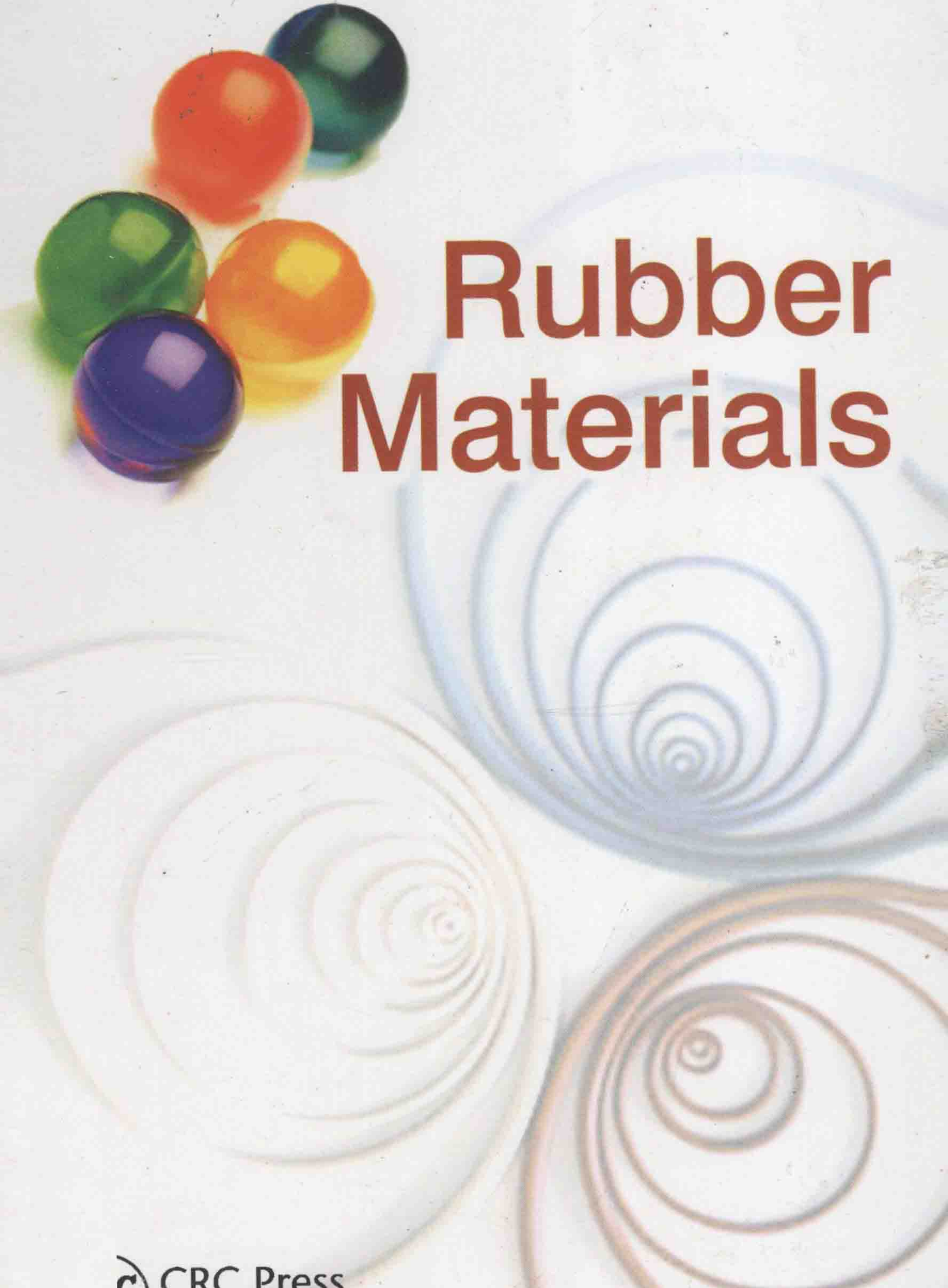


Rubber Materials

CRC Press
Taylor & Francis Group

B. Kothandaraman

Rubber
Materials

By

B. Kothandaraman
Asst. Prof., Rubber & Plastics Technology
MIT Campus, Anna University,
Chennai-600044

Taylor & Francis
Taylor & Francis Group
Boca Raton London New York

CRC is an imprint of the Taylor & Francis Group,
an informa business

Ane Books India

First Published in 2008 by

Ane Books India
4821 Parwana Bhawan, 1st Floor
24 Ansari Road, Darya Ganj, New Delhi -110 002, India
Tel: +91 (011) 2327 6843-44, 2324 6385
Fax: +91 (011) 2327 6863
e-mail: anebooks@vsnl.com
Website: www.anebooks.com

For

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway, NW, Suite 300
Boca Raton, FL 33487 U.S.A.
Tel : 561 998 2541
Fax : 561 997 7249 or 561 998 2559
Web : www.taylorandfrancis.com

For distribution in rest of the world other than the Indian sub-continent

ISBN-10 : 1 42007 159 9
ISBN-13 : 978 1 42007 159 7

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Printed at Brijbasi Art Press, India

Rubber
Materials

Foreword

Rubbers are interesting materials and are extensively used all around us. Many Engineering marvels of today like automobiles, aerospace vehicles, machinery etc. cannot function without rubbers. Rubber have been in existence for the last 200 years and are the fore runners of the polymer industry of today. The need for technologists with knowledge of Rubbers is felt very badly in many industries.

Besides students of Rubber and Plastics Technologies, other engineers too may have to know about these materials so that materials selection can be done more effectively. Presently no good book covering the fundamentals of rubbers and their compounding ingredients is available from Indian publishers. Dr. Kothandaraman has been teaching this subject for a long time and he has attempted to write a short book which will help greatly in understanding about these vital materials.

I am glad that he has made this attempt which will help students of Polymer Science and Technology at Diploma, Bachelors' and M.Sc (Polymer Science and Technology, Materials Science, and Applied/Industrial Chemistry). This book will also help practicing technologists in Industry and will be a great asset to any Library of a University or Rubber Industry.

I wish that all individuals and organizations, dealing with Rubbers in India and third world countries benefit by using this simple book.

Dr. K. Balasubramanian
Professor, Rubber and Plastics Technology
MIT Campus, Anna University,
Chennai-600044

Preface

An index of modernity of a country can be its per capita consumption of Rubbers and Plastics. India falls way behind the advanced in this respect though the potential very much exists. The country also has the necessary technological base for this. With the economy growing fast, the usage of rubbers and plastics is bound to go up. Hence, the Indian Rubber Industry is a very fast growing one.

Advances in the fields of Rubber and Plastics technologies have changed the face of modern life. Rubbers play a vital role in automobile, aeronautics, electrical and electronics, materials handling, health care, power transmission fields besides a host of other applications. Hence, every engineer must know a little about rubber components like—oil seals, gaskets, diaphagms, grommets, belts, etc., and not the least, the pneumatic tyre. Such components must be made of the appropriate raw material otherwise break downs like oil leakage, transmission of vibrations, insulation breakdown etc. can occur.

Appropriate choice of the materials into the making of such rubber components is vital. To understand the properties, a strong understanding of the role played by polymer structure is vital and hence the book begins with a chapter on Structure-property relationships in rubbers.

The Rubber industry began with the naturally occurring material (i.e. Natural rubber - NR). This material still remains unchallenged in a few applications like heavy duty truck tyres, aero tyres though in other areas synthetic rubbers have come in a big way. Hence natural rubber will be the subject matter for the next chapter. This chapter will cover latex tapping, conversion to dry rubber, forms of natural rubber, and its modifications.

The next chapter will be on various general purpose synthetic rubbers-mainly styrene butadiene rubber (SBR), poly butadiene rubber (BR) and other such rubbers like synthetic poly isoprene (synthetic NR) and some aspects of advances made in polymerisation techniques towards development of rubbers comparable to NR like poly alkenamers.

The next chapter will be on special purpose rubbers – EPDM, butyl rubber, oil resistant rubbers - mainly NBR and poly chloroprene. The other speciality rubbers like poly acrylates, chloro sulphonated polyethylene, ethylene vinyl acetate, poly epichlorohydrin, poly sulphide rubber etc., are also covered in the next chapter.

This will be followed by the chapter on high performance rubbers mainly fluorine containing rubbers and silicone rubbers. The need for rubbers which can be processed by unusual techniques is always present. Poly urethanes, the rubbers with unusual processing techniques are also covered in this chapter.

Chapter VI will cover compound ingredients-details about curatives, accelerators, anti degradants, fillers, processing aids etc., are covered in this. The mechanism by which various curatives, reinforcements by carbon black and silica and the action of anti oxidants etc., are covered in this chapter.

The need for rubbers which can be processed like thermoplastics is being realised as the days go by - hence the next chapter will be on Thermoplastic elastomers, which is a very rapid growing area in rubber technology.

The need to understand about polymer blending-blending of rubbers with rubbers and with plastics is more acute today and a chapter on blending is added next. Principles of compounding are also covered in this last chapter.

This book will cover the important aspects of rubber materials. This will be useful for Diploma and Bachelors level students of Polymer Technology besides technologists working in Rubber Industry. This will also help aspirants of Diploma of Indian Rubber Institute exams.

Target readers: Students of Polymer Science and Technology at B.Tech, Diploma and MSc (Polymer Science/Materials Science) besides practising Technologists.

Presently there are very few books which teach the fundamentals of Rubber Materials. A few books were available from abroad-most of them are out of print now. The only available Indian book on Rubber Technology covers Processing and machinery aspects but not so much on the materials side. Thus this book will be a boon for those who want to understand Rubber materials especially from the Chemistry angle.

For understanding the subject a good understanding of the fundamentals of Organic Chemistry is essential and a good student of 10+2 can fit the bill. With this background it will be easy to understand this book.

Author
B. Kothandaraman

Contents

1

Structure–Property Relationships in Rubbers

Rubber means a polymer which is capable of reversible deformations under small applied loads. The elasticity of a rubber comes from the very nature of the chain structure of a polymeric molecule. The stress-strain curves of all rubbers are similar, though exceptions may be seen in some cases. The commonly used theories of rubber elasticity, necessary for engineering calculations, work reasonably well over a limited range of strains (roughly up to 300% elongations) but beyond this, discrepancies are seen and these are due to the chemical structural features of the polymer. Thus, the chemistry has to be considered for explaining the properties of rubbers.

The properties of a rubber are very much related to its molecular structure. Whenever a new polymer is synthesized, the first thing we may know about it, is its structure. Will it be possible to make a reasonable guess about some of its properties, from a knowledge of its structure, is the theme of this chapter.

To describe the basic structural features of polymers is beyond the scope of this book as there are a good number of books available on Polymer Science which the student is advised to refer to. For the same reason it is not proposed to cover the basics of polymerisation reactions in this book. A few basic points will be covered for refreshing the concepts already learned in polymer chemistry, to apply to Rubber Technology, at appropriate places in later chapters.

The words 'rubber' and 'elastomer' are often treated as interchangeable. Often 'rubber' means the raw polymer while elastomer, the compounded material.

If a polymer is to behave as a rubber it has to fulfil the following requirements :

1. The main chain of the polymer must be flexible (over the temperatures of use).
2. The individual chains must be capable of being crosslinked with each other.
3. The main chains must be free of weak links – otherwise they may break so easily that the rubber will be of little use to us.

1. Chain Flexibility :

This is a very important factor. How is the flexibility defined ? Is there any way by which this can be quantified ? There is a measurable property which can directly be related to flexibility.

The back bone of a polymer consists of carbon – carbon bonds (mostly single bonds). The carbon atom in a C— C bond has a tetrahedral configuration. Each single bond is capable of rotation about its axis. Since a polymer chain consists of thousands of C — C bonds, the chains can assume any configuration. This can theoretically even lead to a situation where the two ends of a chain may be the same point. With this, one can imagine to what extent each of these bonds can be straightened – this is the origin of elasticity of a polymer.

Fig. 1.1a. Tetrahedral nature of Carbon atom

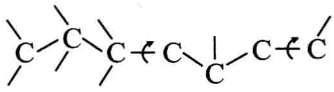


Fig. 1.1b. Any of these bonds can rotate through any angle leading to randam coiling

Fig. 1.1c. Randomly coiled polymer chain

Double bonds are by themselves rigid, but make their neighbouring single bonds more flexible. For rotation of a C — C single bond about its neighbouring bond, it must overcome a rotational energy barrier. The lowest energy barriers are associated with C — C — C bond, C — O — C bond and Si — O — Si bonds. Further, the side chains in these chains must be as light as possible. The rotational energy barriers can be overcome if the temperature in question, crosses a particular value called glass transition temperature (Tg). Thus a polymer with a low Tg value can be considered as a rubber. Tg can be defined as a temperature below which a polymer will be hard and brittle (i.e. glassy state) and above which soft and flexible (rubbery state).

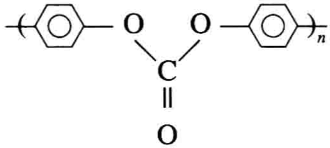
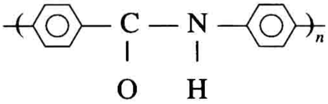
The lightest side chains are H and F atoms – thus poly ethylene (PE) and poly tetra fluoro ethylene (PTFE) which contains only H and F side chains respectively, have highly flexible chains but these polymers, as we know are only plastics – this is due to other reasons which will be discussed in due course.

On the other hand, another polymer with only H as the side chain is a rubber – that is, poly butadiene (BR) especially its predominantly cis and trans forms. Poly butadiene also exists in the 1,2 structure as in medium vinyl grades, which will have a higher Tg.

The Tg of a polymer depends on the following factors :

1. *Chain stiffness*
2. *Inter chain attractions*
3. *Molecular symmetry*
4. *Copolymerisation and its types*
5. *Branching and cross linking*
6. *Presence of solvents/plasticisers*

Chain stiffness can be increased by double bonds or ring structure (as in poly phenylene or poly phenylene oxide or poly phenylene sulphide or PEEK or Poly sulphone) or ladder polymer (as is the case when poly acrylo nitrile – PAN is heated to about 250°C). Though in BR, NR (natural rubber), and CR (poly chloroprene – neoprene) a double bond is present once in 4 carbon atoms, it will not be enough to make the main chains rigid. The Tg values of the following polymers are in the following order (as the chain stiffness increases) :

Structure & Polymer	**Tg**
Poly ethylene $-\!\left(CH_2CH_2\right)\!-_n$	around –80°C (value is uncertain)
Poly butadiene $-\!\left(CH_2CH=CHCH_2\right)\!-_n$	–100°C
Poly carbonate (bisphenol based) 	150°C
Poly phenylene terephthalamide 	327°C

(In the last two cases, the benzene rings are present in the main chain itself – this increases the rotational energy barriers enormously).

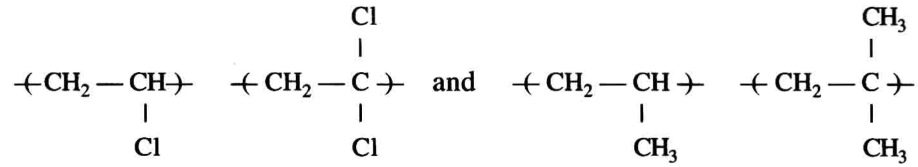
The side chains increase the resistance to rotation of the C — C bonds. Thus when we compare poly ethylene and poly propylene, poly propylene will have a higher Tg value. This in turn will be higher in poly styrene where the side chain is the highly bulky benzene ring.

Restrictions on rotations will also be caused by ***inter chain attractive forces***. For example, presence of electronegative atoms or groups as side chains increase inter chain attractions – this will increase Tg values (comparing PP and PVC, though the side chains do not differ greatly in bulkiness, PVC has a much higher Tg values (PP –20°C while PVC about +82°C). This effect will be magnified by Hydrogen bonding – as in the case of poly acrylonitrile (nearly 100°C). Conversely, increase in inter chain repulsion will lead to a decrease in Tg. If we consider the polymers of the acrylate series :

$$-(CH_2-\underset{|}{CH})_n-$$

COOR the Tg values will show a peculiar trend as the bulkiness of R increases. If R = CH_3 (i.e. poly methyl acrylate) its Tg is 8°C while if R = ethyl (i.e. poly ethyl acrylate –24°C and poly butyl acrylate –54°C. This is opposite the trend which we would expect—i.e. as the bulkiness of the side chains increases Tg, instead of increasing, decreases. This is due to inter chain repulsion caused by the bulkiness of the side chain. Further increase in bulkiness of R beyond the alkyl group with 8 carbon atoms again leads to increase in Tg – this may be due to crystallisation of the side chains.

The role of ***moleclar symmetry*** on Tg is not clear. In the case of Poly vinyl chloride and poly vinylidene dichloride Tg again decreases in the polymer containing two chlorine atoms. Similar is the case with poly propylene and poly isobutylene, though the stiffness of the chains should increase when 2 Cl or methyl sides are present, the Tg decreases.



$$-\!(CH_2-\underset{Cl}{\underset{|}{CH}})\!- \quad -\!(CH_2-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}})\!- \quad \text{and} \quad -\!(CH_2-\underset{CH_3}{\underset{|}{CH}})\!- \quad -\!(CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}})\!-$$

Tg = 82°C Tg = –16 to –22°C Tg = –20°C Tg = –75°C

This is sought to be explained by symmetry caused by, perhaps, reduction in dipole moment due to symmetry.

Similarly cis and trans forms of poly butadiene show almost same Tg (–107° and –106°C respectively) while in case of cis and trans poly chloroprenes the values are markedly different (–20°C and –45°C respectively). These are also difficult to explain.

Similarly tacticity also has, generally, little effect on Tg values.

The type of copolymerisation affects Tg values. Alternating and random copolymers show one Tg value which is in between the Tgs of the corresponding homopolymers (depending on the composition) while block and graft copolymers show 2 Tg values which are the Tg values of the pure homopolymers. SBR, a random copolymer has one Tg value (around –65°C) which can be calculated from the mole fractions of styrene and butadiene present in the copolymer (i.e. about 23.5% of styrene normally). In contrast, in SBS block copolymer which is a thermoplastic elastomer (TPE), two Tgs are seen—one at –100°C i.e. Tg of poly butadiene and another at near +100°C i.e. the Tg of poly styrene.

Cross linking reduces chain flexibility as the individual chains are chemically linked with each other. Thus as sulphur content increases in NR in a series of ebonites, Tg increases with cross link density. As we may recall, ebonite is a hard plastic. The rigidity increases with cross link density.

Branching in chains affect Tg values but the effect is not so straight forward. Branching increases free chain ends which should depress Tg while the branches themselves may act like heavy side chains – these may balance each other. However, the free chain end effect predominates often.

Plasticisers and solvents penetrate the space between the chains and this will increase flexibility of chains – thus Tg will decrease. In case of PVC plasticisation is used to reduce Tg and convert it to a rubbery polymer– Tg decrease from 82°C to, nearly room temperature.

Ability to be cross linked:

This is another important factor. Poly isobutylene has a low Tg of about –75°C but cannot be useful as a rubber as it cannot be cross linked. Hence it is copolymerised with isoprene to be useful as a rubber (butyl rubber). Cross linking may be by sulphur or peroxide or metal oxide or any other chemical or it can also be physical as in TPEs. Physical cross links serve the same purpose as chemical cross links by preventing chains from slipping past each other at ordinary temperatures.

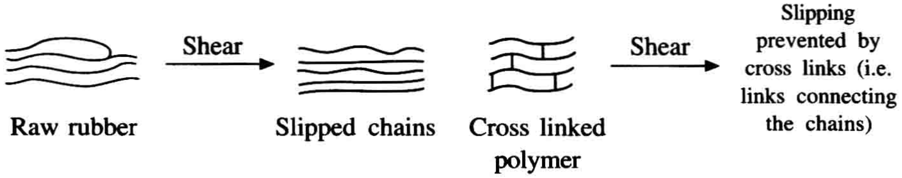
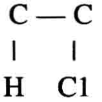


Fig. 1.2

Absence of weak links:

This is a minor requirement in the sense that any polymer with weak links in the main chain will be useless (either as a rubber or as a plastic) as it will have poor life. Examples of weak links are peroxide (— O — O — links). This must be avoided in any polymer chain. Double bonds in the main chains are also weak links – hence rubbers with more double bonds cannot withstand higher temperatures. Similarly  $\underset{H}{C}-\underset{Cl}{C}$ as in PVC can also be considered as a weak link as it can lose HCl easily even at fairly low temperatures which causes double bonds to form rapidly and hence rapid degradation. Hence PVC always requires stabilisers in its compounds.

Effect of structure on other properties:

Heat resistance: Heat resistance depends mainly on bond dissociation energies. Single bonds like C — C or Si — O — Si or C — O — C have high bond dissociation energies, while double bonds weaken their neighbouring single bonds as they can lose H easily and form free radicals which can be easily stabilised by the double bonds besides other factors. This can lead to cross linking or degradation reactions. The details will considered in the chapter on compounding/anti oxidants. In case of silicones, the high heat resistance may be due to lack of an energetically favourable pathway to a stable degradation product (i.e. silica).

$$\left(CH=CH-CH_2\right)_n \xrightarrow[\text{(or heat)}]{\text{light}} \left(CH=CH-\dot{C}H\right)_n \longleftrightarrow \left(CH=CH-\dot{C}H\right)_n$$

Fluorocarbon rubbers are highly heat resistant due to shielding effect of fluorine atoms attached to the main chain carbon atoms.

Benzene rings in main chains as in poly phenylene sulphide or aromatic poly amides or ladder structures impart heat resistance due to their highly rigid structures.

Table 1.2 Bond dissociation energies

	Bond	**Approx. bond dissociation energy (kg mol^{-1})**
1.	— O — O —	145
2.	— S — S —	270
3.	C — C, C — O, Si — O, C — C	325–375
4.	C — F	425
5.	C = C	600
	C = O	740
	C ≡ N	900

Effect of Structure on low temperature flexibility:

The factors to be considered here are Tg and crystallisation. Tg has already been dealt with, in detail earlier and hence now we will look into crystallisation. Crystallisation leads to close packing of the chains and hence restrict rotation of the main chain bonds. Thus poly ethylene, poly propylene, PTFE and trans poly isoprene are all plastics though they have low Tgs.

In polymers, crystallisation is never 100% — often the crystalline polymers may be pictured as having crystalline regions connected to each other by amorphous zones. Factors which lead to crystallinity may be light side chains, regular structures like uniformly *cis* (or *trans* etc) or tacticity (iso and syndiotactic) or alternating copolymerisation. Crystallisation does not affect Tg but increases melting point (Tm). If the Tg:Tm (in $\dot{K}$) ratio is around 2 : 3 such a polymer may be amorphous. Mostly rubbers fall in this category. If the ratio has a smaller value as in HDPE or PTFE or trans poly isoprene, the chains may be having a symmetrical structure. Another thing to note is that the values of Tgs of crystalline polymers are uncertain.

As far as rubbers are concerned, crystallinity is certainly an undesirable phenomenon. Without exception no rubber is a crystalline polymer, in normal conditions. This should not be confused with a property called strain-induced crystallisation seen in NR, CR and IIR (butyl rubber). These polymers have regular structure (NR has 100% *cis* structure, CR predominantly *trans* structure) and hence on stretching, the chains tend to align and then pack closely, leading to crystallisation. Of these, NR and CR also crystallise at low temperatures. IIR does not crystallise on cooling. Strain induced crystallisation confers some advantages in mechanical properties. This will be discussed in a later section.

In general a polymer is useful as a rubber at temperatures above Tg +30°C. Thus NR should be a useful rubber down to about –40°C. Crystallisation on cooling limits the lower temperature use of NR at –22°C instead of –40°C, as the polymer will become stiff (this is reversible as once the temperature is increased, this effect will vanish). For the same reason, the lower service temperature range of some grades of CR may be close to 0°C. In other rubbers, the lower service temperature limit will be about 30°C above Tg.

Crystallisation is usually caused by regular structure – this prevails in NR, CR and IIR. Most of the other rubbers are random copolymers and hence they will have irregular structure and hence will not crystallise. In case of chlorination or chlorosulphonation of poly ethylene, the resulting polymers, due to the addition of the bulky side chains, Cl and SO_2Cl groups respectively, will disrupt crystallisation and hence these polymers will become rubbery. Similarly copolymerisation of ethylene with propylene or vinyl acetate or methyl acrylate will destroy crystallisation and hence these copolymers will be rubbers. In case of vinylidene fluoride, copolymerisation will lead to rubbery polymers.

Effect of Structure on chemical reactivity: A polymer must be reactive enough to be capable of cross linking. Thus NR and BR will cure fast as there is a double bond once in every 4 carbon atoms in the main chains. In case of butyl or EPDM rubbers, the number of carbon atoms between two double bonds will be very large (a few hundreds)—hence they will cure slowly. SBR and NBR will cure slower than NR but much faster than IIR or EPDM (in these cases the number of carbon atoms between main chain double bonds will be around 8–10). In all these cases, the double bond is the cure site (for sulphur or peroxide cure).

For other rubbers, cure sites will not be double bonds but other atoms or groups – in CR, it will be the C linked to Cl in the 1, 2 or 3, 4 structures (the Cl in the 1,4 structure is not reactive for any curing reaction). Other rubbers with Cl containing C as a cure site are epichlorohydrin rubber, poly acrylate rubbers or chlorosulphonated poly ethylene (hypalon or CSM), chlorinated poly ethylene etc.

Reactivity of the rubbers also lead to modification of properties through chemical reactions. Thus many double bond reactions can be used on NR and convert it to polymers with different end use properties.

Some reactive groups may also lead to rapid degradation of polymers especially double bonds – thus NR and BR have poor heat resistance, oxidation resistance, ozone resistance and weather resistance. Double bonds can be easily attacked by oxygen in presence of heating or ozone or UV light – thus NR, SBR, NBR and BR will need protective chemicals against attack by heat, ozone and UV light – this role is fulfilled by anti oxidants, and anti ozonants. Carbon black will protect rubbers against UV radiation, present in the early morning sunlight.

Polymers with no double bonds and other reactive groups will have exceptional chemical resistance e.g. IIR, EPDM, CSM. Fluorocarbon rubbers are heat resistant due to fluorine atoms attached to C atoms. Fluorine atoms 'shield' the main chains from being attacked by chemicals.

If a polymer contains ester or amide groups in the main chains, they may be prone to hydrolysis (common examples are not found in rubber technology except for thermoplastic rubbers of the type, poly urethanes based on polyester polyols and polyesters, while in the plastics world, poly amides, poly carbonates and polyesters are common plastics prone to hydrolysis by strong bases).

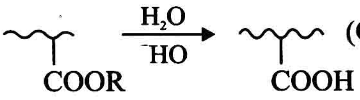
$$\sim\sim\sim \text{CONH} \sim\sim\sim \xrightarrow[H_2O]{OH^-} \sim\sim\sim \text{COO}^- + H_2N \sim\sim\sim$$

(Polyamide)

$$\sim\sim\sim \text{COO} \sim\sim\sim \xrightarrow[H_2O]{OH^-} \sim\sim\sim \text{COO}^- + \text{HO} \sim\sim\sim$$

(Polyester)

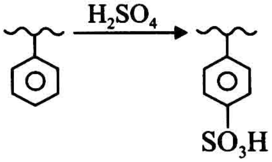
In poly acrylates or EVA or EMA rubbers, the esters are in the side chains and hence these rubber will resist hydrolysis.



(Only side chain is affected here)

(as in EVA, EMA)

Benzene rings may undergo substitution reactions like nitration or sulphonation in its vacant positions without affecting the polymer – as in poly styrene or SBR. In case of poly styrene the substitution of the benzene rings by sulphonate group etc. leads to production of ion exchange resin.



Solvent Resistance: Solvents and plasticizers are special type of chemicals – they are essential in processing. Some rubbers are affected by some solvents. This is important when we choose polymers for hoses or seals. From our earlier education we know that polar solvents will affect polar polymers and non polar solvents will affect non polar polymer ("like dissolves like"). Polarity may be quantified using a property called solubility parameter. This property simply depends on latent heat of vapourisation and molecular weight.

Solubility parameter (M, in $\text{MJ/m}^3 = \sqrt{[(L - RT)/(M/D)]}$

where, L = Latent heat of vapourisation, R = gas constant, T = temperature, M = molecular weight, D = density.

The term under the square root is called cohesive energy density.

Non polar solvents have lower values of solubility parameter while the more polar ones, higher. More polar means more inter molecular attractive forces and hence higher latent heat of vapourisation – this increases solubility parameter.