Klaus Kircher

Chemical Reactions in Plastics Processing

HANSER
PUBLISHERS

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With 44 Figures and 51 Tables

Hanser Publishers, Munich Vienna New York

Distributed in the United States of America by
Macmillan Publishing Company, New York
and in Canada by
Collier Macmillan Canada, Inc., Ontario

English edition of
"Chemische Reaktionen bei der Kunststoffverarbeitung"
by Dr. Klaus Kircher

Translated by Dr. Carla B. Grot, Chadds Ford, PA 19317, U.S.A.

Distributed in USA by
Scientific and Technical Books
Macmillan Publishing Company
866 Third Avenue, New York, N.Y. 10022

Distributed in Canada by
Collier Macmillan Canada, Inc.
1200 Eglington Ave. E, Suite 200, Don Mills, Ontario M3C 3N1 Canada

Distributed in all other countries by
Carl Hanser Verlag
Kolbergerstrasse 22
D-8000 München 80

CIP-Kurztitelaufnahme der Deutschen Bibliothek

Kircher, Klaus:
Chemical reactions in plastics processing / Klaus
Kircher. [Transl. by Carla B. Grot]. - Munich ;
Vienna ; New York : Hanser ; New York : Macmillan, 1987.
Dt. Ausg. u. d. T.: Kircher, Klaus: Chemische
Reaktionen bei der Kunststoffverarbeitung
ISBN 3-446-14279-7 (Hanser)
ISBN 0-02-947520-1 (Macmillan)

ISBN 0-02-947520-1 Macmillan Publishing Company, New York
Library of Congress Catalog Card Number 86-602089

Printed in the Federal Republic of Germany

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Preface

A polymer of high molecular weight is the most commonly used raw material for manufacturing molded articles and semifinished goods. The polymer is heated, molded while still in the melt, and subsequently cooled. This molding process is strictly a physical process; chemical reactions are not considered.

Approximately 10% (by weight) of the molded articles and semifinished goods produced in the polymer processing plant undergo a chemical synthesis during processing; the processor does not start with a finished polymer of high molecular weight but manufactures the polymer during the molding process. Thus, the polymer processor performs the task of a chemist. Other methods which employ polymers in the manufacture of molded articles and semifinished goods start with high molecular weight intermediates, but the molecular weight is increased even further during the molding process, and this alters the properties of the original material. Cross-linking is one of these methods. An additional 14% of all molded articles and semifinished goods are produced by these methods. Altogether, one-fourth of all processing methods employ a chemical reaction. Even during the molding of thermoplastics it is possible for a chemical reaction to occur, for instance, an undesirable decomposition which may lead to end products of diminished quality. The processor must be aware of these undesired chemical reactions.

This book discusses every polymer processing method in which a chemical reaction is an important part of the process. I have relied to a great extent on the following books and publications and have quoted freely from the original texts.

- *Menges, G.* Werkstoffkunde der Kunststoffe, Carl Hanser Verlag, München, 1979
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  - Bd. I: Grundlagen, Aufbau, Verarbeitung und Prüfung der Kunststoffe
  - Bd. II: Polyvinylchlorid
  - Bd. III: Abgewandelte Naturstoffe
  - Bd. IV: Polyolefine
  - Bd. V: Polystyrol
  - Bd. VI: Polyamide
  - Bd. VII: Polyurethane (also available in English version: *Oertel*, Polyurethane Handbook)
  - Bd. VIII: Polyester, gesättigte Polyester, ungesättigte Polyester, Polycarbonate
  - Bd. IX: Polymethacrylate
  - Bd. X: Duroplaste
  - Bd. XI: Polyacetale, Epoxidharze, fluorhaltige Polymerisate, Silikone usw.
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This book has been written during my employment with the Institut für Kunststoffverarbeitung (IKV) in Industrie und Handwerk an der Rheinisch-Westfälischen Technischen Hochschule, Aachen.

It describes parts of IKV’s newest research results in the area of UP resin processing, of UP resin processing, synthesis of PUR foam articles, and cross-linking of polyethylene. I am deeply grateful to my many colleagues at IKV; Dr. E. Roth, Dr. B. Franzkoch, Dr. H. Schwesig, and Dr. A. Behmer. Part of this research has been funded by Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF) and Deutschen Forschungsgemeinschaft (DFG).

Finally I would like to express my sincere gratitude to Professor Dr. Ing. G. Menges, director at IKV, for encouraging me to start this book and his advice and assistance which allowed me to write it.

Spring 1987

Dr. Klaus Kircher

Contents

1 Chemical Reactions in the Polymer Processing Plant

In manufacturing parts and semifinished shapes from synthetic polymers, one usually melts a powdery or granular raw material; the melt is then shaped and subsequently cooled. During this process the synthetic polymer supplied by the chemical manufacturer is transformed into a different physical state; it is then returned to its original physical state by cooling. In the ideal case, such a shaping process is strictly a physical process which is not accompanied by a chemical reaction. But if one looks at all possible processes for the manufacturing of parts and semifinished shapes from synthetic polymers, including both synthetic macromolecular polymers and elastomers, one will find quite a few processes in which the polymer processor determines the chemical structure of the end product simultaneously with the molding process. The products which were used by the polymer processor and the end product differ in their chemical structure. The product which is supplied by the chemical manufacturer undergoes a chemical reaction in connection with the molding process. The manufacturing processes, which are characterized not only by physical change but also by targeted chemical reactions, can be divided into two groups:

(a) Manufacturing processes which, starting with a low molecular weight monomer, synthesize a polymer during the molding process.

(b) Manufacturing processes in which a high molecular weight compound is transformed into a new compound by molecular enlargement through chemical reactions. The high molecular weight compounds used in these processes may themselves be useful plastic materials, for instance, polyethylene. Through chemical reactions a new polymer with certain targeted properties is being produced.

Polymer processing includes, therefore, part of the polymer synthesis. The distinction between polymer producers and polymer processors is not clear-cut; the transition is rather vague. In many cases the processor completes the polymer synthesis which was started by the raw material producer. He therefore takes over tasks which according to popular belief belong to the chemist. Chemical reactions in the polymer processing plant are not limited to synthesis alone. Other chemical reactions also play a more or less important role. These chemical reactions sometimes occur during the manufacturing of parts and semifinished shapes; sometimes they are part of other production steps.

A chemical reaction which frequently occurs (although to a small extent) is molecular degradation. In a few cases this molecular degradation is desired; in most cases it is an unwanted side reaction which sometimes presents processing problems and at other times has detrimental effects on the properties of the end product. The processor has to minimize or eliminate these chemical reactions by optimizing the processing parameters. Molecular degradation is possible not only during the shaping process but also during storage and use of the parts. Even if these reactions do not occur in the processing plant, the polymer processor is still sometimes able, in a few cases (for instance, in the case of polyvinyl chloride) to influence the extent and outcome of subsequent reactions through the use of a suitable additive.

Chemical reactions also occur during surface treatment and during the joining of parts and semifinished shapes. Two-component adhesives, for instance, represent reactive components or component mixtures which will become a high molecular weight compound during the joining process. Sometimes, two-component adhesives are used which are very similar in their principal chemical structure to the reactive resins which are used in the manufacturing of molded parts.

Sometimes surface enhancement of the plastic parts includes several chemical reactions. Frequently this step is preceded by preparation of the surface. For instance, oxidation of the polymer during this treatment will produce polar structures and partial oxidation will roughen the surface. For surface coating one uses lacquers, which are partially reactive systems. Sometimes these reactive lacquer systems show similarities to thermosets which are used for manufacturing of the parts.

Table 1 Chemical reactions in the realm of the polymer processor

Intended chemical reactions during the processing period	- Synthesis of the polymer out of low molecular weight components - Polymer synthesis by modification of high molecular weight components - Degradation of exceedingly high molecular weight polymers (for ex.: mastication of natural rubber) - Surface modification and coating - Joining by reactive adhesives
Unwanted chemical reactions in the form of side reactions during the processing period	- Decomposition, depolymerization of the molecule - Oxidation
Chemical reactions which occur outside of the processing plant but which are still controllable by the processor through the use of additives	- Decomposition (caused by exposure to energy; remedy: addition of stabilizers) - Oxidation on exposure to weathering or fire (remedy: employment of oxidation inhibitors and fire retardant substances)

Polymer processing is a technical process during which very dissimilar chemical reactions can occur. The present text is limited to those reactions which occur during the manufacturing process of parts and semifinished shapes; chemical reactions which occur during the joining and enhancing process will not be discussed.

2 Polymers Produced by the Plastics Processor - An Overview

Table 2 contains a summary of synthetic polymers which are produced in the processing plant during the manufacturing of parts and semifinished shapes by synthesis of macromolecular products. The variety of polymers produced by the processor include many dissimilar products which cannot be identified with a special group of substances. There are several ways of classifying these polymers:

- Economic importance of the polymer
- Physical properties (thermoplastics - thermosets)
- Molecular weights of the original components
- Type of chemical reaction used in the synthesis

Synthetic polymers which are produced through chemical reactions include polymers that differ greatly in their importance. For instance, the cross-linking of elastomers of all types in terms of volume is a very important reaction. The synthesis of polyurethanes (PUR) one of the most widely produced types of polymer and one which is almost exclusively synthesized by the polymer processor) is also a very important chemical reaction in the plastics processing plant. To a large extent, therefore, the large number of plastics processors and not the chemical companies are the producers of polyurethanes.

Table 2 Polymers produced in the polymer processing plant

Synthesis of the polymer from low molecular weight components	Synthesis of the polymer from high molecular weight intermediates by chemical modification (increase in the size of molecule)
non cross-linked polymers: - Polyamide-6 - PMMA - Polycarbodiimide **cross-linked polymers:** - UP resins (cured) - Polydiallyl esters - specialty plastics of high heat distortion temperature - Phenoplasts - Aminoplasts - PUR - Polyisocyanurate - Epoxy resins (cured)	- Cross-linked thermoplasts (especially PE, PP, ethylene-vinyl acetate copolymers) - Elastomers (cross-linking of (ethylene-like) unsaturated natural rubbers, polyethylene sulfochloride, polychloroprene, polyurethane-elastomers, fluoroelastomers, polyisobutylene)

Some polymers which are produced in very small quantities are also made by molding processes which are accompanied by chemical reactions. For instance, polymers with high heat distortion temperatures are manufactured in such small amounts that they are omitted from production or manufacturing output tables. Similarly the polydiallyl esters are specialties which are theoretically very interesting but whose production output is of little importance. The plastics processor produces uncross-linked thermoplastic polymers as well as cross-linked elastic, or thermosetting molding materials.

Polyamide-6 and PMMA are thermoplastic materials which are produced by the manufacturer through reaction casting only in connection with the manufacturing of parts or semifinished shapes. Both polymers are also processed by injection molding and extrusion and the processor obtains the finished materials from the producer of raw materials.

Molded parts and semifinished goods made from polyamide-6 and PMMA can, therefore, be manufactured by means of two fundamentally different processes, each of which offers certain advantages. Thermoplastic processing of a preprocessed polymer can present difficulties for the production of very bulky objects made from these materials. On the other hand, reaction casting can be used to manufacture objects of any size. Parts made from PMMA are usually of higher quality (if the casting process is used), especially in respect to surface finish. It is a disadvantage that the reaction casting processes are difficult to run automatically and are therefore more labor intensive. Reaction casting processes have a distinct advantage over the process that uses finished polymers; they are controllable. In each step the polymer processor theoretically is able to change the composition of the mixture and consequently, up to a certain point, vary the properties of the polymer. This allows the processor to be independent of the variety of polymers that are offered by the chemical companies. It is believed that the processor also produces other thermoplastic polymers by reaction casting. Only a few chemical syntheses are performed in the processing plant, because of the difficulty in handling many of the polymer precursors and additives which are necessary for synthesis.

Processes which yield crosslinked polymers are being used much more than reaction casting processes for thermoplastic polymers. Reaction casting processes which manufacture thermoplastic polymers are in competition with other manufacturing processes; but parts and semifinished goods from cross-linked polymers can be manufactured only by reaction casting. Cross-linked polymers cannot be shaped plastically, and therefore the plastic shaping has to be done in a chemical state which allows molding; this means it is done in the prepolymer state or before the polymer is cross-linked.

Manufacturing parts from cross-linked polymers requires a chemical reaction. The cross-linked polymer can be either formed from low molecular weight reagents or produced from a plastic or thermoplastic polymer by starting new chemical bonds between various chain molecules. Sometimes, very low molecular weight reagents are used for the production of cross-linked polymers in the mold.

In the production of epoxy resins, for example, by hardening of cycloaliphatic resin, components with very low molecular weights are used. Similarly, in the hardening of unsaturated polyester (UP) resins, diallyl phthalate resins and pheno- and aminoplasts use resin components which have low or medium molecular weights. Only through a chemical reaction will they form a polymer; usually the molecular weights of the polyester components in UP resins are not higher than 4000. The same is true for the polyols in the resin which is used for the production of polyurethane.

In addition to cross-linked polymers which have been produced from low to medium molecular weight compounds, other polymers are available which are produced by cross-linking high molecular weight compounds. In a few cases these high molecular weight components are already technically useful polymers which are only modified by the cross-linking, for example, polyethylene. In other cases (like rubber), the high molecular weight starting material is not useful as a polymer for all practical purposes. Only the cross-linking process converts it into a polymer (e.g. rubber). The cross-linking reaction of only a few chain segments of the high molecular weight compound alters the properties of the rubber substantially.

Synthesis of polymers in the polymer processing plant is not limited to a specific variation of a chemical process. All three major methods of synthesis of macromolecules (polymerization, polycondensation, and polyaddition) are also used in the processing plant. In this text the different processing procedures are organized according to the chemical reactions which occur during synthesis. This makes it possible to summarize common characteristics.

3 Importance of the Polymer Synthesis in the Polymer Processing Plant

Up to 1920 practically every type of polymer processing involved a chemical reaction. Only with the development of the thermoplasts and the increasing perfection of the processing plant did the commercial importance of the reaction resins diminish. Today, a large portion of the polycondensates, so dominant in the earlier years, are used in processing applications which have little in common with polymer processing (treating of textiles, paper industry, paint and varnish industry, etc.); on the other hand, even today a considerable amount of the polymerizate is used by the fiber industry. Therefore, the data which are published in regard to production and consumption often do not report the true values for the polymer quantities processed in the processing plant. It is worth mentioning that polymer processing employs only a small portion of the phenoplasts, aminoplasts and epoxy resins; the bulk of it is used as laquers, glues and varnish and sizing material or as encapsulating compounds.

Table 3 lists the most important polymers whose final composition is only first synthesized by the processor; the same table shows the portion used by the processor in comparison to the total production. In contrast to polyurethane which is synthesized almost exclusively by the polymer processor, only one tenth of the urea and melamine resins are fabricated to cured objects.

Polymers modified by a chemical reaction, particularly cross-linked, have to be added to the list of plastics (which are) synthesized by the processor. Approximately 2 million tons of polymers are synthesized annually in polymer processing plants in Western Europe; but in addition to that approx. 3 millions of tons of elastomers (mainly in synthetic rubber factories) are produced by cross-linking of natural rubber. Therefore, the multitude of polymer processing plants represents a significant independant chemical industry.

Table 3 Polymers manufactured in the polymer processing plant by chemical reaction (not counting any specialty products) and their percentage of the total production respectively

Polymer	Percentage (by weight) of the total production carried out by the polymer processor.
Polyamide	trivial amounts
UP-resin, cured, without reinforcement	80
Polyurethane	95
Epoxy resins, cured	20
Phenolresins, cured	20
Urea and melamine resins, cured	10
Polyacrylate and methacrylate	40

Table 4 Organic material manufactured as modified by means of a reaction as percentage (by weight) of the total volume of organic polymer material

Type of material	Percentage in % by weight of the total volume	
Melt fabricable plastic	75	
Reaction molded plastic	10	25
Cross-linked plastic as rubber	15	

Table 4 shows the (percentage) break-down of the total amount of organic polymers: In approx. one fourth of the plastics (including elastomers) the characteristic properties are caused by chemical reactions designed by the processor. The processor is able to intervene in any phase of the reaction, be it by varying the ratio of the components or by altering the conditions of the reactions.

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