The purpose of the present report is primarily to discuss the mechanism of curing, which is not the same for the episulfides as for normal epoxies. Some property data are given.

Experimental

Materials

The following materials were used for the development of a rapid curing epoxy-episulfide system and for the measurement of the reaction kinetics of this new system. The reagents described below are available from manufacturers in the U.S.A.

Epon 828 (conventional DGEBA resin from Shell Chemical Co.).



n = 0.2; gram equivalent weight = 189