

1. Introduction

1.1 Polymer gels and networks – definition and properties

Polymer gels are a fascinating class of materials. Now-a-days, the field of polymer gels is a very active area of worldwide research. Materials scientists, chemists, physicists, chemical engineers and biologists are all working on various kinds of gel. Different gels may have widely different structures and characteristics. However, in the current literature, there is still no generally accepted definition of this term.¹ Flory²⁻³ and Stockmayer⁴⁻⁶ reached an important milestone when they attempted to include structural criteria in the definition of a gel, such as infinite network, three-dimensional structure, coherence etc. The following criteria to distinguish different polymer gels were first proposed by Flory⁷:

- I. Well-ordered lamellar structure, including gel mesophases.
- II. Covalent polymeric networks; completely disordered.
- III. Polymer networks formed through physical aggregation; predominantly disordered but with regions of order.
- IV. Particulate and disordered structures.

It is well known that polymer gels are association of macromolecules. These are generally made, at least formally, by crosslinking simpler linear polymers and their mechanical properties reflect gel network structure. The Encyclopedia of Polymer Science and Engineering gives this definition: “A *gel* is a crosslinked polymer network swollen in a liquid medium. Its properties depend strongly on the interaction of these two components”.⁸ It may be noted here that the above classification of gels as proposed by Flory contains no statement about the minimum number of phases in the system. This implies that undiluted (unswollen) crosslinked rubbers, which ideally consist of one giant molecule, are considered as true gels.⁷ The above concept has been deliberated in this thesis and the term “*crosslinked gels*” referred herein essentially represents the unswollen chemically crosslinked polymer (elastomer) matrix (Flory Type II Gels).

In general, polymer gels and networks possess at least one of the following characteristics,

- a) Infinite molecular weight
- b) Insoluble and infusible
- c) Ability to reversibly swell or shrink (up to even 1000 times in volume)

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However, depending on several factors like polymer matrix, nature of crosslinking, size etc., gels can have very diversified as well as unique set of properties. In many cases, gels exhibit stimuli-responsive behavior under the influence of external stimuli such as pH, pressure, temperature or electric field etc.

Gels can have natural as well as synthetic origins. Examples of typical biological gels which are formed by cooling of solutions are gelatin, pectin, agarose, carrageenan, and agar gels.⁹⁻¹¹ Fibrin clots are also typical biological gels which, however, are formed by polymerization of fibrinogen monomer through a series of enzymatic reactions.¹² A number of synthetically prepared organic systems exhibit similar properties. Dilute solution of polyvinylchloride in di(2-ethylhexyl) phthalate forms gels on cooling.¹³ Typical examples of covalently crosslinked networks are a styrene-divinylbenzene copolymer swollen in an organic solvent¹⁴ and a 2-hydroxyethyl methacrylate ethyleneglycol dimethacrylate copolymer swollen in water (the material used for soft contact lenses).^{15, 16} Silica gel in the swollen state is a typical example of an inorganic gel.^{17, 18} Usage of the term 'gel' has gradually been expanded to include a number of systems that contain no liquid phase. Unswollen crosslinked rubber,¹¹ and aerogels¹⁹ are common examples. Rigid materials have also been characterized as gels. Dried silica gel, which is a very rigid and brittle material, can be mentioned in this context.²⁰ Polyisocyanurate networks with moduli in the order of 10^8 Pa prepared in presence of small quantities of solvent are yet another example.²¹

1.2 Classification of polymer gels and networks

Based on the nature of crosslinking, gels and networks can be divided into three main classes. These are covalently crosslinked gels, entanglement network gels and physical gels.⁵

1.2.1 Covalently crosslinked gels

Covalently or chemically crosslinked gels are formed by a variety of routes including crosslinking or vulcanization of high molecular weight linear polymer chains, addition polymerization of oligomeric multifunctional precursors and end linking of reactive chains with branching units.^{22, 23} These are true macromolecules with nominally infinite molecular weight, and consequently they swell rather than dissolve, if immersed in a good solvent. They also possess an infinite relaxation

process and equilibrium modulus.⁵ Covalently crosslinked gels have been extensively investigated and both the small and large deformation mechanical properties have been characterized. Since network junctions in covalently crosslinked gels are formed by covalent bonds between macromolecules and crosslinking agents, such gels can be destroyed only by bond rupture or by thermal degradation of polymer. Chemically crosslinked gels are characterized by an equilibrium modulus of elasticity.²⁴ The factors responsible for the elasticity of polymer gels are a large amount of solvent and the flexibility of polymer chains. The higher the flexibility, the smaller the polymer concentration in the system, and the longer the distance between network junctions, the higher the elasticity. In the cases, when macromolecules have high chain rigidity and the network is very dense, or it swells in a solvent with a very poor thermodynamic compatibility with respect to a polymer, fragile gels are formed. Of great interest are the gels of swollen hyper-crosslinked polystyrene (PS) in which each phenyl group of PS is involved in crosslinking with divinylbenzene.²⁵ Such gels are capable of absorbing huge quantity of solvent (up to 500% of the polymer mass). Depending on the amount of the solvent, they can be fragile (although they do not occur in the glassy state) or even can exhibit certain degree of elasticity.²⁶ At the same time, there are gels characterized by rubber like elasticity i.e. the ability to sustain a very large amount of deformation reversibly. It is worth mentioning here that hydrogels are a special class of covalently crosslinked gels and are formed by crosslinked three-dimensional hydrophilic polymer network swollen in water or aqueous solution.¹⁵ Reversible hydrogels display reversible sol–gel transitions: a lower transition when sol is converted into gel and higher transition when the gel collapses or shrinks and expels part or nearly all of the solution absorbed by it. Such transitions can be induced by change in temperature, counter ions or their concentration, solvent composition, wavelength or intensity of light, electric voltage, or chemical triggers.¹⁵

As the present work solely deals with this type of gels, more information on the various routes of preparation and properties of chemically crosslinked gels are provided in the later sections.

1.2.2 Entanglement network gels

The second class is the so-called entanglement networks gels. These are formed by the topological interaction of polymer chains either in the melt or in

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solution, when the product of concentration and molecular weight becomes greater than the critical molecular mass for entanglements. This type of entanglement network is normally found in high molecular weight polymers, especially in elastomers. In this case, they behave as “pseudogels” at frequencies higher (at shorter timescale) than the lifetime of the topological entanglements. Entanglement network gels can be dissolved in an appropriate solvent to form a more dilute polymer solution whereas the covalently crosslinked gels will only swell but not dissolve. However, entanglement networks can be identified from covalently crosslinked gel by using simple rheological techniques such as dynamic mechanical analysis.²⁷ There has been much progress in this area since it was recognized that their relaxation behavior can be described by tube (reptation) models. However, detailed discussion on this topic is beyond the scope of the present thesis.

1.2.3 Physical gels

Many systems fall between the above mentioned two categories as they consist of chains which are “physically” crosslinked into networks. The crosslinks themselves are of small but finite energy and/or of finite lifetime. The term ‘physical gels’ includes gels from both the biological and synthetic polymers.^{9, 23} Also, this term, which appears to have been introduced by de Gennes²⁸, is often assumed to imply thermoreversibility, which is by no means the case with every system. The presence of non-covalent crosslinks complicates any physical description of the network properties enormously. This is because their number and position fluctuate with time and temperature. In many cases, the nature of the crosslinks themselves is not clearly known. The reason is that disparate forces are often involved, e.g. Coulombic, dipole-dipole, van der Waals, charge transfer and hydrophobic and hydrogen bonding interactions.²⁵ In biopolymer gels, non-covalent crosslinks are formed by one or more of the forces listed above, combined with more specific and complex mechanisms involving junction zones of known, ordered secondary structure, e.g. multiple helices, ion mediated “egg box” structures etc.⁸ Typically there is a specific and often intricate hierarchy of arrangements, a situation which is more familiar to molecular biologists than to polymer scientists. A physical description of such networks is rather difficult, because the potential number of junction zones per primary chain and the extent (molecular weight) of the junction along the chain profile can be estimated only indirectly. In many cases there is a subsequent lateral

aggregation of the chains. These factors can influence the actual number of physical crosslinks and consequently, the modulus of the final gel. Since the modulus will usually reflect both entropic (rubber-like elasticity) and enthalpic contributions, an a priori description of the modulus and mechanical response of these materials is bound to involve a number of approximations. Examples of biopolymer physical gels are gelatin, seaweed and plant polysaccharides such as agarose, carrageenans and pectin, starches and cellulose derivatives. More details of the structure and properties of these are given elsewhere.²⁸ Physical gels can also be formed from synthetic polymers including isotactic polymers in certain solvents (polystyrene in decalin), ionomers in solvents of low dielectric constant, and a number of A-B-A type block copolymers; aggregation of hetero-structural chains is often a common feature of such materials.

Because their crosslinks are not permanent, some physical gels are thermoreversible, which means they can be melted out and they will reform without any real hysteresis. However, thermoreversibility and irreversibility of a physical gel depend on the type of material.²⁸ For example, “storage” materials possess highly ordered structures even after extraction and purification (e.g. starch granules). In order to gel aqueous solution or dispersion, it is usually necessary to heat the sample first to rupture part of the ordered structure. Cooling can then lead to gelation with a new intermolecular network being formed. The original structure cannot be recovered and as with heat-set mechanisms, the process is generally irreversible. The gelation of ‘structural’ polymers, by contrast, is accompanied typically by a reversible disorder-order transition.²⁹ Such physical gels are usually thermoreversible, because the bindings at junction are rather weak. Conversely, as mentioned earlier, chemically crosslinked gels are thermally irreversible as the crosslinks are strong, permanent point-junctions held together by covalent bonding.

It is interesting to note that in physical gels the length of disordered chain between junction zones is generally shorter and less flexible than the regions of ‘random coil’ in chemical gels.²⁸ Gel networks of the association type (physical) indicated in Figure 1.1a and the point-like representation of chemical crosslinks shown in Figure 1.1b are by no means the only structure involved in gel formation. Some macromolecules in a compact, semi-rigid conformational form can give rise to a particulate network structure. These are then aggregate into random clumps and chains to give a continuous network as shown in Figure 1.1c. These are better known as Flory type IV gels.

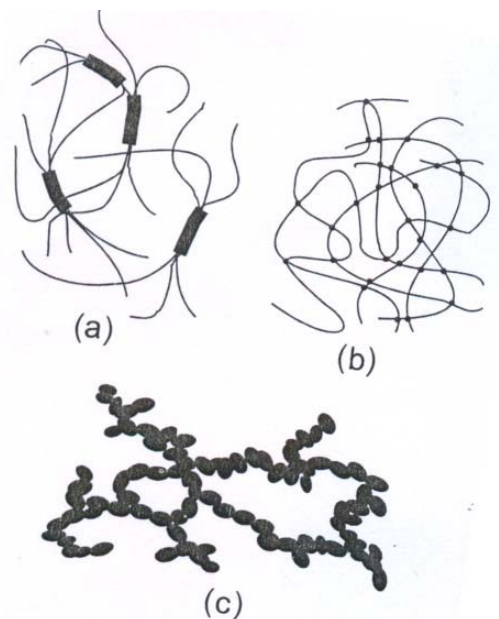


Figure 1.1: Schematic representation of a gel network involving (a) physical junction zones, (b) permanent point-like chemical crosslinks, and (c) particle association (reproduced from reference 28).

1.2.4 Macrogel, microgel and nanogel

Based on the sizes (particle diameter), polymer gels can be further sub-divided into three groups. Individual gel particles having particle diameter of $> 1\mu\text{m}$ are termed as macrogels. Gels in submicron sizes (from $1\mu\text{m}$ to 100 nm) are classified as microgels. Gels having $<100\text{ nm}$ diameters are called *nanogels*. It may be pointed out here that considerable differences of opinions exist among the researchers and above size based classification is neither authoritative nor exhaustive. For example, Murray and Snowden³⁰ extended the size range of microgels to include all intramolecularly crosslinked particles of colloidal dimensions (i.e. 1 nm - $1\mu\text{m}$), while Funke³¹ defined microgels as submicroscopic particles in the size range of 1 - 100 nm . Similarly, gels having size range slightly greater than 100 nm (in the vicinity of nanometer range) may be termed as quasi-nano (near nano) gels.

1.3 Characterization of polymer gels and networks

The characterization techniques which have been applied to the study of polymer gels and networks may be subdivided into (a) those which essentially examine the details of crosslinking at the molecular level and (b) those which probe on the physical state. In order to reveal the molecular structure and bonding of the polymer gels and networks, many spectroscopic techniques such as nuclear magnetic

resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), ultra-violet spectroscopy (UV), etc. are frequently employed.¹⁰ Scattering techniques namely small-angle neutron scattering (SAN) and small-angle X-ray scattering are also used to determine the ordered structure of microlattices.³²

Static and dynamic light scattering (DLS) measurements are extensively used for the determination of gel particle sizes and their distribution.³⁰ Various microscopic methods like scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are often used to visualize the finer morphology of the polymer gel particles.^{28, 30} Figure 1.2 shows a typical SEM photomicrograph revealing the morphology of microgel particles. In order to measure the gel content and crosslinked density of the gels, especially chemically crosslinked gels and networks, solvent swelling technique is employed universally.

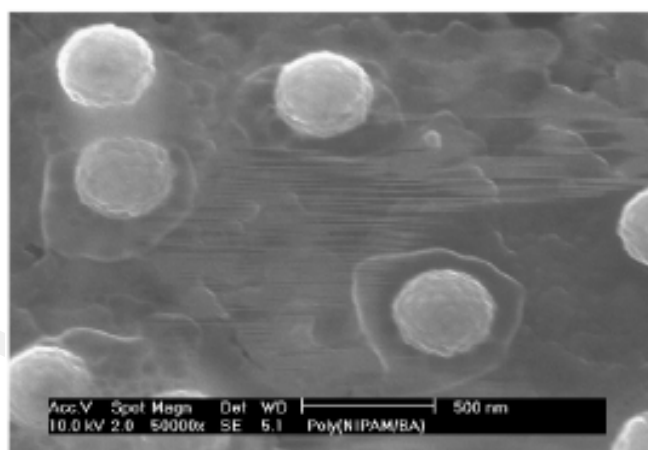


Figure 1.2: A high resolution SEM of poly-N-isopropylacrylamide microgel particles (reproduced from reference 23).

Dynamic mechanical analysis (DMA) is also an excellent technique for the characterization of different gels.²⁹ Using small deformation, an oscillatory strain (usually in shear) is applied to the material and shear storage modulus (G') and loss modulus (G'') are measured. A typical plot is illustrated in Figure 1.3a-b. For the entanglement networks, at low frequency (ω), $G' \sim \omega^2$ and $G'' \sim \omega^1$, while as the frequency is increased there is a “cross-over” in G' and G'' .²⁹ At the very low frequencies, in the “terminal zone” they flow as high viscosity liquids. In the case of chemically crosslinked gels and networks, generally there is no entanglement effects, and G' and G'' are parallel, and largely frequency insensitive, i.e. G' and $G'' \sim \omega^0$.²⁹

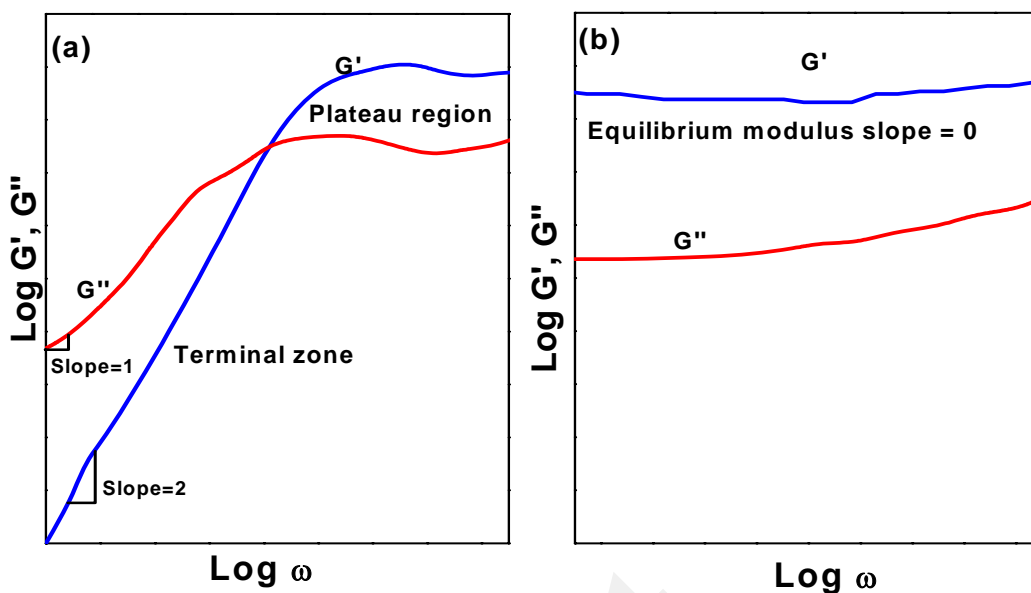


Figure 1.3: Dynamic mechanical spectra expected for the real (G') and imaginary (G'') parts of the shear modulus for (a) entanglement networks systems and (b) covalently crosslinked networks [adapted from reference 29].

1.4 General applications of polymer gels

Gels are commonly used for a great deal of applications such as controlled release drug delivery system, tissue engineering and regenerative medicine, materials responsive to specific molecules (glucose or antigens used as biosensors), diapers, contact lenses, medical electrodes, water gel explosives, breast implants, paints, coatings, adhesives, recyclable absorbents, bioreactors containing immobilized enzymes, bioassay systems, display devices, actuators, valves, sensors, artificial muscles for robotic devices, chemical memories, optical shutters, molecular separation systems, toys and as rheological or flow modifier for polymers.

1.5 Chemically crosslinked gels and networks: Routes of synthesis

Chemically crosslinked gels can be prepared by direct polymerization of monomers/co-monomers, free-radical polymer grafting, and crosslinking a polymer using suitable crosslinking agents such as sulfur, peroxide or radiation energy. Details of these processes are described below.

1.5.1 Polymerization

It is well known that polymerization of polyfunctional compounds can lead to insoluble, crosslinked polymer networks. At first the formation of three dimensionally

crosslinked polymer is indicated by a sharp rise in the viscosity of the system. Over a narrow interval of degrees of conversion, the polymerizing system loses its mobility due to chemical crosslinking of the macromolecules, and is transformed from the liquid to the highly viscous gelled state. The degree of conversion at which formation of spatially crosslinked polymer begins is called the degree of conversion for gel formation or simply the gel point, and the time required for the process, to reach this degree of conversion is called the gel time. The conditions for formation of gel in polycondensation reactions have been well studied. For example, the gel point is predicted satisfactorily by the statistical theory of Flory.^{2,33} In an elaborated form, this theory has been applied a number of times for determining the gel point in radical polymerization also.^{4, 34-38} Here, the gel point has been taken as the degree of conversion at which the weight average chain length (consequently the polydispersity index) approaches infinity. This phenomenon is also known as the auto-acceleration effect, Trommsdorff, Norrish-Smith effect or gel effect.³⁹⁻⁴¹

The gel effect is more effectively manifested in undiluted monomers than in diluted systems where the non-ideal or unusual effect may be minimized or even eliminated. In some monomer systems, the gel effect may be so high as to be accompanied with large rise in temperature. Using undiluted methyl methacrylate, acrylic acid and acrylonitrile, the gel effect associated with the polymerization process may even lead to explosion.³⁹ It is widely accepted that gelation is well described by the theory of percolation.^{42, 43} This theory has also been extended to include predictions for how the dynamic properties are expected to scale with time or frequency.^{44, 45}

Thus at the gel point, the frequency dependence of the dynamic complex shear modulus, G^* , and the storage (G') and the loss (G'') moduli, are expected to obey a power law over a large frequency range.⁴⁶

$$G^* \sim G' \sim G'' \sim \omega^n, \quad (1.1)$$

where the loss angle, δ , (defined from $\tan \delta = G''/G'$) is related to the power law exponent n as,

$$\delta = n\pi/2 \quad (1.2)$$

Further, the steady state viscosity, η_s , and the equilibrium shear modulus, G_s , are expected to scale with the reduced extent of reaction, ε as:

$$\eta_s = \eta_0 \varepsilon^i \quad (1.3)$$

and

$$G_s = G_0 \varepsilon^j \quad (1.4)$$

where, η_0 and G_0 are linked to the microscopic properties of the system and the exponents i and j relate to n as ($n = j/i + j$). Prior to gelation, the system is expected to behave as Newtonian liquid (with $G' \sim \omega^2$ and $G'' \sim \omega$) and after gelation as Hookean solid ($G' \sim \omega^0$ and $G'' \sim \omega$). Experimentally, Eqs. 1.1 and 1.2 have been verified for a large number of systems⁴⁷⁻⁴⁹ whereas fewer results have been reported for the relations described by Eqs. 1.3 and 1.4.⁴⁶ This reflects the experimental difficulties involved in determining the zero-time viscosity and modulus for reacting systems.

1.5.2 Polymer grafting

Free radical polymer-polymer grafting may also lead to gel formation. Due to the different possible combination and termination reactivities of each polymer backbone radical, polymer chains are crosslinked in a non-random manner. Such polymer-polymer grafting often takes place via free-radical mechanisms in solution or in melt phase. Chemical initiators such as peroxides and azo compounds and γ or electron beam radiation can initiate the radical generation. The initiator molecules are decomposed into primary radicals at an elevated temperature. These primary radicals and γ -rays or electron beams have sufficient energy to abstract or eject atoms from polymer backbones, thus generating backbone radicals. For a binary polymer system, two types of backbone radicals are formed: R^I and R^{II} with the radical centers located on the base polymer (I) and on the graft polymer (II), respectively. The radicals are terminated by combination to form cross-linkages. There exist three types of possible crosslinkages (I-I, II-II, I-II). In the case of a I-II type of crosslinkage, a graft polymer chain is said to be grafted onto a base polymer. Backbone radicals are continuously generated and terminated during the course of free-radical grafting. Successive crosslinking eventually leads to gel formation.⁵⁰

1.5.3 Crosslinking

Crosslinking is the process of chemically joining two or more molecules by a covalent bond. Crosslinks can be formed by chemical reactions those are initiated by heat, pressure, or radiation. For example, mixing of an unpolymerized or partially polymerized resin with specific chemicals called crosslinking agents results in a

chemical reaction that forms crosslinks. Crosslinking can also be induced in materials that are normally thermoplastic through exposure to a radiation source, such as electron beam, gamma-radiation, or UV light. For example, electron beam processing is used to generate crosslinked polyethylene, commercially known as XLPE.

The process of vulcanization is a type of chemical crosslinking reaction and changes the property of an elastomer to the tough and durable material which is required in many finished products such as tyres. This process is often called sulfur curing, and the term vulcanization originates from Vulcan, the Roman God of fire. However, sulfur curing can be a slow process taking around 8 hours to complete. The curing time can be substantially reduced by the addition of accelerators such as 2-mercaptobenzothiazole or tetramethylthiuram disulfide. Both of these contain sulfur atoms in the molecule that initiates the reaction of the sulfur chains with rubber. Accelerators increase the rate of cure by catalyzing the reaction of sulfur chains to rubber molecules.

Crosslinks are also the characteristics of thermosetting plastic materials. In most cases, crosslinking is irreversible, and the resulting thermosetting material will degrade or burn if heated, rather than melt. Especially in the case of commercially used plastics, such as epoxy and unsaturated polyester, once a substance is crosslinked, the product is very hard or impossible to recycle.

Crosslinking agents are employed in order to carry out crosslinking reactions. The term “crosslinking agent” is a very general one and covers molecules which bridge two polymer molecules during crosslinking, initiate a crosslinking reaction, are purely catalytic in their action and attack the main polymer chain to generate active sites. The first type includes vulcanizing agents, such as sulfur, selenium and sulfur monochloride, for diene rubbers, formaldehyde for phenolics, diisocyanates for reaction with hydrogen atoms in polyesters and polyethers, and polyamines for fluoroelastomers and epoxide resins. Perhaps the most well-known crosslinking initiators are peroxides, which initiate crosslinking in unsaturated polymers. Catalytic agents include acid for phenolic resins and amino-plastics and certain amines in epoxides. Peroxides are very useful active site generators, abstracting protons from the polymer chains. With some polymers, this leads to scission but in other cases crosslinking occurs.

1.6 Crosslinking of elastomers

In this thesis, chemically crosslinked gels and networks have been prepared by crosslinking or curing of various elastomers (more specifically rubber latices). The first commercial method of crosslinking has been discovered by Charles Goodyear in 1839.⁵¹ His process of heating rubber with sulfur, was first successfully used in Springfield, Massachusetts, in 1841. Thomas Hancock used essentially a similar process about a year later in England.⁵² Heating natural rubber (NR) with sulfur resulted in improved physical properties. However, the vulcanization time was still too long (>5 h) and vulcanizates suffered from certain disadvantages, e.g., age quickly. Since these early days, the process and the resulting vulcanized articles have been greatly improved. In addition to NR, many synthetic rubbers have been introduced over the years. Furthermore, many substances other than sulfur have been included as components of curing (vulcanization) systems. Figure 1.4 illustrates the timeline for the development of vulcanization technique.⁵³ The sulfur based crosslinking of elastomers has been well reviewed in the literature.⁵⁴⁻⁵⁶

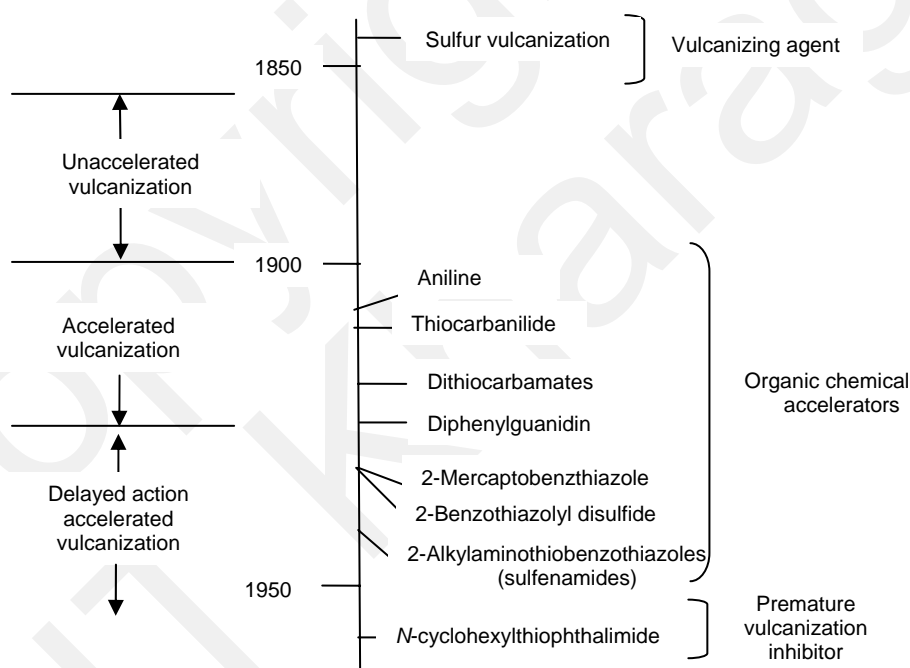


Figure 1.4: The timeline of development of the process of rubber vulcanization (adapted from reference 53).

The accelerated sulfur vulcanization of general-purpose diene rubbers [e.g., NR, styrene butadiene rubber (SBR), and butadiene rubber (BR)] and other rubbers, which are vulcanized by closely related technology [(e.g., ethylene–propylene–diene monomer (EPDM) rubber, butyl rubber (IIR), halobutyl rubber (XIIR) and nitrile

rubber (NBR)] comprises more than 90% of all vulcanizations. Frequently employed curing systems used in crosslinking of common elastomers are briefly reviewed in the following section.

1.6.1 Sulfur based curing systems

Initially, vulcanization was accomplished by heating elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr) for 5 h at 140°C. The addition of zinc oxide reduced the time to 3 h. Accelerator in concentrations as low as 0.5 phr have since reduced time to 1–3 min.⁵⁴ As a result, elastomer vulcanization by sulfur without accelerator is no longer of commercial significance. An exception is the use of about 30 or more phr of sulfur, with little or no accelerator, to produce molded products of hard rubber called ebonite. Organic chemical accelerators were not used until 1906, 65 years after the Goodyear–Hancock development of unaccelerated vulcanization (Figure 1.4), when the effect of aniline on sulfur vulcanization was discovered by Oenslager.⁵² Aniline, however, is too toxic for use in rubber products. Its less toxic reaction product with carbondisulfide and thiocarbanilide was introduced as an accelerator in 1907. However, most dithiocarbamates accelerators give little or no scorch resistance and therefore cannot be used in all applications. The history of the progress toward faster vulcanization with better control of premature vulcanization or scorch is illustrated in Figures 1.4. Accelerated sulfur vulcanization is the most widely used method. This method is useful to vulcanize NR, SBR, BR, IIR, NBR, chloroprene rubber (CR), XIIR, and EPDM rubber. The reactive moiety present in all these rubbers is essentially $(-RC=CR-)_n$, where R = H, X, CH₃.

Functionally, accelerators are classified as primary or secondary. Primary accelerators provide considerable scorch delay, medium fast cure, and good modulus development. Secondary accelerators, on the other hand, are usually scorchy and provide very fast cure. There are a wide variety of accelerators available to a compounder including accelerator blends. Zinc oxide (ZnO) is added to rubber compounds to activate sulfur vulcanization and thereby reduces the vulcanization time further. It is believed that accelerators and activators (ZnO and stearic acid) form an active accelerator complex, which subsequently interacts with sulfur to produce active sulfurating species necessary for subsequent crosslinking reaction.⁵²

Rubber latex can be cured efficiently by a simple method. Prevulcanized latex (PVL) is a very convenient source for the latex goods manufacturing industry. It is

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especially attractive for small-scale business units since it can be used directly for the manufacture of latex dipped goods, thus eliminating the need for extensive compounding other than the addition of antioxidant or pigment. The crosslinking of rubber in latex can be effected by the reaction with sulfur,^{57, 58} sulfur donors,⁵⁹ peroxides,⁶⁰ or radiation.⁶¹ Production of sulfur PVL involves heating of raw latex with various compounding ingredients such as an accelerator and sulfur until the required degree of crosslinking is obtained. Drying of prevulcanized latex produces a crosslinked film without the need for further vulcanization. The rate of prevulcanization varies with different vulcanization systems and the extent of prevulcanization has a profound influence on the final properties of the vulcanizate. The crosslinking reaction in latex takes place over a range of conditions such as temperatures from 20 to 90 °C for appropriate periods.⁶² As temperature is lowered, crosslinking takes place very slowly. By proper stabilization of latex, prevulcanization conducted at higher temperatures reduces the vulcanization time appreciably. Normally prevulcanization of rubber latex is carried out at 70-80 °C for 2-3 h duration.

1.6.2 Peroxide curing

NR can be transformed into a crosslinked state with dibenzoyl peroxide. However, little interest in peroxide cross-linking evolved until the development of fully saturated ethylene-propylene copolymers in the early 1970s.⁶³ The use of peroxides for the crosslinking of elastomers is limited to those that are stable during storage, safe to handle during processing but, on the other hand, decompose sufficiently fast at cure temperatures. In order to meet these requirements peroxides containing tertiary carbon atoms are most suitable, whilst peroxy groups bonded to primary and secondary carbon atoms are less stable.

Organic peroxides that are suitable for crosslinking elastomers are di-*tert*-butyl peroxide, dibenzoyl peroxide, dicumyl peroxide etc. In addition to the symmetrical peroxides, asymmetrical peroxides are also in use, as for example, *tert*-butyl perbenzoate, *tert*-butylcumyl peroxide, and some polymeric peroxides.⁶⁴ A further limitation with regard to the suitability of peroxides concerns the efficiency of crosslinking. Higher efficiencies are observed for those peroxides that form allylic radicals during homolytic decomposition.⁶³

Rubber latex can also be prevulcanized using organic peroxide. For example, NR latex has been cured by compounding with tert-butyl hydroperoxide and then heating at 60 °C for specific period of time.⁶⁵

1.6.3 Radiation crosslinking

Radiation crosslinking of polymers by various radiation sources, e.g. X-rays (soft and hard), gamma (γ) and ultraviolet (UV) rays and electron beam (EB), is a continuous process, which accomplishes a variety of reactions within a very short span of time.⁶⁶ It has been used in the cross-linking and modification of polymers for several decades successfully. Its major advantages are a high speed of conversion, cleanliness and very accurate process control. However, the unique advantage of ionizing radiations is that they provide a means of generating crosslinked structure from thermoplastics and elastomers without the aid of any chemical agent and heat, thus improving the mechanical and chemical properties of the original polymer. Physical and chemical changes in some polymers and mechanisms of crosslinking and chain scission under exposure to radiation energies have been investigated first in the 1950s.⁶⁷⁻⁷² The efforts are however still continuing today.

Crosslinking of polymers is done routinely by radiation technology. During radiation processing of polymers, free radicals are formed that can initiate a continuous process, in which monomers and polymers can lead to polymerization, crosslinking, back bone or side chain scissions, structural rearrangements etc. The final outcome of the reaction depends on the structure of polymer, dose absorbed and presence of other compounds in the material. The other factors influencing the crosslinking or the efficiency of crosslinking of polymeric materials are: presence of α -H (alpha hydrogen) in polymer backbone, ambient temperature, presence or absence of oxygen during irradiation, dose rate of radiation employed, degree of crystallinity of polymers, presence of crosslinking promoter or crosslinking enhancer such as maleimides, thiols, acrylic and allylic compounds etc.⁷³ The changes in polymers during the irradiation are rather complex. In general, there are always competing reactions occurring simultaneously. For example, crosslinking and main chain scissions compete, and the final outcome depends on which of the two prevails. The response of different elastomers to ionizing radiation is summarized in Table 1.1.

Table 1.1: Classification of elastomers according to their response to ionizing radiation

Elastomers predominantly crosslinking
Styrene butadiene rubber (SBR)
Chlorinated polyethylene (CM)
Chlorosulfonated polyethylene (CSM)
Polybutadiene rubber (BR or PB)
Natural rubber (NR)
Polychloroprene rubber (CR)
Acrylonitrile butadiene rubber (NBR)
Hydrogenated NBR (HNBR)
Ethylene propylene rubber (EPR)
Ethylene propylene diene monomer rubber (EPDM)
Polyurethanes (PUR)
Polydimethyl silicone (MQ)
Polydimethylphenylsilicone (PMQ)
Fluorocarbon elastomers based on vinylidene fluoride (FKM)
Elastomers predominantly degrading
Isobutylene isoprene rubber or butyl rubber (IIR)
Chlorobutyl rubber (CIIR)
Bromobutyl rubber (BIIR)

Radiation vulcanization of rubber latex especially that of NR latex (RVNRL) is a well established technique. RVNRL has several advantages over the sulfur prevulcanized latex, like the absence of nitrosoamines compounds,⁷⁴ better transparency,⁷⁵ very low cytotoxicity⁷⁶ and less rubber proteins those cause allergic response.⁷⁷ Radiation prevulcanization can be performed by using γ -rays as well as EB. Nevertheless, it needs more than 200 kGy to achieve maximum tensile strength.⁷⁸ In practice, radiation vulcanization accelerators or sensitizers are used to reduce the radiation dose at which maximum tensile strength could be obtained (D_v). Polyfunctional monomers which contain more than two polymerizable C=C double bonds within the molecule,^{79, 80} and monofunctional acrylic monomers are used as sensitizers.⁸¹ Among the monofunctional monomers, n-butyl acrylate (BA)

is the most effective sensitizers because it not only imparts superior physical properties at lower D_v but also unreacted BA is not retained in the final product.⁸² It can effectively bring down the D_v of NR latex to as low as 20 - 30kGy.

1.7 Nanofillers, nanocomposites and nanocomposite gels

1.7.1 Nanofillers

The nanofillers, which have at least one dimension in nanometric level, used in polymer nanotechnology are usually inorganic fillers, carbon nanotubes, carbon nanofibers etc.

Nanofillers can have different shapes which can be categorized as:

- ❖ **Spherical** [e.g., nanosilica, polyhedral oligomeric silsesquioxanes (POSS)]
- ❖ **Rod / fibre** (e.g., synthetic whiskers, carbon nanotubes, boehmite, sepiolite)
- ❖ **Sheet / platelet** (e.g., layered silicates such as smectite group clays, synthetic mica etc.).

In this thesis, layered silicate namely *unmodified montmorillonite clay* has been used to prepare *nanocomposite gels*. Hence, details of unmodified montmorillonite clay are elucidated below.

The silicates are the largest, the most interesting and complex class of minerals by far. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates. The maximum varieties of layered silicates are aluminosilicates with a layered structure of silica (SiO_4^{4-}) tetrahedral sheets bonded to alumina (AlO_6^{9-}) octahedral ones. These sheets can be arranged in a variety of ways; in smectite clays, a 2:1 ratio of the tetrahedral to the octahedral is observed. *Montmorillonite* (MMT) is the most common smectite group of clay.^{83, 84}

The structure of montmorillonite $((\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2, n\text{H}_2\text{O})$ is derived from the original pyrophyllite structure by partial substitution of the trivalent Al-cation in the octahedral layer by the divalent Mg-cation. Because of the difference in charge between the Al and Mg ions, the central layer of these 2:1 silicates is negatively charged and the negative charge is balanced by group I or II metal ions present between the 2:1 sheets. These ions do not fit in the tetrahedral layer such as in mica and the negative charge is located in the octahedral layer, thus making the attractive forces between the layers weaker. Therefore, the layers are not collapsed upon each other such as in mica. Montmorillonite can absorb water between the

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charged layers because of this weak binding and the large gallery spacing, and it is therefore a member of a group of water-expandable clay minerals known as smectites or smectite clays. As clearly shown in Figure 1.5, in MMT, oxygen atoms from each alumina octahedral sheet also belong to the silica tetrahedral ones, the three of them consisting of ~1 nm thin layer.

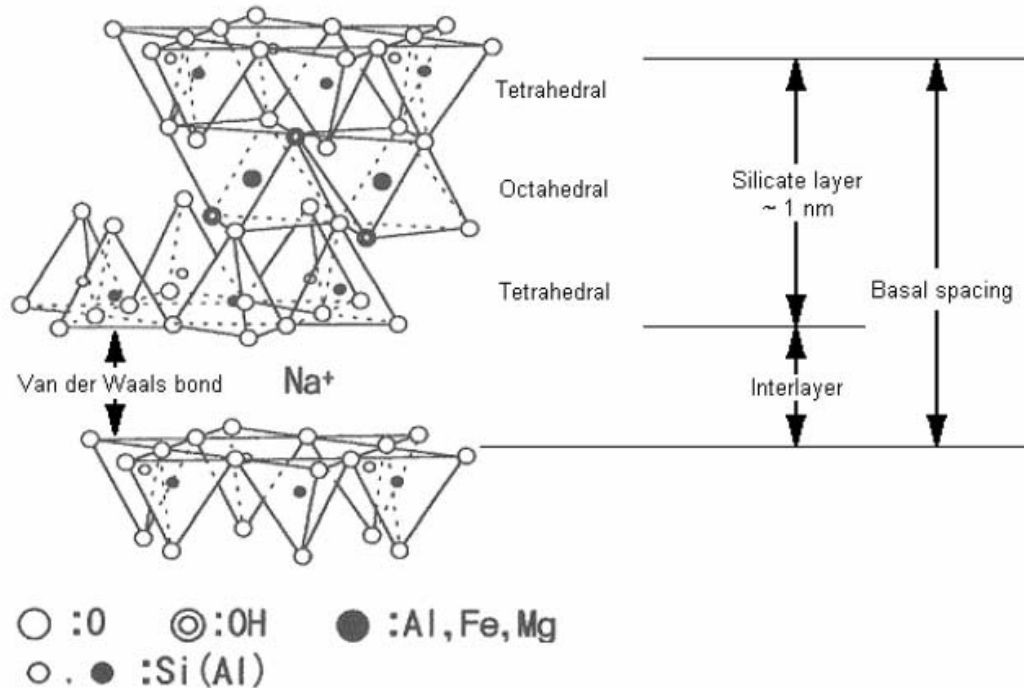


Figure 1.5: Structure of a typical MMT layer (adapted from reference 84).

These layers are in turn linked together by van der Waals forces and organized in stacks with a regular gap between them called 'interlayer' or 'gallery'. Within the layers, isomorphic substitution of Al^{3+} with Mg^{2+} or Fe^{2+} generates an excess of negative charge, the amount of which characterizes each clay type and is defined through the cation exchange capacity (CEC). The CEC value for smectite depends on its mineral origin and is typically 65-150 meq/100g. In natural clays, ions such as Na^+ , Li^+ or Ca^{2+} in their hydrated form balance this excess negative charge; this means natural MMT is only compatible with hydrophilic polymers. General characteristics of these materials include 20 layers of ~1 nm thickness and lateral dimensions ranging from ~25 nm to ~5 μm .⁸³

The mechanical properties of a single silicate layer are often assumed similar to materials like glass and mica, and elastic moduli around 170-250 GPa are frequently mentioned in the literature.⁸⁵ These silicate layers allow for the retention of

aspect ratios in excess of 100-1000 during normal polymer processing, something that is exceedingly difficult to achieve with conventional fillers. On the other hand, such systems also benefit from the extremely large amount of available interface and interphase polymer produced due to full dispersion of nanometer thick silicate layers in polymer matrix.

1.7.2 Nanocomposites

The term 'nanocomposite' refers to every type of composites materials having nanofillers as one of the components. More specifically, polymer nanocomposites are polymeric composite materials that are reinforced with rigid inorganic/organic particles, which have at least one dimension in the nanometer size-range. Extensive research has been done in the field polymer based nanocomposites in the last two decades.⁸⁶⁻⁹⁰

Nanocomposites show excellent properties at very low filler loadings (<10 wt %). Nanofillers are necessarily nanoscopic and have a high specific surface area. The large specific surface area is one of the reasons why the nature of reinforcement is different in nanocomposites.⁹⁰ In conventional micro- and macro-composites, the properties are dictated by bulk properties of both matrix and filler. This relationship between the properties of the composite and the properties of the filler is what leads to the stiffening of the matrix and lowering of overall elongation. In the case of nanocomposites, the properties are more tied to the interface. The terms like "bound polymer", and "interphase" have been used to describe the polymer at or near the interface. Interfacial structure is known to be different from bulk structure, and in polymers filled with nanofillers with extremely high specific surface area, most of the polymer are present near the interface, even with only a small weight fraction of filler. If the interaction at the interface is a strong one, or if the structure of the interfacial polymer is very different from the bulk, markedly different properties in the material as a whole can be observed. These changes have a fundamentally different origin than those found in micro- and macrocomposites, where the volume of the interphase is only a small fraction of the overall volume of the material.

Over a period of time, this research laboratory has made significant contribution to this emerging field, especially in elastomer based nanocomposites.⁹¹⁻¹⁰⁰ These include but not limited to NR,⁹¹ SBR,⁹²⁻⁹⁴ NBR,⁹⁴ PBR,⁹⁴ Brominated isobutylene-co-p-methylstyrene (BIMS) rubber,⁹⁵ Acrylic rubber,⁹⁶ Epoxidized

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Natural Rubber (ENR),⁹⁷ FKM rubber,⁹⁸ Ethylene Vinyl Acetate (EVA),⁹⁹ and Polyurethane¹⁰⁰ based nanocomposites, using unmodified and organically modified layered silicate clays, sepiolite clay, nanosilica, carbon nanotubes, carbon nanofibers, POSS, nano Zinc Oxide (ZnO) etc. The additional benefits of nanocomposites compared to the polymers filled with traditional fillers (besides the general benefits of conventionally filled polymers) are as follows:

- Increased tensile modulus at very low filler concentration; 5 % nanofiller can typically provide the similar increase in modulus as 40 % conventional filler (such as carbon black, silica, talc) or 15 % glass fibres¹⁰¹
- Lower density, because the nanofillers are used in much smaller quantities
- Increased barrier properties¹⁰⁰
- Reduced rate of moisture uptake in polymers such as in polyamides, because of the barrier property⁸⁶
- Improved thermal stability and reduced flammability¹⁰²⁻¹⁰⁴

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when layered clay is associated with a polymer as shown in Figure 1.6a-c. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite (Fig. 1.6a) is obtained, whose properties stay in the similar range as traditional microcomposites. Beyond this classical family of composites, nanocomposites with two different types of structures can be recovered. Intercalated structure (Figure 1.6b) in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained (Figure 1.6c).^{88, 89}

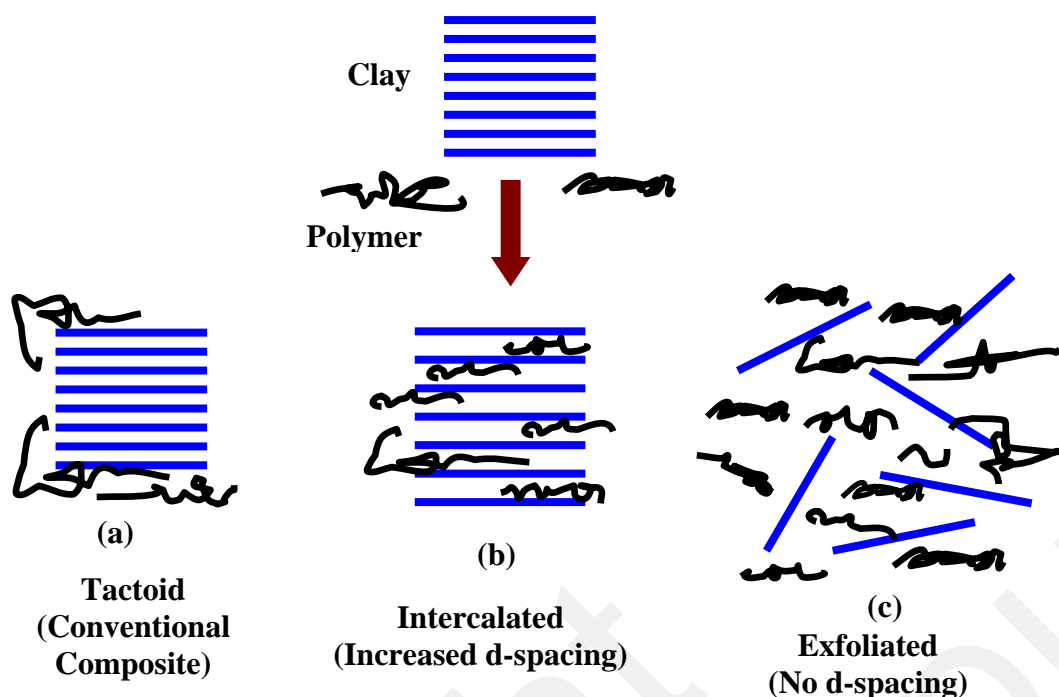


Figure 1.6: Different microstructures of polymer-clay nanocomposites: (a) phase separated aggregated macro or micro-composites, (b) expanded inter-layer spacing in intercalated microstructure and (c) completely separated / de-laminated clay platelets in exfoliated morphology.

1.7.3 Nanocomposite gels

Nanocomposite gels (NC) are the most recent addition to the family of polymer gels. NC gels are mostly clay/polymer nanocomposite hydrogels joined by clay platelets without organic crosslinkers.¹⁰⁵ The NC gels have an important advantage of simplicity of synthesis. The mechanical strength of NC gels increases with increasing clay content as illustrated in Figure 1.7 and it could overcome the limitations of the mechanical properties of conventional polymeric hydrogels.¹⁰⁶ However, most NC gels have been synthesized with low clay contents because of the high viscosity of the aqueous clay dispersion at higher clay concentrations. The nanocomposite gels consisting of poly-*N*-isopropylacrylamide (PNIPA) and inorganic clay have been made to achieve the best mechanical properties together with excellent swelling, optical transparency, and stimuli sensitivities.¹⁰⁶ Haraguchi et al. have extensively studied NC gel systems and revealed that NC gels having a unique organic (polymer)/inorganic (clay) network structure, and consisting of exfoliated clay uniformly dispersed in an aqueous medium with a number of flexible polymer chains linking them together.¹⁰⁶⁻¹⁰⁹ These have mechanical and swelling properties that can be controlled to a large extent by altering their compositions.^{106, 108} Also, a

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mechanism for forming the organic/inorganic network structure during NC gel synthesis was proposed.¹¹⁰ Further, it was found that NC gels with such excellent properties could not be prepared using other procedures such as mixing and using other inorganic nanoparticles such as silica and titanium. That is, NC gels were only realized by free-radical polymerization in the presence of inorganic clay. NC gels exhibit great potential as advanced soft materials, as reported elsewhere, such as temperature-sensitive actuators¹¹¹ and raw materials for layered porous solids.¹¹² However, there is no reported work on chemically crosslinked elastomer based NC gels prepared by latex blending and prevulcanization process.

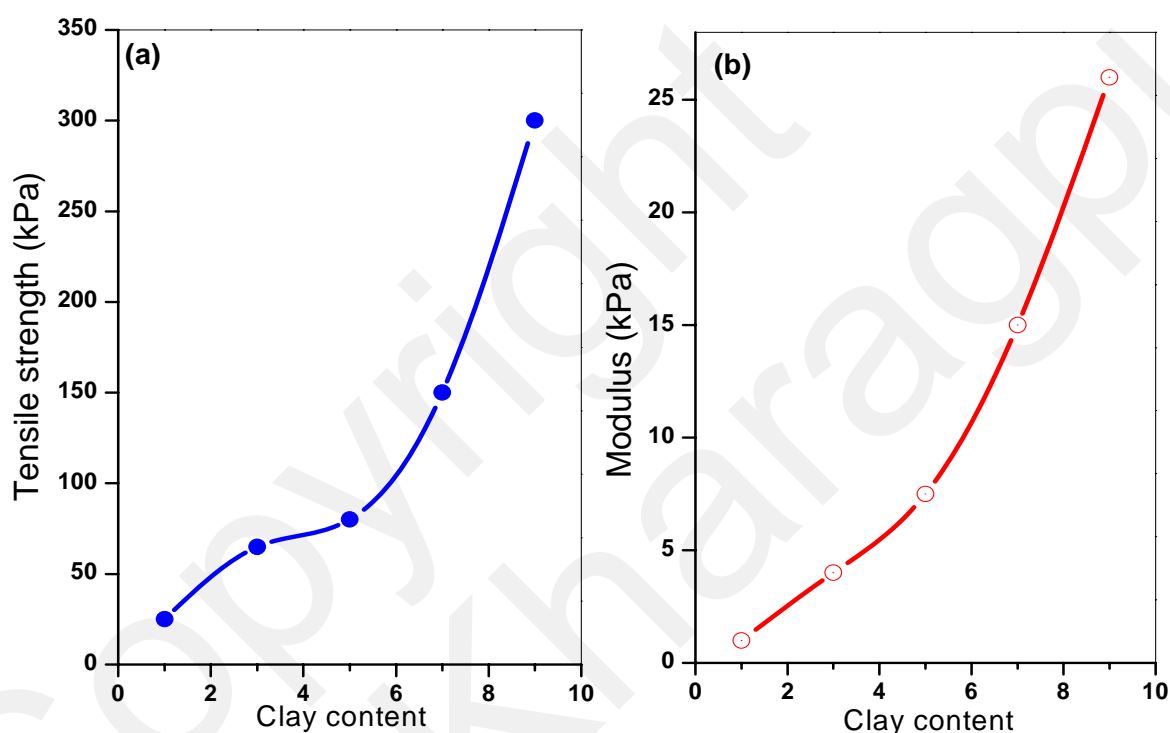


Figure 1.7: Variation in mechanical properties such as (a) tensile strength and (b) modulus, by changing clay content of PNIPA based NC gels (adapted from reference 106).

1.8 Effect of gels in elastomers

The open literature on elastomeric gels and its effect on elastomer properties are strikingly scanty. However, the subject is of great importance especially from the industrial application point of view. It is well known that crosslinked gel particles are added into the elastomers in order to influence various properties such as processability of virgin elastomers. It is an industrial practice to incorporate gels in to rubber to reduce die swell, to have better profile and higher extrusion rates. The

advantages of such process have been described by Hofmann.¹¹³ In general, the improvements are in elastic responses, such as decreased swelling of extrudates, smoother surface finish, and better shape retention. These effects are similar to the ones produced by the addition of carbon black or other particulate fillers. In some cases a decreased time and energy of mixing with carbon black are achieved with the use of gels.

Using this concept, several researchers studied the rheological properties of gel filled elastomers. Rosen and Rodriguez¹¹⁴ measured the steady-state viscosities of poly (ethylacrylate) containing up to 40% of its own of gel particle, over a wide range of shear rates. The data were summarized in a master curve with two empirical parameters, one being the assumed value of the yield stress and the other a modified expression for the zero-shear viscosity. Both parameters increased with increase in crosslink density. However, the yield stress decreased and the zero-shear viscosity increased with increasing particle size of the gel particles. In a similar study, Nakajima and Collins reported the flow behavior of nitrile rubber (NBR) containing divinyl benzene crosslinked gel particles prepared by emulsion polymerization.¹¹⁵ The gel loading in the NBR was varied from 25-100%. The flow behavior of these materials was examined with a capillary rheometer at 70,100, and 125 °C for the shear rate range of 3-3000 s⁻¹. It was observed that within the experimental shear rate range, the viscosity decreased with increasing gel content. The reduction in viscosity was attributed to the presence of supra-molecular flow units which have larger size than the gel particles. In another work, an investigation on the effect of gel and nonrubber constituents on the extrusion behavior of Guayule rubber was carried out.¹¹⁶ It was found that at 140 °C, presence of gel increases the viscosity of guayule rubber at low shear rates. It was also noted that at 120 °C, the effect of gel is noticeable at high extrusion rates in increasing the viscosity. This was attributed to the onset of flow-induced crystallization. From the above examples, it is quite clear that the effect of gel particles on the rheological properties of rubber is not the same for all elastomers. Moreover, the properties will depend very much on the size, shape and chemical nature of gel particles, which are not so easy to characterize. Although a few researchers including those from this laboratory have worked on the subject of crosslinking of elastomers, gels and their influence on elastomers, no study can be found on the topic of this research, especially on nanogels and nanocomposite gels.

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Hence, further study is needed in this area to investigate the effect of well characterized gels in elastomers.

In addition to processing behavior, crosslinked gel particles greatly influence various physical properties of virgin elastomers. The influence of gel on the crystallization, stress relaxation and orientation behavior of NR was investigated by Bhowmick et al.¹¹⁷ It was found that the gels reduce the overall crystallinity as measured by differential scanning calorimetric experiments. Gels also had a stiffening effect on the tensile relaxation modulus and decreased the rate of relaxation significantly. Birefringence, which is a measure of orientation and stress-induced crystallization, increased with time for samples containing gels especially at high elongation. Similar observation was also noted in stress relaxation experiments of unfilled virgin NR.¹¹⁸ The gels increased the relaxation modulus and slightly decreased the rate of relaxation in NR. The effect of individual microgel particles and macrogel phase was found to be similar. The effect of gel on the green strength of NR during storage was studied by Kawahara et al.¹¹⁹ Formation of chemical crosslinks between phospholipids was attributed to the increase in green strength during storage. In order to study the mechanical and dynamic mechanical properties of microgel containing elastomers at low strain, polystyrene and polybutadiene microgels were incorporated into NR and SBR matrix.¹²⁰ It was observed that depending on its chemical nature, microgels increase the Young's modulus and dynamic storage modulus of virgin elastomers. The mechanical effects were qualitatively related to the state of clustering of microgels which is governed by the particle size and the interfacial tension. In another work, the strain-time correspondence principle for large deformations was successfully tested for NBR containing gel particles.¹²¹ Also, the effect of different types of gels on the deformational behavior of polyvinyl chloride and NBR blend was investigated by dynamic shear measurements.¹²² It was noted from the experiments that the sample having higher gel content appeared to be more elastic. Additionally, it was found that highest degree of strain hardening was observed with the blend containing macrogels followed by the blends containing microgel. *However, as described above the current literature is devoid of any investigation concerning the effect of quasi-nanogel and nanogel particles on the properties of virgin elastomers. Moreover, literature reports relating the crosslink density of the gels with the properties of gel filled elastomers are completely missing.*

Several patent literature also describe the usefulness of gels in elastomers from the practical application point of view. It has been reported that conventional fillers such as carbon black and silica in rubber mixtures can be replaced quantitatively or partially by elastomeric gels.¹²³ Due to the low density of the rubber gels ($\rho < 1$ g/cc), corresponding vulcanizates have a lower weight than the mixtures filled with carbon black ($\rho < 1.8$ g/cc) or with silica ($\rho < 2.1$ g/cc). In addition, polybutadiene rubber gels contribute to high rebound resilience at different temperatures.¹²⁴ This property is useful in preparing low-damping rubber articles, especially tire components. Again, use of styrene butadiene rubber gels leads to improved tire tread formulations which show advantageous wet-skid behavior/rolling resistance relationship.¹²⁵ The presence of NBR microgel particles in uncrosslinked butyl rubber contributes to the development of molded vulcanizates which have low gas permeability and acceptable mechanical properties coupled with good processability.¹²⁶ Crosslinked particulate gels made from NR, SBR, PBR, NBR and CR and their mixtures are now added in tire sidewall compound formulations up to about 30phr for attaining benefits already outlined above.¹²⁷ These compounds show reduced hysteresis loss and improved abrasion resistance along with increased modulus. In all these cases, gels are formed by emulsion polymerization in latex state or by post crosslinking after polymerization. The process of post crosslinking has been already described in the preceding sections. Use of hydrogels for making elastomeric seal materials for well-bore application is also listed recently in the patent literature.¹²⁸

1.9 Scope and objectives of the present work

The literature search carried out reveals that the addition of gel particles in various elastomer matrices generally improves the processability along with many physical properties. A great deal of such works has found important industrial applications. However, there is a dearth of literature investigating the effect of well characterized gels in elastomers. It was pointed out earlier that proper characterization of gels is often difficult due to many reasons. Hence, researchers of earlier works have mostly used gels of different chemical nature (physically crosslinked as well as chemically bonded) and of a wide range of sizes (from microgels to macrogels) without much control. As a result, any insight on the inter-relations between the properties of individual gels (like modulus, crosslink density, particle size etc.) and

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the properties of gel filled elastomers is obscure. But these are the key factors for understanding the performance of gel filled elastomers. Also, the reinforcement aspect of crosslinked gels has not been reported in the literature till date. Moreover, conventional rheological studies of virgin polymer have been conducted with fillers or particulate inclusions which are rigid with very high modulus (in GPa). Extensive research work has not been carried out to elucidate the effect of relatively low modulus and semi-rigid or deformable gel particles on the viscosity of virgin polymer. Additionally, there is no reported work showing the effect of elastomeric nanogels and nanocomposite gels on the properties of virgin elastomers. In this thesis, an attempt has been made to bridge these gaps.

Considering all the above points, an in-depth investigation has been carried out to understand the effect of well characterized gels in virgin elastomers in this thesis. For this purpose, quasi-nano (near nano) and nano-sized gels have been prepared from NR latex and SBR latex, respectively, using sulfur prevulcanization technique. Rubber latices have been used to gain control over the particle sizes of gels and to generate discrete gel particles. NR and SBR matrices have been chosen due to their easy availability and commercial importance. Sulfur to accelerator ratio in the prevulcanization recipes has been varied to form gels having gradient in physical and chemical properties. These as-prepared gels have been extensively characterized using dynamic light scattering (DLS) technique for particle diameter and size distribution, solvent swelling for gel content and crosslink density, atomic force microscopy (AFM) and transmission electron microscopy (TEM) for morphology of gel particles, and measurements of mechanical and dynamic mechanical properties. The influence of these well characterized gels on the rheological and processing behavior of NR and SBR has been studied in detail using a capillary rheometer, at different shear strain rates and temperatures corresponding to practical processing conditions. The mechanical and dynamic mechanical properties of these gel filled systems have also been examined extensively. In order to compare the influence of the chemical nature of crosslinking in the gels, electron beam (EB) crosslinked gels have been prepared from the NR latex. These gels have carbon-carbon crosslinks instead of sulfidic and carbon-sulfur crosslinks found in sulfur prevulcanized gels. These EB crosslinked NR gels have been characterized following the aforementioned procedures as well. Moreover, the influence of EB crosslinked NR gels on the properties of virgin NR has been reported in this thesis, for the first time.

In a logical continuation of the above work, inter-mixing of gels and matrices has been carried out in order to ascertain the role of dissimilar gel-matrix interaction. Crosslinked NR gels have been added into the virgin SBR matrix and SBR gels have been incorporated in the virgin NR matrix. The morphology of the gel filled elastomers has been studied using a combination of energy dispersive X-ray sulfur mapping, AFM and TEM. Mechanical, dynamic mechanical and thermal properties of the gel filled systems have been investigated in detail with an emphasis on rheological properties and processing behavior. Contemporary particulate composite reinforcement models have been used to understand the reinforcement behavior of these nanogels. This type of investigation is not available in the current literature.

Literature review reveals that no published work is available on the preparation of nanocomposite gels from rubber latices and their effect on properties of virgin elastomers. In the later part of the thesis, nanocomposite (NC) gels have been prepared from NR and SBR latices by a unique latex blending technique using unmodified montmorillonite clay and have been subsequently characterized. The influence of these NC gels on the properties of the virgin elastomers has also been studied in great detail.

Also in this thesis, an important elastomeric property, which is intimately related to the processability, namely dynamic stress relaxation behavior, of the above-mentioned systems has been explored elaborately. There is no reported work on the stress relaxation behavior of nanogel and NC gel filled elastomers. Moreover, an attempt has been made to understand the mechanism of stress relaxation behavior.