DEVELOPMENTS IN RUBBER TECHNOLOGY—3

Thermoplastic Rubbers

Edited by

A. WHELAN and K. S. LEE

London School of Polymer Technology
(*formerly National College of Rubber Technology*),
Holloway, London, UK

WITH 33 TABLES AND 89 ILLUSTRATIONS

© APPLIED SCIENCE PUBLISHERS LTD 1982

DEVELOPMENTS IN RUBBER TECHNOLOGY—3

Thermoplastic Rubbers

CONTENTS OF VOLUMES 1 and 2

Volume 1: Improving Product Performance

Volume 2: Synthetic Rubbers

PREFACE

Elastomers which are vulcanised after being shaped were covered in the two previous volumes of this series. This volume deals with the relatively new class of materials which has been given the label 'thermoplastic rubbers or elastomers'. This term has been taken to include blends of polymers as well as those homopolymers and copolymers which exhibit rubbery behaviour.

Despite the recent appearance of these polymers they are already making significant inroads into markets such as the automotive and adhesives industries. As the properties of these materials become known and appreciated new applications are being found in which these materials either replace traditional polymers or create new uses for polymers. Because of their usage the book will be of interest to both rubber and plastics technologists.

All the contributors to this volume were chosen because of their extensive experience in their subject area and we would like to express our thanks to them and to their companies for participating in this book. Grateful thanks are also tended to the Governors of the Polytechnic of North London for allowing us to act as editors and for providing the facilities without which this book could not have been produced.

<div align="right">

A.W.

K.S.L.

</div>

LIST OF CONTRIBUTORS

J. A. BRYDSON

London School of Polymer Technology, The Polytechnic of North London, Holloway, London N7 8DB, UK

D. J. ELLIOTT

Malaysian Rubber Producers' Research Association, Tun Abdul Razak Laboratory, Brickendonbury, Hertfordshire SG13 8NL, UK

G. W. GILBY

Imperial Chemicals Industries Limited, Petrochemicals and Plastics Division, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD, UK

D. J. HARROP

Elastogran UK Limited, Alfreton Trading Estate, Wimsey Way, Somercotes, Derby DE55 4NL, UK

I. R. LLOYD

Du Pont (UK) Limited, Polymer Products Department, Maylands Avenue, Hemel Hempstead, Hertfordshire HP2 7DP, UK

F. MISTRALI

Enoxy Chimica S.p.A., Assago, Milan, Italy

A. PRONI

Enoxy Chimica S.p.A., Assago, Milan, Italy

R. RANALLI

Montepolimeri S.p.A, SAP/POL/SVP, Largo Donegani 1/2, 20121 Milan, Italy

CONTENTS

Chapter 1

THERMOPLASTIC RUBBERS—AN INTRODUCTORY REVIEW

J. A. Brydson

London School of Polymer Technology,
The Polytechnic of North London, Holloway, London, UK

SUMMARY

In order to produce a thermoplastic rubber it is necessary to produce what is, in effect, a cross-linked molecular network over the proposed range of service temperatures but which breaks down reversibly at higher temperatures. Thus these materials have the characteristics of a rubber at service temperatures and of a thermoplastic material at processing temperatures.

Effective networks can be obtained in a variety of ways including ionic bonding, hydrogen bonding, crystallisation and by the use of block copolymers.

Block copolymers for thermoplastic rubbers contain 'soft blocks' and 'hard blocks'. The soft blocks, consisting of highly flexible chains, impart rubberiness whilst the hard blocks, which can be glassy or crystalline, provide the effective heat-fugitive cross-links. The principles and problems involved in producing such block copolymers involving such techniques as double bond polymerisation, condensation polymerisation, rearrangement polymerisation and mechanochemical reactions are discussed. The principles of methods, other than the use of block copolymers, for making thermoplastic rubbers are also briefly considered.

The chapter concludes with some general comments concerning the advantages, disadvantages and applications of thermoplastic rubbers.

1

1. INTRODUCTION

Since the Second World War, natural and synthetic rubbers have been replaced in many applications by thermoplastics. Areas in which there has been a substantial replacement include flooring, belting, shoe soling, protective sheeting and cable applications. In many of these applications the property of high elasticity, the primary characteristic of a rubbery material, was not a fundamental requirement for the application. In these cases, the basic requirement was met by a flexible material. In itself, the over-specification by the use of an elastic material does not of necessity lead to replacement of an elastic by a flexible material. For example, if the product made from rubber had been cheaper to produce and had met all the requirements of the product, then a change to a thermoplastics material would be unlikely.

Whilst general purpose rubbers such as natural rubber and styrene–butadiene rubber are amongst the cheaper polymers and even cheaper compounds may be made from them by use of oils and fillers, compared with thermoplastics they do possess one serious disadvantage. This is the requirement that after shaping, it is necessary to involve a chemical cross-linking process (vulcanisation) which consumes both time and energy. Furthermore, it is not possible to regenerate the original uncross-linked material from any scrap or rejected product. For this reason, the concept of a rubber which behaved as if it were cross-linked at room temperature but which flowed like a thermoplastics material at elevated temperatures is a very attractive one. Over the past 25 years a number of developments have occurred which have brought about the realisation of this concept. For reasons which will be explained later, this has not led to the general replacement of conventional vulcanised rubbers but rather has led to the creation of new markets.

2. THE HEAT-FUGITIVE CROSS-LINK

In a conventional rubber vulcanisate the flexible chains of the rubber molecule are highly cross-linked by covalent bonding, most commonly involving sulphur but not exclusively so. For a thermoplastic rubber, it is necessary for any cross-link that exists at ambient temperature to lose its identity when the material is heated so that the polymer molecules can behave just like the molecules of a molten thermoplastics material. There

are many ways by which this may be achieved of which the most important
are the following:

(i)   ionic cross-linking;
(ii) cross-linking by hydrogen bonding;
(iii) cross-linking by thermally unstable covalent bonds which reform
      on cooling;
(iv) linking of molecules via small crystalline structures;
(v)   the use of block copolymers.

2.1. Ionic Bonding

Ionically bonded polymers have been known for many years. Perhaps the
most well-known are the ionomers which were introduced by Du Pont in
the early 1960s. The commercial materials, marketed under the trade name
Surlyn, are copolymers primarily composed of ethylene molecules but with
a small amount of a second monomer which contains carboxylic acid
groups. When this material is blended with metal salts, ionic cross-links are
formed which are strong at normal room temperatures but which disappear
on heating.

2.2. Hydrogen Bonding

Similar effects can occur with hydrogen bonding. This probably occurs
with some types of polyurethane material, although these are masked by
other effects. There are also some grounds for believing that there is some
hydrogen bonding between PVC and plasticiser molecules such as tritolyl
phosphate, diisooctyl phthalate, and diisooctyl adipate. In these cases it
would seem that PVC molecules are to some extent linked together via
plasticiser molecules. The differences in the behaviour of the three types of
plasticiser in PVC can be explained in terms of the differences in hydrogen
bonding characteristics of the three plasticisers.

2.3. Reformable Bonds

During the manufacture of some polyurethane materials, it is believed that
allophanate groups are formed. Furthermore, these are believed to break
down on heating but reform on cooling. A more deliberate application of
thermally unstable bonds for cross-linking has recently been developed by
the Polysar Corporation who have introduced styrene–butadiene rubbers
to which tertiary-amino groups have been attached. When these are reacted
with a dihalide a cross-link involving a quaternary salt is produced. These
materials also break down on heating and reform on cooling. Rubbers of

this type cannot be considered as thermoplastic rubbers but they do have good green strength.

2.4. Crystalline Links

That polyethylene is a flexible thermoplastic rather than a rubber is due to the presence of crystal structures in the polymer mass. The greater the percentage of crystalline material, the harder and stiffer is the polymer. If, on the other hand, the level of crystallisation is reduced, for example by copolymerisation with a second monomer such as vinyl acetate, then the materials become almost rubber-like. It has also been found that if a crystalline polymer such as polypropylene is blended with an ethylene–propylene rubber a thermoplastic elastomer may be produced. The effective cross-linking here appears to be associated with the crystal structures that may be present.

2.5. Block Copolymers

The most spectacular results in the search for thermoplastic elastomers have, however, been achieved using block copolymers. With these materials, the polymer chains are split up into blocks or segments which have a very low glass transition temperature, i.e. well below room temperature, and into other blocks or segments which have got either a glass transition temperature or a crystalline melting point well above room temperature. Prominent amongst these polymers are the so-called SBS triblocks, the polyether–ester thermoplastic elastomers and some of the thermoplastic polyurethane rubbers. Some of the general principles involved with these materials will be discussed in the next section.

3.   BLOCK COPOLYMERS AS THERMOPLASTIC ELASTOMERS

3.1. Basic Requirements

For a block copolymer containing two basically different block types to show the behaviour of a thermoplastic elastomer, it is necessary for the two blocks to be sufficiently dissimilar for phase separation to occur with one phase being rich in one block and the second rich in the other. In practice, the compatibility between polymers is so low that such phase separation tends to occur even when the differences, as assessed for example by differences in cohesive energy density, are quite small. It is reasonable to

expect that the point in the chain where the blocks link together should, in the mass, be found at or near the interface between the two phases.

A second requirement is that one of the blocks be composed of a material with a T_g (and a T_m in the case of a crystallisable block) below ambient temperature or, more specifically, below the temperature range in which the material is to be used as a rubber. At the same time the other block should have a T_g, or a T_m in the case of a crystallisable block, well above the required service temperature range. These two blocks are often referred to, respectively, as 'soft segments' and 'hard segments'.

3.2 Tri-block Copolymers

Even where a polymer meets these requirements the block copolymer may not behave as a thermoplastic elastomer. One block copolymer that does is the SBS triblock copolymer with SBS ratios of 14:72:14. In this case the styrenic chain ends congregate into spherical (or perhaps cylindrical rod) domains embedded in a rubbery polybutadiene segment matrix (Fig. 1).

Since the polystyrene segments have a T_g of about 70–80 °C and the polybutadiene segment a T_g of about −100 °C, at room temperature the chains are in effect tied together or 'cross-linked' by the polystyrene domains. Since the domains have a diameter of about 300 Å they also act like reinforcing fillers. When the material in the mass is raised to above the T_g of the polystyrene block, the domains disappear and provided the
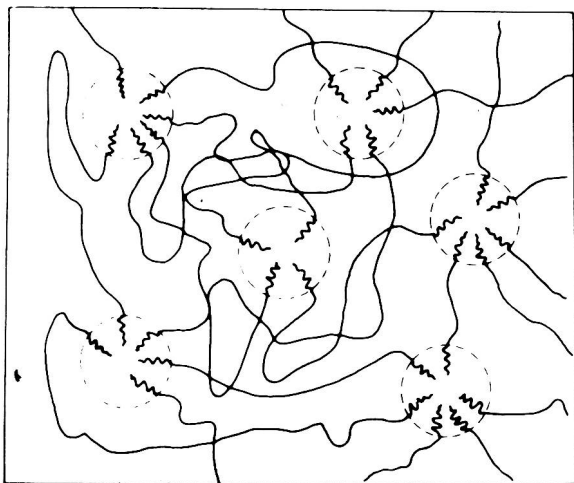

FIG. 1. Schematic representation of the polystyrene domain structure in styrene–butadiene–styrene triblock copolymers. (After Holden et al., 1969.[1])

molecular weight is not too great, the material flows like a conventional thermoplastics material. On cooling, the domains reform and the material behaves as a thermoplastic elastomer. Clearly, by using a monomer to give a block with a higher T_g than polystyrene, for example α-methyl styrene, the resistance to heat softening will be improved.

If, on the other hand, the polymer was of the BSB triblock type, it is not to be expected that a useful rubber would be obtained since the free polybutadiene ends would not be part of a network and hence not load-bearing at normal ambient temperatures. A simple SB diblock will also be unsuitable for similar reasons.

3.3. Multi-block Polymers

With some block copolymers there may be many more than the three blocks per chain possessed by the SBS triblocks. For example, with the polyether–ester thermoplastic elastomers there may be well over a dozen. In this case the nature of the terminal group is not so crucial since each chain will be expected to pass through a series of hard and soft zones. The morphological structure of spherical domains in an amorphous matrix is only one of several possibilities. For example, in ABA type triblock copolymers, a sequence of products may be envisaged as the proportion of A increases (Fig. 2). At low concentrations of A the A segments are to be found in spherical domains. As the proportion of A increases, the spheres are replaced by cylindrical rods and in turn these will be replaced by lamellae. As A becomes predominant, it becomes the continuous phase with B segments embedded either as rods or as spheres. To some extent a specific polymer may be driven from one form into another by blending

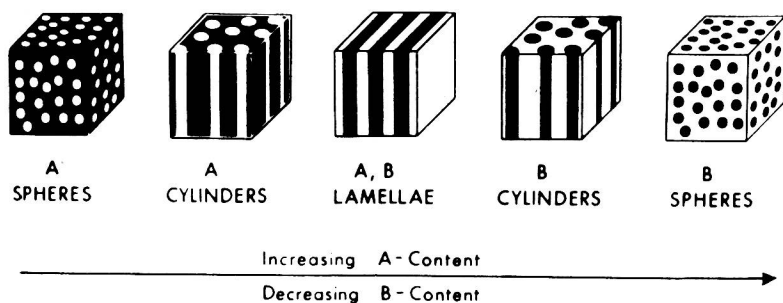| A | A | A, B | B | B |
| SPHERES | CYLINDERS | LAMELLAE | CYLINDERS | SPHERES |

Increasing   A - Content

→

Decreasing   B - Content

FIG. 2. Schematic representation of the dependence of block copolymer morphology on the volume fraction of the blocks. A and B denote the two chemical species forming the molecule without reference to a particular system. (From Molau, 1970.[2])

with, say, an oil compatible with the soft segment or a resin compatible with the hard segment.

The simple domain concept (be it spherical, rod-like or laminar) is unlikely to apply to block copolymers with several blocks per chain and here one can envisage complex morphologies with intermingling of phases.

4. BLOCK COPOLYMERS—PRINCIPLES OF MANUFACTURE

A wide range of possible approaches exists for the preparation of block copolymers using such techniques as double bond polymerisation, condensation polymerisation, rearrangement polymerisation and mechanochemical reactions.

4.1. Double Bond Polymerisation

Block copolymers may be made from unsaturated monomers by anionic polymerisation techniques. In the first stage the polymerisation of monomer A is initiated by the addition of an anionic initiator such as butyl lithium. One end of the chain consists of an active anion on to which additional monomers add to form a longer anionic chain. When all of the first monomer, A, has been consumed, the second monomer, B, is added to the reactor and molecules of B add on to the still reactive chain. When in turn, all of the B molecules have been consumed, additional monomer A is added. This technique is known as sequential anionic polymerisation (Fig. 3).
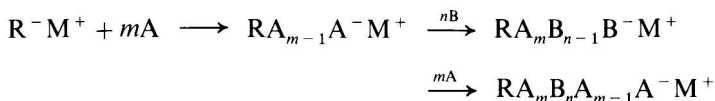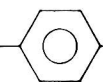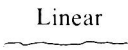
$$R^- M^+ + mA \longrightarrow RA_{m-1}A^- M^+ \xrightarrow{nB} RA_m B_{n-1} B^- M^+$$
$$\xrightarrow{mA} RA_m B_n A_{m-1} A^- M^+$$

FIG. 3.

By modifications of this technique, polymer growth may be stopped at the $A_m B_{n-1} B^- M^+$ stage. The living polymer that exists at this stage may then be coupled by difunctional coupling agents to give linear polymers, trifunctional agents to give T-shaped polymers, tetrafunctional agents to give X-shaped materials and with agents of higher functionality, star-shaped polymers will be produced (Table 1).

At the present time the most important block copolymers made by sequential anionic polymerisation are those of the SBS types. Also available are SIS triblock materials in which isoprene is used for the central

TABLE 1

EFFECT OF TYPE OF COUPLING AGENT ON SHAPE OF BLOCK COPOLYMER

Coupling agent	Functionality	Polymer shape
$ClCH_2$—⬡—CH_2Cl	2	Linear
PI_3	3	T-shaped
CH_3SiCl_3	3	T-shaped
$SiCl_4$	4	X-shaped
Divinyl benzene	7–14	Star-shaped

block instead of butadiene. Triblocks also exist in which the central polybutadiene chain has been hydrogenated. These materials have somewhat better ageing and weathering resistance. (It should be noted that as the butadiene units have joined together by both 1,4- and 1,2-addition the hydrogenated centre block has the structure of an ethylene–butene copolymer, hence the abbreviation SEBS which is used for these polymers.)

An alternative method of preparing block copolymers using unsaturated monomers is the technique of graft copolymerisation. A commercial example of this is the ET polymer at one time produced by Allied Chemicals. With these materials butyl rubber is grafted onto polyethylene chains using a phenolic material such as brominated hydroxymethyl