COATED TEXTILES

Principles and Applications

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Preface

COATED textiles applications are found in defense, transportation, healthcare, architecture, space, sports, environmental pollution control, and many other diverse end-product uses. I developed an insight into the breadth of the subject during my long association with the Defense Materials and Stores Research and Development Establishment (DMSRDE, Kanpur, India) while working on the development of protective clothing and related equipment. The opportunity to visit and work at several coating facilities has given me a feel for the complexity of the coated textile industry. The world production of coated fabrics used for defense alone every year is on the order of several billion dollars. Extensive research is being done on a global basis, and many new products, such as breathable fabrics, thermochromic fabrics, and charcoal fabrics, are entering the market. The subject is spread over a wide range of literature in polymer science and textile technology, with no single comprehensive book available. The motivation to write this book was to fill this void and to create a general awareness of the subject. This book is meant for scientists and technologists in academic institutions as well as in the coating and textile industry. The purpose of this book would be served if it could create additional interest in the coated textile industry and stimulate R&D activity to develop newer and better coated textile products.

A.K. Sen
Kanpur
2001

Acknowledgements

I had a long tenure with Defense Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, India, as a research scientist, which has recently ended. DMSRDE, Kanpur, is a premier research establishment under the Defense Research and Development Organization (DRDO), Government of India, and is primarily responsible for research and development in nonmetallic materials required for the defense forces. The scope of R&D activity of the establishment encompasses a wide range of scientific disciplines including polymers, composites, organometallics, lubricants, anticorrosion processes, biodegradation studies, textiles and clothing, tentage, and light engineering equipment. It is one of the best equipped laboratories with various sophisticated analytical instruments.

The Department of Science and Technology (DST), Government of India, granted me a project to write a book on "Coated Textiles and their Applications." I am grateful to DST for this opportunity. I am also grateful to Professor G. N. Mathur, Director, DMSRDE, for permitting me to continue as Emeritus Scientist and for providing me access to a library and other facilities. His encouragement and help have been a source of inspiration. I am particularly thankful to my colleague Mr. N. Kasturia who first suggested that I write a book on the subject and for the help rendered at different stages in writing the book. I am indebted to Drs. V. S. Tripathi, L. D. Kandpal, Messrs. Anil Agrawal, T. D. Verma, Dhannu Lal, Darshan Lal, R. Indushekhar, G. L. Kureel, Miss Subhalakshmi, and several other colleagues at DMSRDE for their spontaneous help, suggestions, and input on specialized subjects. I also wish to acknowledge useful discussions and literature provided by Mr. A. K. Mody, Entremonde Polycoaters, Mumbai; Mr. M. L. Bahrani, Southern Group of Industries, Chennai; Mr. A. Narain, Swastik Rubbers, Pune; Mr. M. K. Bardhan, Director, SASMIRA, Mumbai; Professor P. Bajaj, I.I.T., Delhi; and Professor A. Nishkam, Principal, GCTI, Kanpur. Above all, I am thankful for the encouragement, inspiration, and valuable suggestions given by my wife, Sutapa.

Introduction

THE use of coated textiles for protective clothing, shelters, covers, liquid containers, etc., dates back to antiquity. Historically, the earliest recorded use of a coated textile was by the natives of Central and South America, who applied latex to a fabric to render it waterproof. Other materials such as tar, rosin, and wax emulsions have been used over the years to prepare water-resistant fabrics. Due to their vastly superior properties, rubber and other polymeric materials have become the preferred coatings. Today, coated fabrics are essentially polymer-coated textiles. Advances in polymer and textile technologies have led to phenomenal growth in the application of coated fabrics for many diverse end uses. Coated fabrics find an important place among technical textiles and are one of the most important technological processes in modern industry.

Textiles are made impermeable to fluids by two processes, coating and laminating. Coating is the process of applying a viscous liquid (fluid) or formulated compound on a textile substrate. Lamination consists of bonding a preprepared polymer film or membrane with one or more textile substrates using adhesives, heat, or pressure. Fibrous materials are also used for reinforcing polymeric materials to form composites for use in tires, conveyor belts, hoses, etc. The scope of this book has been restricted to coated and laminated textiles and does not address polymer fiber composites.

Several methods of production are used to manufacture a wide range of coated or laminated fabrics. Broadly, they are spread coating, dip coating, melt coating, and lamination. They not only differ in the processing equipment used, but also in the form of polymeric materials used. Thus, paste or solutions are required for spread coating; solutions are required for dip coating; and solid polymers such as powders, granules, and films are required for melt coating and lamination. The basic stages involved in these processes include feeding the textile material from rolls under tension to a coating or laminating zone, passing the coated fabric through an oven to volatilize the solvents and cure/gel the coating, cooling the fabric, and subsequently winding it up into rolls.

The properties of a coated fabric depend on the type of polymer used and its formulation, the nature of the textile substrate, and the coating method employed. The subject of coated textiles is thus interdisciplinary, requiring knowledge of polymer science, textile technology, and chemical engineering. The organization of this book is based on these considerations.

Among the various polymers used for coating and laminating, three classes are mainly used for coating: rubber, polyvinyl chloride, and polyurethane. These polymeric materials are specifically formulated with additives and compounded into a paste suitable for coating. The production of a polymeric coating fluid is one of the most important functions of the coating industry. The chemistry of these polymers, the additives used, and their processing for coating compounds and fluids have been described in Chapter 1. Conventional solvent coatings are losing favor, as they lead to environmental pollution. Several alternative processes, such as the ecofriendly aqueous polyurethane and radiation-cured coatings, are included in this chapter. The various adhesive treatments for improved elastomer-textile bonding have also been discussed in Chapter 1.

For many years, cotton was the primary fabric used for coating; however, today's coating industry uses diverse substrates made of rayon, nylon, polyester, polyester-cotton blends, and glass fibers that may be produced in woven, knitted, or nonwoven constructions. The physical properties of a coated fabric are affected by the nature of the fiber and the construction of the textile substrate. The choice of the substrate depends on the application of the material. Chapter 2 discusses the different fibers and their conversion into textile materials of various constructions used in the coating industry. The coating methods employed by the industry are discussed in Chapter 3. Emphasis is placed primarily on the principles, rather than on the engineering aspects, of the machinery. Chapter 4 describes the changes that occur in the physical properties of a fabric when it is coated. A brief account of rheological factors affecting the coating has been presented in Chapter 5. Thus, the raw materials, the coating methods, and the properties of the end product are presented in chronological sequence.

The large, ever-increasing variety of applications of coated fabrics is covered in the three subsequent chapters. Protective clothing for foul weather is one of the major applications of coated fabrics. In the last two decades, particularly after the development of GORE-TEX® laminates, there has been an explosion of development in breathable fabrics. Chapter 6 discusses all types of coated fabrics for foul weather protection with special emphasis on the developments in the field of breathable fabrics. Coated textiles used in synthetic leather, upholstery fabrics, fabrics for fluid containers, backcoating of carpets, and architectural textiles are discussed in Chapter 7.

In various applications of coated fabrics, a functional material such as dye, pigment, or carbon is applied on the textile materials with polymeric binders. These fabrics are being used as camouflage nets, thermochromic fabrics, protective clothing for toxic chemicals, etc. This specialized category of coated fabrics is included in Chapter 8. Metal coatings are finding newer uses in EMI-RFI shielding and radar responsive fabrics. These fabrics are also discussed in this chapter.

The test methods pertaining to coated fabrics have been discussed in Chapter 9. The references are given at the end of each chapter. Properties of common polymers used for coating are separately provided in Appendix 1, and a few typical formulations are given in Appendix 2.

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CHAPTER 1

Polymeric Materials for Coating

1.1 RUBBER—NATURAL AND SYNTHETIC [1–4]

1.1.1 INTRODUCTION

IN ancient times, Mayan Indians waterproofed articles of clothing and footwear by applying (coating) gum from a tree (rubber tree) and drying it over smoke fires. Modern day history of coating rubber on fabrics dates to 1823, when the Scotsman Macintosh patented the first raincoat by sandwiching a layer of rubber between two layers of cloth [3].

Since then, there have been great advances in rubber-coated fabric technology. Coated fabrics are now used for diverse applications. Almost all types of rubbers are used for coating, but the discussion here will be restricted to the more popular kinds.

Rubber is a macromolecular material that is amorphous at room temperature and has a glass transition temperature, T_g, considerably below ambient. Raw rubber deforms in a plastic-like manner, because it does not have a rigid network structure. It can be cross-linked by vulcanization to form an elastomer with the unique ability to undergo large elastic deformations, that is, to stretch and return to its original shape. For natural and most synthetic rubbers, vulcanization is accomplished with sulfur.

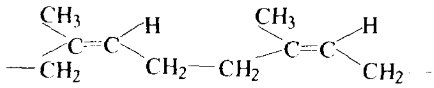
Elastomers that have stereoregular configuration and do not have bulky side groups or branching undergo crystallization. Crystallization cannot occur above melt transition, T_m. The rate of crystallization is greatest at about halfway between T_g and T_m. For natural rubber, for example, this is about $-25°C$. The crystallites embedded in the elastomeric matrix act as physical cross-links, like reinforcing fillers. Most importantly, crystallinity can be induced by stress. Formation of crystallites enhances the strength of the rubber.

Vulcanization lowers the crystallinity as three-dimensional networks create obstacles in segments entering the crystal lattice. Lower crystallinity is also observed in random copolymers.

1.1.2 PRODUCTION, STRUCTURE, AND PROPERTIES

1.1.2.1 Natural Rubber (NR)

NR is obtained from the exudation of the rubber plant, *Hevea brasiliensis*. The rubber is obtained from the latex by coagulation, sheeting, drying, and baling. There are various internationally recognized market grades, common among them are ribbed smoked sheets and pale crepe. Natural rubber contains about 90% rubber hydrocarbon as *cis*-1,4-polyisoprene along with naturally occurring resins, proteins, sugars, etc., that precipitate during latex coagulation. The average molecular weight of polyisoprene in natural rubber ranges from 200,000 to 500,000, with a relatively broad molecular weight distribution. As a result of its broad molecular weight distribution, NR has excellent processing behavior.

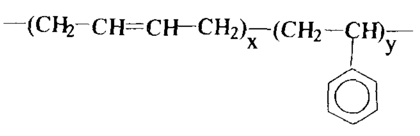


cis-1,4-Polyisoprene unit

The α-methylene group of the polyisoprene units is reactive for vulcanization with sulfur. NR vulcanizates combine a range of properties that are of great technological interest. The individual property can be improved by the use of synthetic rubber, but a combination of high tensile strength, resilience, dynamic properties, and good low temperature flexibility make NR indispensable for several applications. The high tensile strength and tear resistance of NR vulcanizates is due to strain crystallization. Being nonpolar, NR swells in nonpolar solvents. Reaction of the double bond in the polyisoprene unit with oxygen or ozone results in degradation of the polymer.

1.1.2.2 Styrene-Butadiene Rubber (SBR)

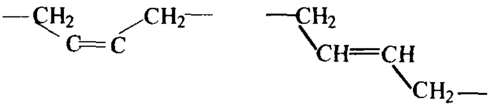
SBR is a copolymer of styrene and butadiene. The styrene content ranges from about 25 to 30 wt.%. The structure is given as



SBR

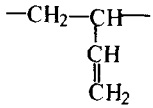
SBR is mainly prepared by emulsion polymerization, The monomers are randomly arranged in the chain, and the butadiene part is mainly in the *trans* configuration (~75%). Some 1,2-addition products are also formed. Depending on the temperature of polymerization, SBR may be classified into hot-polymerized and cold-polymerized grades. The hot grades are highly branched compared to the cold grades.

SBR can also be copolymerized in a solution process using alkyl lithium catalysts in a nonpolar solvent. These rubbers have much higher *cis*-1,4-butadiene content (50–55%), less chain branching, and narrower molecular weight distribution.



cis *trans*

1,4-Butadiene

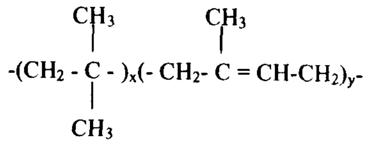


1,2-Addition product

SBR does not crystallize even on stretching their vulcanizates, therefore, pure gum strength is generally low. It has better heat and aging resistance than NR and is usually used in combination with NR and other rubbers.

1.1.2.3 Isoprene-Isobutylene Rubber, Butyl Rubber (IIR)

Butyl rubber is a copolymer of 97 to 99.5 mole % of isobutylene and 0.5 to 3 mole % isoprene. The isoprene unit provides the double bond required for sulfur vulcanization.



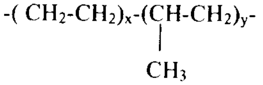
$$-(CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-)_x(-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2)_y-$$

IIR, Butyl rubber

It is produced by cationic polymerization in methylene chloride with $AlCl_3$ as catalyst, at subzero temperatures (−90°C to −100°C). The isobutylene monomer units polymerize mainly in head-to-tail arrangements, and the isoprene units in the polymer chains polymerize in *trans* 1,4-configuration. The molecular weight ranges between 300,000 to 500,000. On halogenation of IIR in an inert organic solvent, a rapid electrophilic substitution takes place, and one halogen atom is substituted per isoprene unit, mainly in the allylic position. Thus, a small number of halogen atoms are incorporated into the polymer chain. These are known as chlorobutyl rubber (CIIR) or bromobutyl rubber (BIIR) depending on the halogen substituted. The polymer chains are highly saturated and have a very regular structure due to the symmetrical nature of the monomer. As a result, butyl rubber exhibits very low gas permeability, ozone, heat, weathering, and chemical resistance. Butyl rubbers are self-reinforcing with a high gum tensile strength. The halobutyl rubbers cure faster than butyl rubber. Bromobutyl has much lower gas permeability and better resistance to aging, weathering, and heat than butyl rubber. Butyl and bromobutyl rubbers are especially used where low gas permeability is required.

1.1.2.4 Ethylene Propylene Polymers (EPM) and Terpolymers (EPDM)

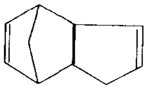
Copolymers of ethylene and propylene EPM are made by solution polymerization using vanadium containing alkyl aluminum, Ziegler-type catalyst. These are elastomers, but they do not contain any double bonds.



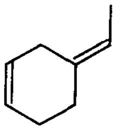
$$-(CH_2\text{-}CH_2)_x\text{-}(\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2)_y\text{-}$$

EPM

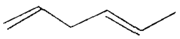
For good elastomeric properties, the ethylene propylene ratio ranges from 45–60 wt.%, and the monomers are arranged randomly. Consequently, these polymers are predominantly amorphous, and the pure gum strength is low. The molecular weight ranges between 200,000 to 300,000. Because EPM is saturated, the polymeric chain is cured by peroxides. The terpolymer EPDM contains, in addition to the olefin monomers, a nonconjugated diene as the third monomer, which renders EPDM able to be vulcanized by sulfur. The common third monomers are dicyclopentadiene, ethylidene norbornene, and 1,4-hexadiene. In these dienes, one double bond is capable of polymerizing with the olefins, but the other is not a part of the main chain.



Dicyclopentadiene



Ethylidene norbornene



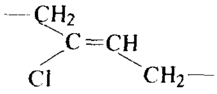
trans-1,4-Hexadiene

Both EPM and EPDM have excellent resistance to oxygen, ozone, heat, and UV radiation.

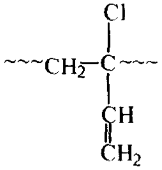
1.1.2.5 Polychloroprene Rubber (CR)

These rubbers are produced by the emulsion polymerization process of 2-chloro-1,3-butadiene. The polymer chains consists of approximately 98%

1,4-addition products which are mostly *trans* in configuration, and the rest are 1,2-addition products. The 1,2-addition product contains a chlorine atom attached to a tertiary allylic carbon atom that is highly activated and thus becomes the curing site in the polymer chain.



trans-Polychloroprene unit



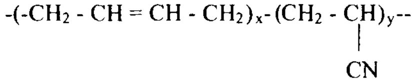
1,2-Addition product

The temperature of polymerization has an important bearing on the polymer structure. At higher temperatures, there is less uniformity in the chain due to large proportions of 1,2 and 3,4 moieties and other isomers in the monomeric sequences. On the other hand, at lower temperatures, the polymeric chain is more regular. The CR is also available in sulfur-modified grades. The polymer chains have Sx groups, and this aids processing due to easy depolymerization. Unlike the diene rubbers, CRs are not vulcanized by sulfur but are vulcanized by metal oxides—a combination of MgO and ZnO.

Polychloroprene stiffens at low temperatures. This is due to second-order transition and crystallization. The rate of crystallization is most rapid at −10°C. Though the stiffening is reversible, it is detrimental for the production of certain goods. Incorporation of low temperature plasticizers like butyloleate can lower the stiffening temperature of CR compounds. CR produced by high temperature polymerization has a much lower rate of crystallization than that produced at a low temperature. The high crystallizable grades are useful as adhesives. For production of coated fabrics, materials with long crystallization times are chosen, as softness and flexibility are more important than ability to withstand heavy stress. The gum vulcanizates of CR show high tensile strength because of strain crystallization, but the resilience is lower. Polychloroprene rubbers are resistant to oxidation, ozone degradation, and flex cracking, and, because of the chlorine atom in the molecule, are inherently flame resistant. Because of its polar nature, the rubber is resistant to hydrocarbons, fats, oils, and most chemicals. It is used for applications requiring weather, oil, ozone, and flame resistance.

1.1.2.6 Nitrile Rubber (NBR)

NBR is a copolymer of acrylonitrile and butadiene obtained by emulsion polymerization. The acrylonitrile content varies from 18–50%, depending on the properties desired. The molecular weight ranges from 20,000 to 100,000.



$$-(-CH_2 - CH = CH - CH_2)_x - (CH_2 - \underset{CN}{\underset{|}{CH}})_y --$$

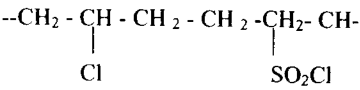
NBR

Like SBR, varying temperatures of polymerization produce different grades of NBR. NBR produced at low temperatures shows less branching than hot rubbers. The steric configuration, i.e., *cis*-1,4, *trans*-1,4, and *trans*-1,2 structures are also influenced by polymerization temperature. The lack of compositional uniformity along the polymer chains prevents formation of crystallites on extension. This results in poor tensile properties of NBR gum vulcanizates.

Nitrile rubbers are of special interest because of their high degree of resistance to fuels, oils, and fats. An increase in acrylonitrile (AN) content increases its oil resistance because of enhancement of polarity of the rubber. NBR has a low gas permeability. Increase of AN percentage in NBR lowers its gas permeability but adversely affects its low temperature flexibility and resilience. NBR is extensively used where oil resistance is required.

1.1.2.7 Chlorosulfonated Polyethylene Rubber (CSM)

CSM is produced by reaction of polyethylene solution with chlorine and sulfur dioxide in the presence of UV radiation.



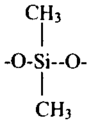
$$--CH_2 - \underset{Cl}{\underset{|}{CH}} - CH_2 - CH_2 - \underset{SO_2Cl}{\underset{|}{CH_2}} - CH---$$

CSM unit

Commercial grades contain 25–40 wt.% of chlorine and about 1% of S. The chlorine and sulfur are randomly distributed along the polymer chain. It is cross-linked by metal oxides through chlorine atom and chlorosulfonyl group. These rubbers are characterized by a unique combination of special properties like ozone resistance, flame retardance and resistance to corrosive chemicals and oxidizing agents.

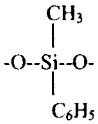
1.1.2.8 Silicone Rubber

Silicone rubber is obtained from silicones. Chemically, silicones are polysiloxanes containing Si-O- bonds. The most important polymers are polydimethyl siloxane, polymethyl phenyl siloxane, and vinyl methyl siloxane. They are manufactured by the hydrolysis of the appropriate dichlorosilane R_2SiCl_2. Silicones are available in a wide range of molecular weights and viscosities, from fluids to gums.



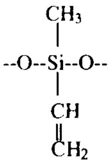
$$-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$$

Dimethyl siloxane unit



$$-O-\overset{CH_3}{\underset{C_6H_5}{Si}}-O-$$

Methyl phenyl siloxane unit

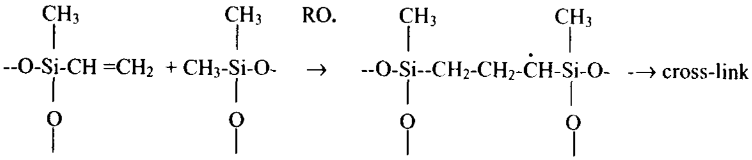


$$-O-\overset{CH_3}{\underset{CH=CH_2}{Si}}-O-$$

Vinyl methyl siloxane unit

There are three major ways of curing silicone rubbers, viz., peroxide cure, hydrosilation, and condensation cure [5,6].

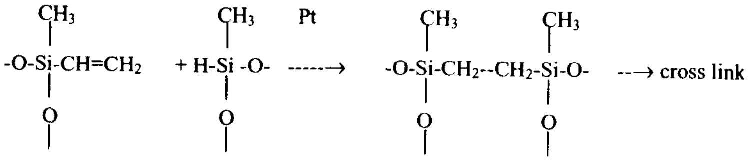
(1) Peroxide initiated cure: $ROOR \xrightarrow{\Delta} 2R\dot{O}$



$$-O-\overset{CH_3}{\underset{O}{Si}}-CH=CH_2 + CH_3-\overset{CH_3}{\underset{O}{Si}}-O- \xrightarrow{RO.} -O-\overset{CH_3}{\underset{O}{Si}}-CH_2-CH_2-\dot{C}H-\overset{CH_3}{\underset{O}{Si}}-O- \longrightarrow \text{cross-link} \quad (1)$$

This is a one-part system where the peroxide is activated on heating above 100°C. The vinyl group facilitates free radical reaction with the formation of vinyl to methyl and methyl to methyl bonds.

(2) Hydrosilation: an addition reaction occurs between vinyl siloxane and siloxane containing Si-H group catalyzed by Pt (chloroplatinic acid). The cross-link occurs due to multiple functionality of both reactants. This is a two-part reaction with one part containing vinyl siloxane with Pt catalyst and the other containing silicone with Si-H functionality. The two liquid parts permit direct processing including coating without solvent and are known as liquid silicone rubber LSR.



$$-O-\overset{CH_3}{\underset{O}{Si}}-CH=CH_2 + H-\overset{CH_3}{\underset{O}{Si}}-O- \xrightarrow{Pt} -O-\overset{CH_3}{\underset{O}{Si}}-CH_2-CH_2-\overset{CH_3}{\underset{O}{Si}}-O- \longrightarrow \text{cross link} \quad (2)$$

PDMS with Si-H group

(2)