EFFECT OF *IN-SITU* VULCANIZATION OF STYRENE MODIFIED NATURAL RUBBER IN ADHESIVE AND RUBBER TOUGHENED POLYSTYRENE APPLICATIONS

by

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[I]	Concentration of initiator
[S]	Concentration of surfactant
[M]	Concentration of monomer in the monomer-polymer particles
^{60} Co	Cobalt-60
a	Total notch length
A	The absorbance peak height of stretching vibration of carbon-carbon double bond of aromatic group in styrene at 1600 cm^{-1}, which appear in SNR samples and
A_1	Mass of styrene monomer used for the polymerization reaction
A_2	Mass of non-reacted styrene
a’	Intrinsic flaw size
A_0	The absorbance peak at 1600 cm^{-1}, which appear in the monomer styrene.
B	Sample depth
E	Young’s modulus
E’	Storage modulus
E”	Loss modulus
E_f	Flexural modulus
F	Maximum force in the force-deflection trace
Fmax	Load at crack growth initiation
I	Initiator (Chapter 2, section 2.1.2)
I	Impact strength (Chpter2, section 2.4.6)
Kc	Fracture toughness

k_p	propagation rate constant
M	Monomer
$M_j\bullet$	Propagating free radical
N	Number of the particles per unit volume
P	Polymer
P^*_n	Polymer chain with reactive site (*) and degree of polymerization of n
P^*_{n+1}	Polymer chain with a reactive site (*) and degree of polymerization of n+1
P_c	Load at failure
P_{gy}	The load at the general yield point
phr	Part per hundred
$R\cdot$	Radical
R_i	Rate of initiation
R_p	Rate of propagation
R_t	Rate of termination
S	Initiation stiffness (Figure 2.12)
S	Beam span (Figure 2.8 a)
sec.	seconds
T	Temperature
t_{90}	Optimum cure time
U	Elastic energy
U_c	Elastic energy at critical stage
U_p	Elastic energy corresponds to the area under the rectangle as shown in Figure 2.10

U_y	Elastic energy at yield point
U_y*	Elastic energy for ductile behavior Type B
V_1	Value of the property after aging
V_2	Value of the property before aging
W	Sample width
W_p	Work done in deforming the bar plastically
wt.	Weight
X	Deflection at the center of the beam
X/S	Deflection to span-ration
X_c	Rupture of the bar occurs at a critical deflection to-span ration
X_n	Number-average number of units per chain
X_p	The deflection subsequent to general yield
γ	gamma
σ_c	Critical stress in a centrally loaded and simply supported beam(three point bending)
σ_{max}	Maximum stress
σ_y	Yield stress in a centrally loaded and simply supported beam(three point bending)

LIST OF ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene
ATR	Attenuated total reflectance
AXO	**A**ntioxidant used is butylated reaction product of p-cresol and dicyclopentadiene
CBS	N- cyclohexyl benzothiazole 2-sulpheamide
CMC	Carboxymethylcellulose (Section 2.5.1)
CMC	Critical micelle concentration
CV	Conventional vulcanization system
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DPG	Diphenylguanidine
DPNR	Deproteinized natural rubber
DR	Diffuse reflectance
DRC	Dry rubber content
DSC	Differential scanning calorimeter
EB	Elongation at break
E-DPNR	Enzymatic-deproteinized natural rubber
EPDM	Ethylene propylene diene methylene
EV	Efficient vulcanization system
FTIR	Fourier-transform infrared spectroscopy
H	Allylic hydrogen
H_2O	Water

HANR	High ammonia natural rubber
HIPS	High impact polystyrene
IPN	Interpenetrating polymer network
IPPD	N-Isopropyl-N-phenyl-p-phenyllendiamine
KBR	Potassium bromide
KOH	Potassium hydroxide
LEFM	Linear elastic fracture mechanics
LIPN	Latex interpenetrating polymer network
MBT	2-mercautobenzothiazole
MBTS	Dibenzothiazol disulfide
MMA	Methyl methacrylate
MMT	Montmorillonite clay
$N_2H_8O_8S_2$	Ammonium persulfate
n-BA	n-butyl acrylate
NH3	Ammonia
NPSBR	Nano powdered styrene-butadiene rubber
NR	Natural rubber
OsO_4	Osmium tetraoxide
PBA	Poly (n-butyl acrylate)
PE	Polyethylene
PI	Polyisoprene
PIB	Polyisobutylene
PMMA	Polymethyl methacrylate

PP	Polypropylene
PS	Polystyrene
PSA	Pressure sensitive adhesive
R	Rubber chain
R1	Refers to mixed system where potassium oleate (aqueous) and antioxidant(aqueous) is added by using *in situ* process in SNR latex, and the dry SNR film is subsequently mix with sulfur (solid) by two roll mill.
R2	Refer to the system where sulfur (aqueous), potassium oleate (aqueous) antioxidant (aqueous) is added by using *in situ* vulcanization.
R3	Refer to SNR4 recipe in Table 3.11, basically is the sulfur vulcanization formulation of the *in situ* vulcanization.
Ref.R	Refer to Table 3.8. SNR is mixed by two roll mixed, and subsequently melt blending with PS. This type of mixing sequence is known as modified dynamic vulcanization.
RSxR	Initial polysulphidic crosslinks
RSyX	Rubber bound intermediate
S	Sulfur
SAN	Styrene-co-acrylonitrile
SB	Styrene butadiene
SBR	Styrene butadiene rubber
SEM	Scanning Electron Microscopy analysis
Semi-EV	Semi-efficient system
SNR	Styrene modified natural rubber
TBSS	N-tert-butyl-2-benzothiazylsulphenamide
TMTD	Tetramethyhhiuram disulphide

TPE	Thermoplastic elastomer
TS	Tensile strength
TSC	Total solid content
U-DPNR	Urea-deproteinized natural rubber
UFPR	Ultra fine powdered rubber
X	Accelerator residue
ZDC	zinc dithiocarbamates
ZDEC	Zinc-diethyldithiocarbonate
ZDEDC	Zinc diethyldithiocarbamate
ZDMC	zinc dimethvldithiocarbamate.
ZnO	Zinc oxide
***DPNR**	Is a control batch contain DPNR, prepared by *in situ* vulcanization with sulfur vulcanization system
^{13}CNMR	Carnon-13 Nuclear magnetic resonance
^{1}HNMR	Hydrogen-1 Nuclear magnetic resonance

KESAN PEMVULKANAN *IN SITU* BAGI GETAH ASLI TERUBAHSUAI DENGAN STIRENA SEBAGAI APLIKASI-APLIKASI PELEKAT DAN POLISTIRENA DIPERKUAT GETAH

ABSTRAK

Kajian ini mengenai pencapaian penyediaan formulasi pemvulkanan bagi getah asli terubahsuai dengan stirena (SNR) dengan teknik pemvulkanan *in situ* . Sintesis bagi SNR telah disediakan dengan pempolimeran emulsi. Getah asli teryahprotein (DPNR) digraftkan dengan monomer stirena dengan penambahan amonium persulfat sebagai pemula. SNR vulkanizat telah disediakan dengan kaedah pemvulkanan dan agen-agen pemvulkanan yang berbeza. Peringkat pertama kajian ini melibatkan penyediaan SNR dengan pempolimeran emulsi dalam nisbah monomer stirena dan DPNR sebanyak 25%:75%. Untuk aplikasi pelekat, kesan tiga sistem pra-pemvulkanan, pemvulkanan lazim (CV), pemvulkanan separa cekap (*semi*-EV) dan penvulkanan cekap (EV) terhadap sifat-sifat tensil SNR pra-vulkanizat diperhatikan. Sistem pemvulkanan *semi*-EV menunjukkan ciri-ciri yang sesuai sebagai pelekat SNR pra-vulkanizat. Sistem pemvulkanan *semi*-EV menunjukkan keputusan yang sama pada pemanjangan takat putus (EB) berbanding dengan sistem pemvulkanan CV dengan kekuatan tensil yang rendah. Kesan pengubahsuaian pH dalam sistem pemvulkanan *semi*-EV menunjukkan sifat pelekatan yang baik dalam SNR pada pH 12 dan sesuai untuk digunakan dalam aplikasi pelekat. Bagi aplikasi bahan diperkuat getah, proses pemvulkanan dengan sulfur sebagai agen sambung-silang telah meningkatkan kekuatan hentaman adunan PS/SNR vulkanizat.

Keputusan menunjukkan adunan dengan kandungan getah 20% mempunyai kekuatan hentaman hampir sama dengan HIPS manakala adunan dengan kandungan getah sebanyak 30% adalah lebih liat daripada HIPS. Apabila komposisi getah dalam adunan ditingkatkan dari 10% hingga 30%, tenaga dalaman dan takat pemutusan pelenturan juga konsisten dengan kekuatan hentaman yang diperolehi. Morfologi pada PS/SNR20% dan PS/SNR30% menunjukkan fasa getah adalah dalam taburan berterusan dan sekata berbanding dengan adunan PS/DPNR. Kalorimetri pembezaan penskanan (DSC) menunjukkan terdapat pencangkukkan berlaku pada SNR9H. Walau bagaimanapun, adunan PS/SNR20% and PS/SNR30% adalah tidak serasi dan fasa terpisah wujud dalam adunan. Analisis dinamik mekanikal (DMA) menunjukkan adunan PS/SNR30% mempunyai interaksi yang baik antara SNR dengan matrik PS, dengan meningkatkan maksimum tanδ dalam kawasan getah. Pada fasa kaca PS di bahagian suhu (90 ^{0}C-150 ^{0}C), adunan PS/SNR30% mempunyai modulus simpanan dinamik terendah berbanding dengan PS/SNR10% dan PS/SNR20%. Kehadiran kandungan getah yang tinggi dalam adunan telah mengurangkan kekakuan rantaian PS. Keliatan rekahan bagi adunan PS/SNR20% mempunyai nilai Kc yang rendah berbanding HIPS tetapi menunjukkan keliatan yang tinggi kerana mempunyai takat putus kelenturan yang lebih tinggi. Rintangan penuaan bagi adunan PS/SNR dengan 20% dan 30% kandungan getah telah menunjukkan kekuatan hentaman yang lebih baik daripada HIPS selepas prosess penuaan. SNR yang disediakan dengan pemvulkanan *in situ* menunjukkan peningkatan yang baik dalam sifat-sifat pelekat sensitif tekanan dan kekuatan hentaman. Aplikasi-aplikasi SNR sebagai pelekat dan pengubahsuaian hentaman telah tercapai.

EFFECT OF *IN SITU* VULCANIZATION OF STYRENE MODIFIED NATURAL RUBBER IN ADHESIVE AND RUBBER TOUGHENED POLYSTYRENE APPLICATIONS

ABSTRACT

In this research, establishment of vulcanization formulation of styrene modified natural rubber (SNR) vulcanizates by using *in situ* vulcanization technique was investigate. The synthesis of SNR was prepared through emulsion polymerization. Deproteinized natural rubber latex (DPNR) was grafted with styrene monomer with the addition of ammonium persulfate as initiator. SNR vulcanizate was prepared with different vulcanization methods and vulcanization agents. The first stage of the work involved in established the emulsion polymerization of SNR with ratio of styrene monomer and DPNR ratio 25%: 75%. For adhesive application, the effect of three pre-vulcanization systems, conventional vulcanization (CV), semi-efficient vulcanization (semi-EV), and efficient vulcanization (EV) on tensile properties of SNR pre-vulcanizates were observed. The semi-EV vulcanization system showed suitable properties as SNR pre-vulcanizates adhesives. It showed similar trend in elongation at break (EB) compared to CV system with low tensile strength (TS). The effect of pH modification on semi-EV pre-vulcanized system showed the SNR with good anchorage ability at pH 12 suitable for adhesive application. For rubber toughened material application, *in situ* vulcanization process with sulfur as crosslinking agent had improved the impact strength of the PS/ SNR vulcanizates. The results showed at 20% of rubber content has comparable impact strength with HIPS while 30% of rubber content showed more ductile than HIPS. Addition of more rubber contents from 10% increased to 30% showed an increased in internal energy and deflection at break which consistent with the impact strength

obtained. The stained photographs of PS/SNR20% and PS/SNR30% showed co-continuous rubber phase and more homogenous than PS/DPNR blend. Differential scanning calorimetry (DSC) analysis showed the occurring of grafting in SNR9H, however the blends of PS/SNR20% and PS/SNR30% showed incompatible and phase separated exist in the blends. Dynamic mechanical analysis (DMA) showed the PS/SNR30% had more interaction between SNR and PS matrix hence the maximum tan δ increases in the rubber region. At glassy PS temperature region (90 ^{0}C-150 ^{0}C), PS/SNR30% had lowest dynamic storage modulus compared to PS/SNR10% and PS/SNR20%. This large amount of rubber molecule had reduced the rigidity of the PS chain. Fracture toughness of PS/SNR20% had lower K_c value than HIPS but showed better ductility with higher deflection at break. Aging retention property of PS/SNR blends contained 20% to 30% of rubber content showed better impact strength after aging compared to HIPS. *In situ* vulcanization of SNR had shown great improvement in pressure sensitive adhesion properties and impact property. The applications of SNR as adhesive and impact modifier had achieved.

CHAPTER 1
INTRODUCTION

1.1 Latex based adhesive

The bonding agents used in paper product are known as adhesive which mostly is latex based. Other than paper products, leather goods and textiles, latex based adhesives also had been used in rigid substrates such as wood, floors, metal, glass, plastic and ceramic. The advantages of latex based adhesive are as follow:

- Reduced cost of production.
- Able to formulate adhesive with a wide range of total solid contents and viscosities, such as adhesive with high total solid content at relatively low viscosity for easy handling.
- Absence of flammable and toxic solvents
- Utilizing polymer of high molecular mass
- Superior resistance to deterioration during aging.
- Ease of wetting on solid substrate and to penetrate on porous substrate.

Generally the copolymer lattices are more effective used as based for latex adhesive than the unmodified polymer lattices. Adhesive with graft copolymer or a block should adhere well to different adherend. The adhesive need to fulfill the condition where the degree of separation of the two (or more) types of the repeat unit in a copolymer should have sufficiently large domain with two types of polarity. Secondly, the block of the copolymer should able to migrate from each other to enable strong adhesive bonds can be formed at the respective adherend surfaces. The copolymer need to have adequate size with no extensive crosslinking that can separate at the respective adherend surfaces.

Basically the adhesive bond formed from the latex based adhesive have to withstand the influence exposure such as sunlight, hydrocarbon oil, ozone and heat in which these bonds are strongly depends on the polymer component. Furthermore, latex based adhesive bond able to withstand high humidity and water through nature and the amounts of hydrophilic substances in the latex. Some polymers used for the production of latex-based adhesive are inherently capable of being crosslinked. The crosslinking are formed if appropriate reagents are included in the adhesive formulation and physical conditions for crossliking are established, or the reagents can migrate into the adhesive films from the adherend substrate. The advantages of crosslinking are to improve the resistance of adhesive towards aging, reduced sensitivity of bond strength and flexibility on changes temperature, improve the resistance to deterioration by water and organic solvents. There are also adhesion modifiers in latex based adhesive such as aqueous solution and dispersions of resin, tackifiers, plasticizer, crosslinking agents, fillers, thickeners and other additives (Blackley, 1997)

Among the other substances are added in the latex based adhesive are:

- Surface active substances
- Antioxidants
- Anti-forming agents, anti-freezes and freeze-thaw stabilizers
- Fungicides, corrosion inhibitors, flame-retarders
- Colorants, de-odorants and re-odorants.

Gazeley and Mente (1985) describe the preliminary investigation of tackifying additives in reducing the molecular mass of the natural rubber. In the case of pressure sensitive adhesive, the adhesive has to be sufficiently soft in the dry state, and able to deform under low pressure so good surface contact can be achieved. However, the sufficient cohesive strength is also required for adhesive application. Unfortunately both tack and cohesive are inversely correlated. So higher level of resin is needed for development of good tack compared to equivalent solution-based pressure sensitive adhesive.

In some latex-containing adhesive, the latex component is present in only small amount. The function of adhesive is to improve or develop existing properties possessed by the adhesive, rather than to convey distinctive characteristics of its own (Blanckley,1997).

Characteristic and process of vulcanized NR based adhesive:

- May used chemical catalysts/accelerators at ambient temperatures or heat curing to vulcanize the adhesive, as to improve strength and temperature resistance.
- Additives such as tackifiers, fillers and plasticizer and antioxidants are often used to improve the ageing of adhesive
- Can be set by solvent/ water evaporation/ vulcanization.
- Process involved NR emulsion contains stabilizers, wetting agents and other component. Adhesive may cured by heat or at room temperature, provided a suitable accelerator is used.

According to Petrie (2006), unvulcanized adhesive tends to lose its strength at temperature 66^{o}C and the vulcanized adhesive has maximum service temperature at 93 ^{o}C. Caution must be taken as exposure of adhesive to higher temperatures can cause permanent softening.

1.1.1 Pressure sensitive adhesive

Pressure-sensitive adhesives (PSA) are fluid applied. These types of adhesives are viscoelastic material and do not undergo a chemical reaction. PSA remains in the gel state which is tackiness capable of being removed rather than a permanent bond after wetting the substrates. In order to have good surface contact, PSA has to be sufficiently soft in the dry state to deform under low pressure and has sufficient cohesive strength contact to react as adhesive. However, in most cases the tack and cohesive strength are inversely correlated (Blackley, 1997).

In the 19th century, the discovery of natural rubber as the first solvent based PSA and its usage are widely recognized in tapes and labels industries. Recent development such as control of adhesive properties through structured particles design of water –borne PSA are studied by Andrew *et. al.*(2009). For further improvement over the joint strength, the mixed adhesive joint technique can offer a good combination of strength and ductility (Silva & Lopes, 2009).

Nanocomposite PSAs also one of the new growth adhesive materials which are popular among the studies of researcher. There is published study that deals with synthesis of acrylic polymer/montmorillonite (MMT) clay nanocomposite PSAs by suspension polymerization (Kajtna & Sebenik, 2009). For medical grade application, the design of new water soluble PSA for patch preparation are reported by Minghetti *et al.*(2003). Mixture of polyisobutylene (PIB) and sodium carboxymethylcellulose (CMC) are physiologically inert and both yield a special moisture absorbing PSA, thus suitable for medical application as patch preparation. The rheological properties of PIB and CMC are studied by Piglowski and Kozlowski (1985).

Polymer mostly use as PSAs are block copolymers of elastomer with styrene, natural rubber, polyacrylate, random polymer butadiene-styrene rubber or butyl rubber (Andrew & Khan,1990; Satas,1989). For example, carboxylated butadiene-styrene rubber and butadiene-styrene rubber are used as base for PSA and styrene-2-ethyl hexyl acrylate copolymer containing 14 mass% of styrene is used as PSA modifier (Florian and Novak,2004).

1.1.2 The effect of nature of adherend surface

Latex based adhesives usually contain substances of widely different polarities, which some of the substances are hydrophobic and others are hydrophilic. This is common in latex based adhesive due to minor amount of various substances, such as surface active substances and hydrocolloids which essentially hydrophilic in nature. It is known that latex based adhesives are hydrophobic colloidal dispersions which contain at least two phases which are aqueous phase and polymer particles. There is a dispersed phase in latex based adhesives which can be occurred due to the filler particles. In principle, predominantly polar surface of adherend encourage the polar component of adhesive to accumulate at the interface between the adherend and the adhesive. Similarly, the surface which is predominantly non polar encourage the non polar component of the adhesive at the interface between the adherend and the adhesive (Comyn et.al,1992).

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1.1.3 The effect of the high humidity and liquid water upon strength of adhesive bonds

Water is highly polar small molecule. The present of the water will further weaken the adhesive bond strength between the adhesive film and the adherend surface. If the adhesive film is in contact with water, surface active substances presence in adhesive may dissolve in the contiguous aqueous phase. Thus, the surface free energy of the water and the thermodynamic work of adhesion of the adhesive bond are reduced (Comyn et.al, 1993). So when produce a new adhesive, the adhesive which is least affected by the humidity is favored when strong adhesive bonds is desired.

1.2 Rubber toughened plastic

1.2.1 Compatibility effect Test

In order to determine whether a polymer-polymer mixture has separated into two phases, light scattering, microscope and measurement of glass transition temperatures are often used as a standard test method for compatibility. For most binary pairs, in which the polymers are completely incompatible, these method can distinguish by difference in refractive index and glass transition temperature (Tg). However, it is difficult to distinguish a single homogeneous phase from a fine dispersion of one polymer in another. The existing analytical methods differ in their ability to make this distinction and give contradictory results. As a result, calorimetry may indicate a single glass transition for a sample while dynamic mechanical testing detects two separate transitions. Sometime, electron microscopy can resolve this problem provided there is sufficient electron contrast between the two components. If there are differences in chemical reactivity which enable one constituent to be stained or etched preferentially, then it is a useful aid to analysis the compatibility. Kinetic effect further complicated the problem. In principle, the concept of compatibility is refer to thermodynamic and related to the equilibrium state of the mixture. Caution must be taken as mixing and demixing of polymeric systems are diffusion-controlled process which can take longer time to reach equilibrium. For second kinetic effect, the partially miscible system between its bimodal and spinodal compositions can exist indefinitely as a metastable homogeneous phase in the absence of a nucleation mechanism. Thus, some caution is necessary to prevent wrong interpreting experimental evidence as failure to mix is not necessary an indication of thermodynamic incompatibility, nor is the existence of an homogeneous phase proof of complete thermodynamic compatibility (Bucknall,1977).

1.2.2 Graft-copolymerization reaction

A specialized type of block copolymer in which blocks of one monomer units are covalently bonded to a main-chain polymer comprising exclusively units derived from other monomer is known as graft copolymer. It is said to be grafted on to the main chain polymer when the monomer units constituting the attached blocks. The aims of producing graft-copolymerization reaction in natural rubber latex are for production of self-reinforced and thermoplastic natural rubber.

A few of published reports (Bloomfiled, 1956; Merrett & Wood, 1957; Allen et al.,1959; Sekhar,1958; Ceresa,1973; Pendle,1973) stated that the amount of grafting of a second polymer such as PS and polymethyl methacrylate (PMMA) onto NR backbone is low (less than 50%). This is due to the presence of protein layer which prohibit the graft copolymerization of vinyl monomers onto natural rubber. In this case, deproteinized natural rubber latex (DPNR) is more suitable as a grafted polymer compared to high ammonia natural rubber latex (HANR). This is due to the removal of protein layer in natural rubber and replacement of surfactant in lattices which increase the degree of grafting and furthermore increase the physical properties of copolymer (Ceresa, 1962; Allen, 1963; Ceresa, 1973; Pendle, 1973).

Emulsion polymerization can be used to produce grafted copolymer. For emulsifier-free emulsion polymerization, the minimum number of component essential for the creation of an aqueous emulsion polymerization reaction system is three, rather than four: monomer(s), water and initiator. The present of colloid stabilizer is unnecessary. The initiator used in the emulsion polymerization reaction will generate radical –anions end groups which provide colloid stability at the surface of the polymer particles (Blackley, 1997). According to Nguyen (2000), during emulsion polymerization, if the DPNR used as main chain polymer for grafting and with already contains amount of surfactant which lower than critical micelle concentration (CMC) value during its manufacturing, hence, the used of addition surfactant in the system can be neglected. Such system will avoid the formation of micelles and has high degree of grafting which known as emulsifier-free emulsion polymerization.

The reaction time in emulsion polymerization depends on the reaction temperature used in the system. Some studies on modification of HANR latex with vinyl monomer had reported using temperature range from 50-70^{o}C for different initiator and surfactant system. According to Nguyen (2000), modification of DPNR latex with styrene monomer with balance of properties can be achieved in the modified DPNR films by using 60^{o}C of reaction temperature together with initiator concentration of 2% by weight of styrene in the system,.

Based on study by Nguyen (2000), the total solid content (TSC) of 40% is recommended for the emulsion polymerization reaction of grafted styrene on natural rubber for ratio of natural rubber to monomer styrene at 75%:25%. Above the 40% of TSC, the rubbers tend to collide more frequently due to the distance between the rubber particles reduce and thus the system will easily coagulated.

Another established graft copolymer example was self reinforced rubber obtained from graft-copolymerization with methy-methacrylate (Bloomfield 1952). It is well known as ‘Heveaplus MG’ in industry. Typical formulation for graft-coplymerization of methyl methacrylate and of styrene in ammonia-preserved natural rubber latex using a hydroperoxide-polyamine initiation system are shown in Table 1.1.According to Bloomfield (1952), significant extents of grafting occur if hydroperoxide-polyamine combination or dibenzoyl peroxide is used as initiator. However, if azobisisobutyronitrile and peroxodisulphates are used as initiator, almost no grafting occurs for the former, and low grafting occurs for the latter. The dependence of the extent of grafting upon the nature of the initiator is inconsistent with the reaction mechanisms in which grafting occurs principally hydrogen-abstraction by interaction between a propagation polymer chain and a rubber macromolecule or copolymerization; neither of these reactions would be expected to depend upon the nature of the free radical which initiated the polymerization. Thus, it is believed that grafting occurs primarily by interaction between rubber molecules and the primary radicals which form from the initiator.

Table 1.1: Typical formulation for graft-coplymerization of methyl methacrylate and of styrene in ammonia-preserved natural rubber latex (Bloomfield ,1952)

	Part by mass			
	Methyl methacrylate		Styrene	
Ingredient	Dry	Actual	Dry	Actual
Natural rubber(as 30%m/m latex,0.4% m/m ammonia	100	333	100	333
Non-ionogenic stabilizer (as 20% aqueous solution)	-	-	3	15
Methyl methacrylate	33	33	-	-
Styrene	-	-	55	55
Tert-butyl hydroperoxide	0.18	0.18	0.25	0.25
Tetraethylenepentamine (as 10% m/m aqueous solution)	0.21	2.1	0.1	1.0
Time of polymerization/hour	3		6.5	
Polymerization temperature/^{o}C	12		55	
Conversion/%	90		95	

A combination of tert-butyl hydoperoxide and tetraethylenepentamine showed rapid initiation and smooth polymerization of both methyl methacrylate and styrene in ammonia-preserved natural rubber latex. Bloomfield (1952) indicated that methyl methacrylate could be used to polymerize natural rubber latex with the used of dibenzoly peroxide only if the ammonia was removed, the temperature need to nearly 80^{o}C, and a substantial quantity of a non-inorganic stabilizer need to add to prevent colloidal destabilization.

Allen *et.al.* (1959) reported that the polystyrene, having a greater tendency to mix with natural rubber than with polymethyl methacrylate, which less tendency to phase-separated to form micro-aggregates. Thus the distribution of monomer styrene within the composite latex particles is expected to be more uniform.

Recently, Pukkate *et. al.* (2007) study the graft-copolymerization of styrene onto natural rubber in order to form nano matrix structure. Nano-matrix structure is formed by graft-copolymerization of styrene onto urea-deproteinized natural rubber (U-DPNR) latex. The grafted U-DPNR is characterized by Fourier-transform infrared (FT-IR) spectroscopy, Hydrogen-1 nuclear magnetic resonance (^{1}H NMR) spectroscopy and transmission electron microscopy. Conversion and grafting efficiency of styrene are more than 90% under the best condition of the graft-copolymerization. In transmission electron micrograph of film specimen stained by OsO4, it is found that natural rubber particle of about 0.5 μm in diameter is dispersed in polystyrene matrix of about 15 nm in thickness. The conversion and grafting efficiency for the grafted U-DPNR are compared with those for a control sample prepared from enzymatic deproteinized natural rubber (E-DPNR) with styrene. Figure 1.1 shows the preparation of grafted styrene-copolymer. Graft-copolymerization of U-DPNR and E-DPNR are carried out with tert-butyl hydroperoxide /tetrethylenepentamine as an initiator in latex stage. The highest conversion and grafting efficiency of styrene for U-DPNR-g-PS copolymer is achieved at 1.5 mol/kg-rubber feed of styrene to be about 90 and 90 w/w%, respectively, as shown in Figure 1.2 and Figure 1.3.

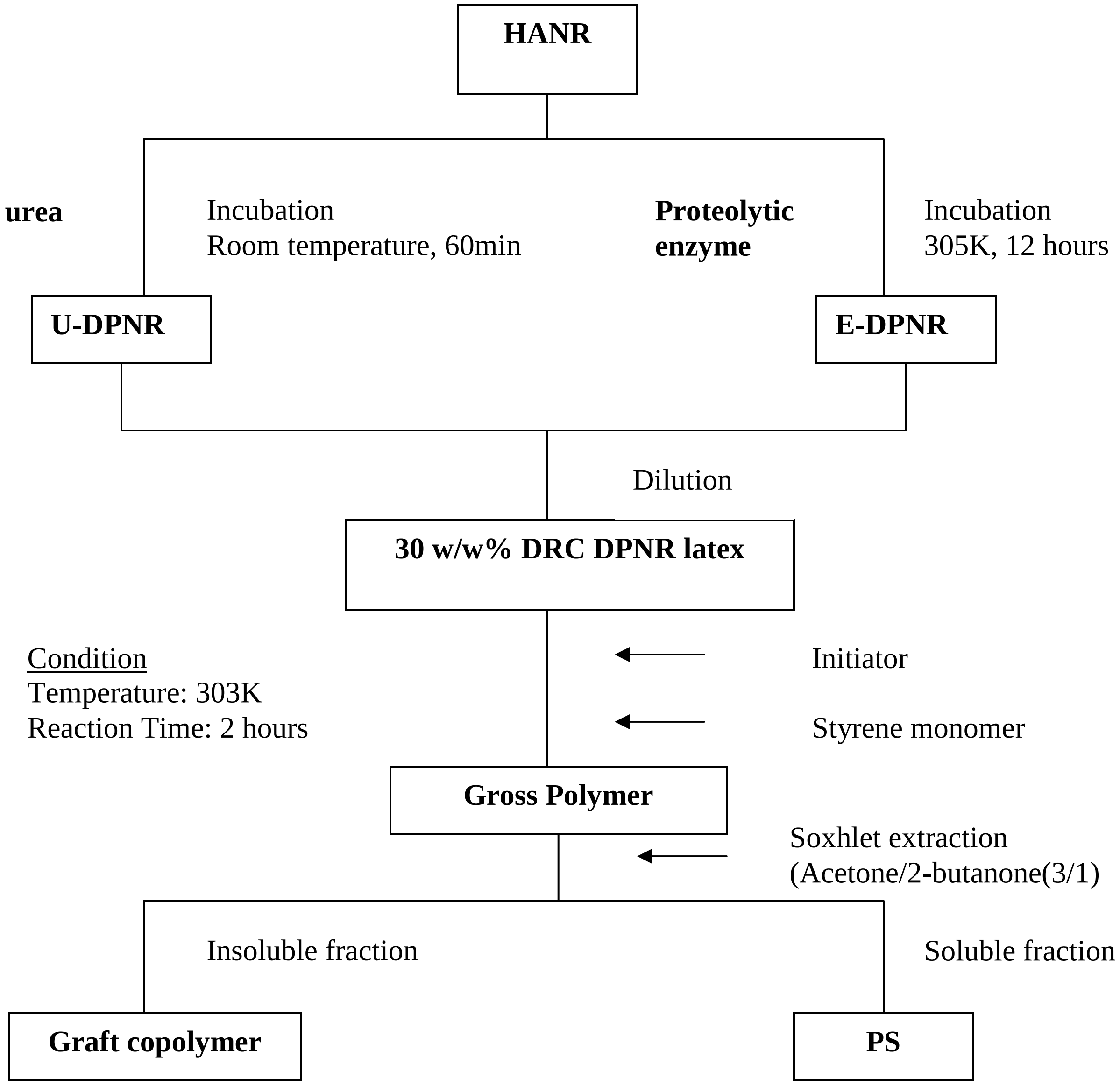

Figure 1.1: Preparation of U-DPNR-g-PS and E-DPNR-g-PS copolymers (Pukkate *et. al.*, 2007).

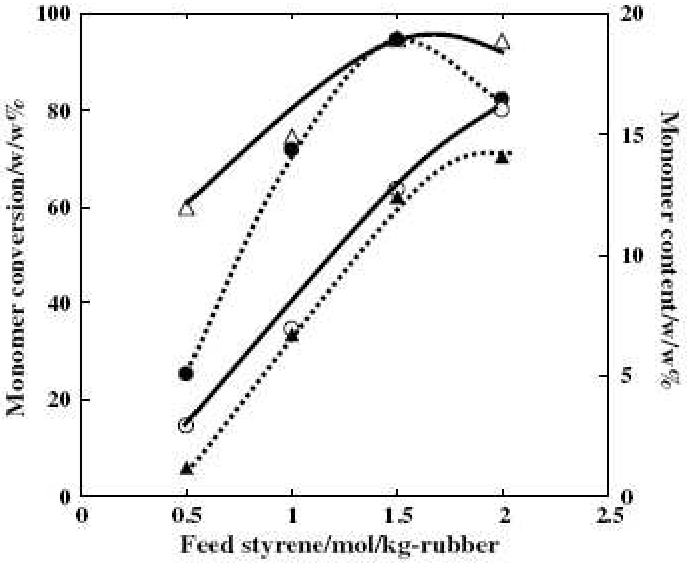

Figure 1.2: Content of styrene units and conversion of styrene for U-DPNR-g-PS and E-DPNR-g-PS copolymers;(Δ), conversion of styrene for U-DPNR-g-PS copolymer; (●), conversion of styrene for E-DPNR-g-PS copolymer; (○), content of styrene for U-DPNR-g-PS copolymer; (▲), content of styrene for E-DPNR-g-PS copolymer(Pukkate *et. al.*,2007).

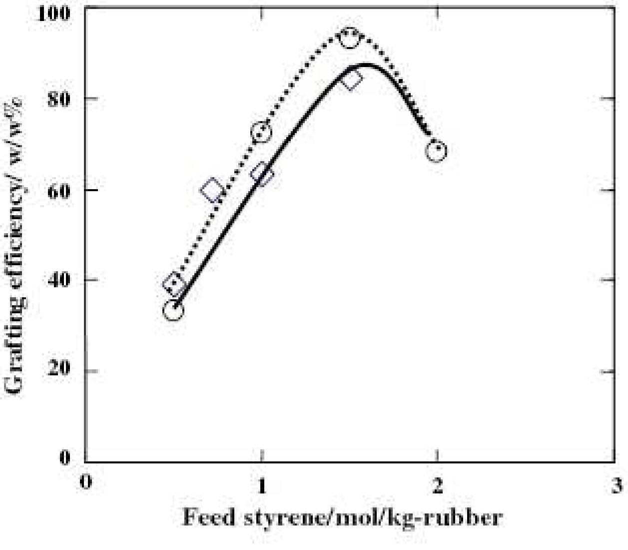

Figure 1.3: Value of grafting efficiency of styrene for (□),U-DPNR-g-PS and (○), E-DPNR-g-PS copolymer (Pukkate *et. al.*,2007).

Graft copolymer also can be prepared by radiation. Asaletha *et.al.*(1998) prepared graft copolymer of NR and PS (NR-g-PS) by polymerizing styrene in rubber latex using ^{60} Co γ- radiation as initiator. Styrene monomer is added into emulsion which is then mixed with NR latex. The dose rate is 0.1166 MRadmin^{-1}. The free homopolymers natural rubber and polystyrene are removed by extraction with petroleum ether and methyethylketone.

1.3 Problems statement

High ammonia natural rubber latex (HANR) is commonly used in latex dipped products but has allergy issue (Dairlymple & Audley, 1992; Yip *et. al*.,1995; Pendle,1993).Thus, deproteinized natural rubber latex (DPNR) become the focus of studies to solve the protein issue. The production of DPNR is by subjecting the natural rubber latex (NR) to enzymatic treatment and centrifugation (Ichikawa *et.al.*,1993). Most of the proteinaceous substances are removed from NR after the deproteinization process. Protein plays an important role in stabilizing the rubber particles and film forming properties of latex. In order to maintain the stability of DPNR, surfactant is added into DPNR to stabilize the lattices. In comparison of HANR and DPNR, the former is stabilized by protein and lipid layer (Gazeley *et.al*., 1988), as the latter is virtually stabilized by surfactant.

Most graft-copolymerization process favors the used of DPNR than HANR. According to Nakason *et.al* (2003), the grafting efficiency percentage decrease with an increase of MMA concentration when the DPNR or HANR is grafted with methyl methacrylate (MMA). In comparison with the two type of lattices, DPNR provides higher grafting efficiency which contains larger quantity of grafted poly (methyl methacrylate),a larger average particle size, and few free natural rubber molecules are observed in the grafting system. These differences are attributed to the removal of proteins. The protein layer can act as free-radical scavengers and terminate the free-radical species during graft copolymerization. Thus DPNR becomes the focus of the recent studies.

The discovery that brittle plastics can be toughened by using minor portion of rubber has led to the commercialization of high impact thermoplastics. One of the leading commodity thermoplastic materials is high-impact polystyrene (HIPS). However, the commercial HIPS were prepared by mass suspension polymerization of poly-butadiene with styrene which is a copolymer of styrene and butadiene usually has a rubber content of 8-14 wt% (Bucknall, 1977).

PS is known to be difficult to compatibilize with natural rubber (NR). Thus, it could be expected that the mechanical properties of PS/NR blend could be further enhanced via the incorporation of a suitable compatibilizer. Natural rubber /polystyrene (NR/PS) blends with the addition of compatibilizer which is NR-g-PS had improved the mechanical properties of NR/PS blends (Chuayjuljit et al, 2005). Research on dynamic vulcanization of NR/PS blends are well established by Asaletha et.al.(1999). Dynamic vulcanization of the blends is carried out by different curing agent, ie: sulfur, peroxide (DCP) and mixed system (sulfur with peroxide). All blends are prepared by melt mixing and solution casting technique.

The study reported here is an investigation of PS-modified NR (SNR) prepared by using emulsion polymerization. Instead of vulcanized the SNR by dynamic vulcanizaion, *in situ* vulcanization in SNR latex is recommended to prepare the SNR vulcanizate. *In* *situ* vulcanization process is carried out immediately after the emulsion polymerization of SNR latex in room temperature. SNR vulcanizate is left to dry in room temperature and then leached with deionized water to remove all the water soluble impurities in SNR vulcanizate. The formulation recommended for *in situ* vulcanization is sulfur based vulcanization. This SNR vulcanizate is ready to be used as impact modifier.

Part of the study involved the application of SNR vulcanizate as pressure sensitive adhesive (PSA). The ratio of accelerator to sulfur used from three type of pre-vulcanization system which are conventional vulcanization system (CV), semi-efficient system (semi-EV) and efficient vulcanization system (EV). Pre –vulcanization were carried out immediately after the emulsion polymerization at 60^{o}C. The focus in this work was to develop a PSA with good performance in anchorage properties, good mean maximum load results and longer average time to fail.

Another application of SNR vulcanizate in the industry is rubber toughened material. The vulcanization system used is semi-EV vulcanization system. Polystyrene (PS) make up a large proportion of total tonnage of plastic currently being used mainly for consumer products or non load bearing application. In order to improve the toughness property of PS glassy polymer and divert the application of PS to high impact applications, small amount of rubber as impact modifier is recommended to add in to PS matrix. SNR vulcanizate which contains highly grafted PS portion is believed to have better interaction with PS in PS/SNR vulcanizate blend and act as impact modifier.

1.4 Objectives of studies

The focus of the study reported here is concerned with the application of SNR as pressure sensitive adhesive and rubber toughened PS. Both applications are using chemical modified DPNR with styrene monomer. The main objectives of this study are:

1. To investigate the *in situ* vulcanization system for SNR vulcanizates by using sulfur based vulcanization. The effect of the vulcanization systems will be studied for both applications.
2. To study the effect of SNR pre-vulcanizate as pressure sensitive adhesive in PS-PS, PS-NR and NR-NR substrates. The formulation of SNR pre-vulcanizate with optimum improvement in anchorage properties, good mean maximum load results and longer average time to fail are to be determined.
3. To investigate the effect of SNR vulcanizate as impact modifier in PS blends. The optimum rubber composition of PS/SNR blends are to be determined in order to achieve higher reinforcement and toughening effect on PS matrix.
4. To compare the PS/SNR vulcanizate with commercial HIPS and to study the compatibility of PS/SNR vulcanizate blends.

CHAPTER 2
LITERATURE REVIEW

2.1 Emulsion polymerization

There are four components in conventional reaction system for the aqueous emulsion polymerization: monomer, water, initiator and colloidal stabilizer. Sodium-n-dodecyl sulphate is colloidal stabilizer (emulsifier or surfactant) of non-polar monomers of low solubility such as styrene. Initiator is water soluble and functions as free radical generator. The common water soluble initiator used is peroxodisulphates (persulphates) of monovalent cations, such as potassium, ammonium and sodium. When the surfactant is added into the aqueous solution, it will saturate the water phase and then aggregated to form micelles, thus, critical micelle concentration (CMC) occur. According to Gerrens & Hirsch (1975), CMC has to be above 2.6 g/*l* H_2O, to ensure that micelles are formed for polymerization (Flory, 1956; Gordon, 1970; Blackey, 1975; Eliseeva *et.al* .,1981; Rosen, 1982; Odian, 1991; Painter & Coleman, 1994; Kumar & Gupta,1998).

In processing the styrene butadiene as example, both styrene and butadiene monomer added will diffuse through the water phase and into the micelles until equilibrium is obtained. Most polymerization occurs within the monomer-swollen micelles. The polymerization begins after the addition of initiator. Initially, the free radicals are formed with the presence of initiators. Free radical reacts with the monomer double bonds, and the chain growth began. The hydrophobic chain migrates to the swollen micelles with further increase of molecular weight is observed. Majority of polymerization occurs in the swollen micelles (Rander, 2006). Figure 2.1 shows concept of the free radical emulsion polymerization

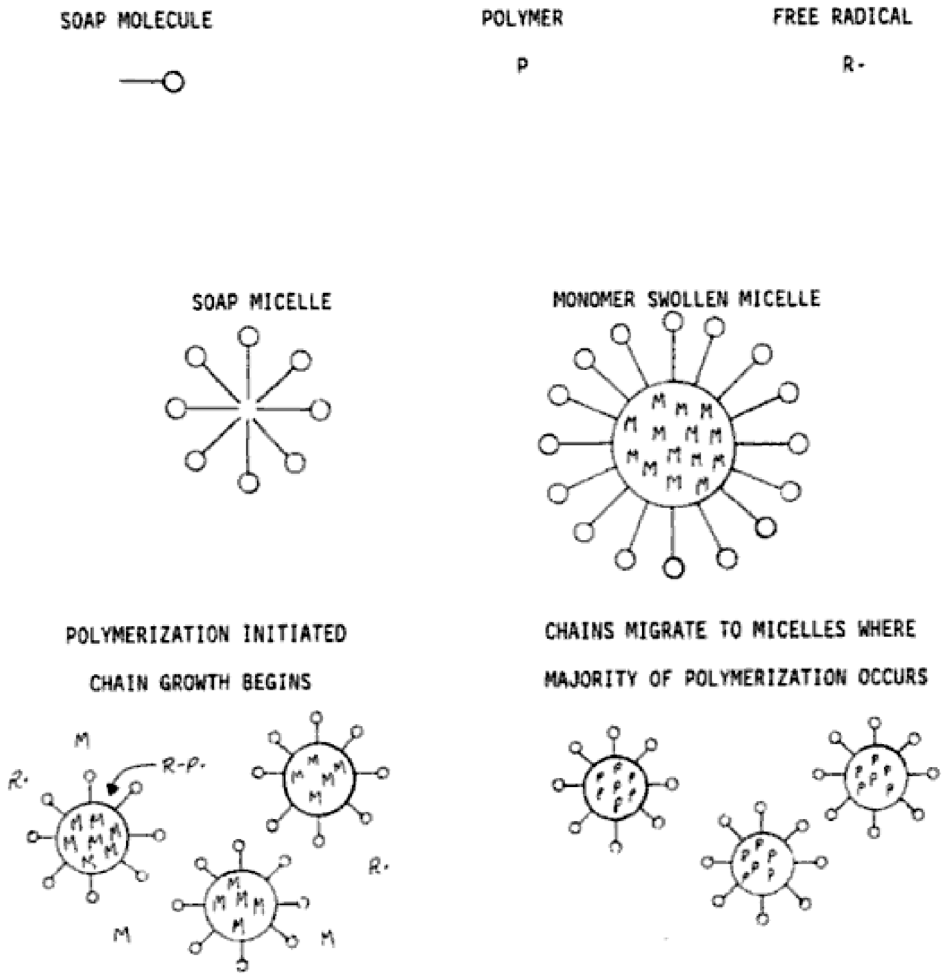

Figure 2.1: Concept of free radical emulsion polymerization (Rander, 2006)

The application of styrene-butadiene (SB) latex in coating industry such as paperboard coating, textile coating, as binder and coating for flooring felts, and as carpet backing. Typical properties of SB latex are shown in Table 2.1

Table 2.1: Properties of styrene-butadiene latex (Rander 2006)

Property	Value
Solids	50% wt.
pH	7-9
Brookfield viscosity	< 500cp at 25^{o}C
Average particle diameter	20,000
Surface tension	45 dynes/cm
Specific gravity (at 25^{o}C)	1.01
Styrene/butadiene ratio	50:50
Film properties:	
Tensile strength (at break)	550psi
Elongation	520%

2.1.1 Smith-Ewart theory

An ideal emulsion polymerization occurs when radicals entering individual latex particles successively initiate and terminate the growing chains. At any given time, the number of growing chains will be one-half the number of particles. It is to be noted, the high radical concentration does not affect the radical lifetime. The number of polymer particles depends on both the initiator concentration and the surfactant concentration (Roderic *et.al.*,1994),

$$N \alpha [I]^{2/5} [S]^{3/5} \qquad (2.1)$$

Where,[I] = Concentration of initiator,[S] = Concentration of surfactant

In the case of the diene, where the classical method of photoinitiation poses difficulties, a rather elegant method for obtaining the absolute value of the propagation rate constant k_p from emulsion polymerization system (Roderic *et.al.*,1994), as

$$R_p = k_p [M] N/2 \qquad (2.2)$$

Where, N = Number of the particles per unit volume, R_p = Propagation rate constant, [M] = Concentration of monomer in the monomer-polymer particles,

2.1.2 Chain-growth polymerization

Chain growth polymerization occurs when there is an addition of monomer to reactive sites on the growing chain molecules.

$$P^*_n + M \longrightarrow P^*_{n+1} \quad +M \qquad (2.3)$$

Where, P^*_n = Polymer chain with reactive site (*) and degree of polymerization of n, M= Monomer unit, P^*_{n+1}= polymer chain with a reactive site (*) and degree of polymerization n+1

The reactive species which initiate such chain reactions must be capable of opening one of the bonds in the monomer and may be a radical, an electrophile, a nucleophile, or an organometallic species. Hence this polymerization may proceed by a variety of possible mechanisms depending on the electronic nature of the chain-carrying species, viz., free radical, cationic, anionic, and coordination, as illustrated in Figure 2.2 (Roderic et.al.,2005).

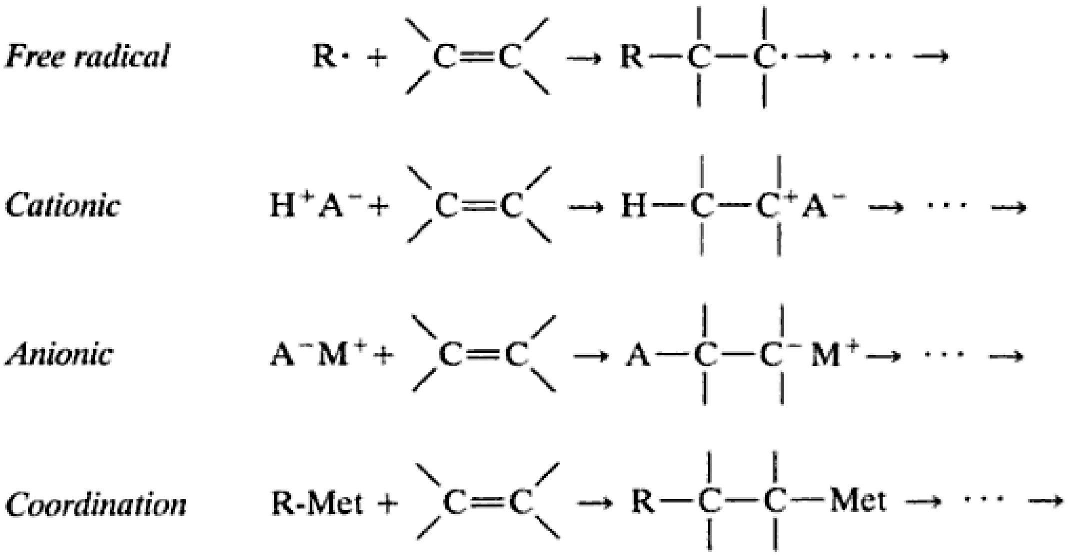

Figure 2.2 : The reactions of double bonds with various types of initiating species. (Roderic et.al, 2005)

The general kinetics for chain propagation by free radical mechanism involve three primary steps, i.e., initiation, propagation, and termination as shown in Figure 2.3 (Roderic et.al, 2005). Where I= initiator, M=monomer, R= initial free radical, and $M_j\cdot$ = propagating free radical.

This sequence of steps then leads to the following simple kinetic treatment:

Rate of initiation $R_i = 2k_i\,[I]$ (2.4)

Rate of propagation $R_p = k_p\,[M_j\cdot]\,[M]$ (2.5)

Rate of termination $R_t = 2k_t\,[M_j\cdot]^2$ (2.6)

Assuming a steady-state condition where the rate of formation of radicals is equal to their rate of disappearance, i.e., $R_j = R_t$,

$$[M_j\cdot] = k_i^{1/2}\,k_t^{-1/2}\,[I]^{1/2} \qquad (2.7)$$

And

$$R_p = k_p\,k_i^{1/2}\,k_t^{-1/2}\,[M][I]^{1/2} \qquad (2.8)$$

Equation 2.8 thus illustrates the dependency of the overall rate of polymerization on the concentration of initiator and monomer. Another important aspect of the free radical polymerization is the dependency of the number-average degree of polymerization on initiator concentration, increases the rate of polymerization but decreases the degree of polymerization, X_n, which corresponds to the number-average number of units per chain.

$$X_n = k_p k_i^{-1/2} k_t^{-1/2} [M][I]^{-1/2} \tag{2.9}$$

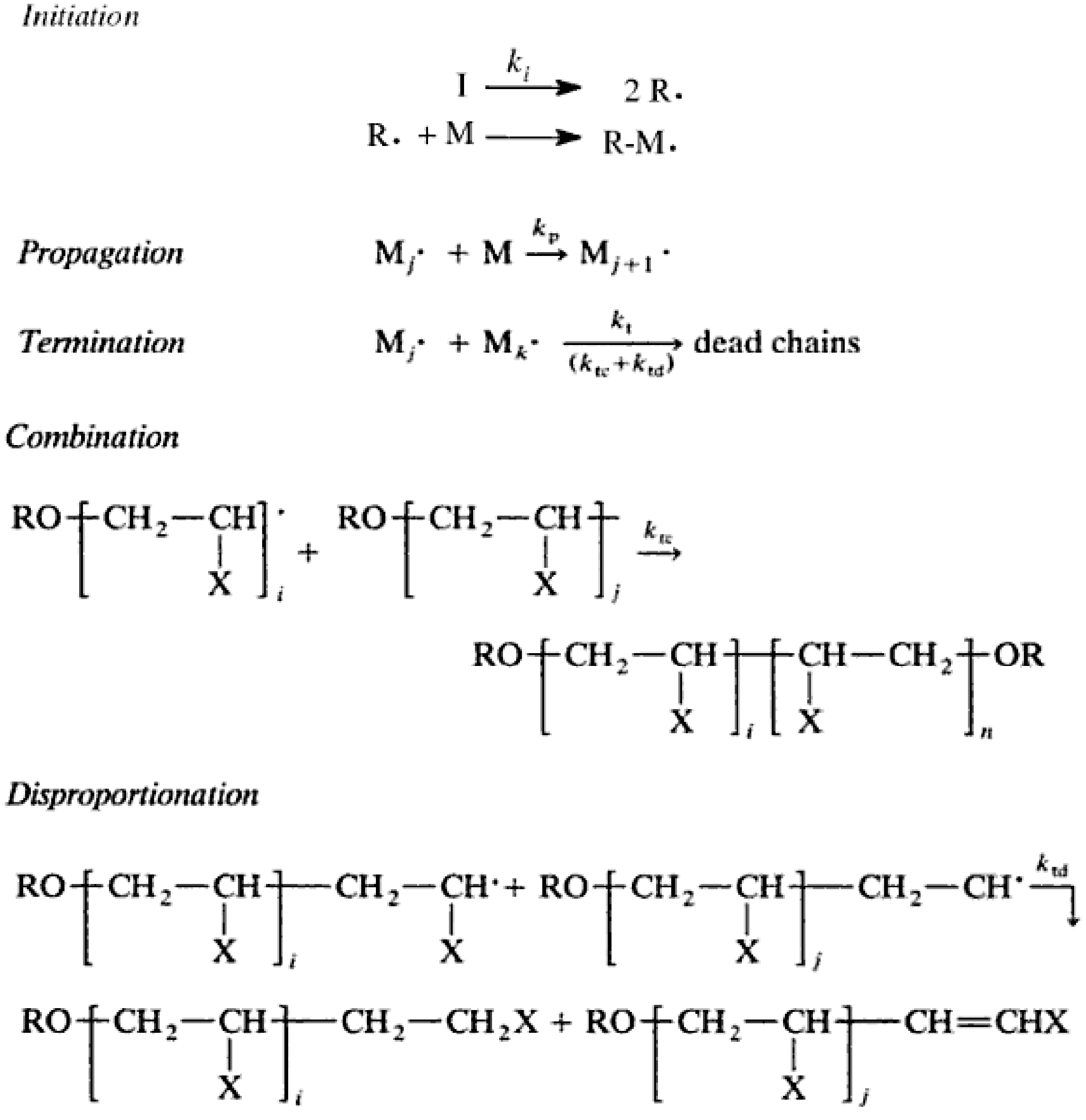

Figure 2.3: Kinetics for chain polymerization by free radical mechanism (Roderic et.al, 2005)

2.2 Latex Compounding Ingredients

Lattices require addition of compounding ingredients for a finished product. The range of compounding ingredients used for latex are divided into the following categories (Howard,1999; Blackley,1997):

(a) **Vulcanization agents:** These agents are necessary for vulcanization as the chemical crosslinking reaction can improve the physical properties of the latex compound.

(b) **Accelerators:** The function of these chemical with the combination of vulcanizing agents will reduce the vulcanizing time (cure time) or increase the rate of vulcanization. In most cases, the physical properties of the products are also improved.

(c) **Activators:** These ingredients form chemical complexes after react with accelerators. These chemical complexes further increase vulcanization rates and improve the final product properties.

(d) **Stabilizer including surfactants:** These chemicals are used to reduce the surface free energy of aqueous media against air, and the interfacial free energy of aqueous media against immiscible organic liquids. This is due to the majority of lattices of industrial has aqueous dispersion media.

(d) **Antioxidants:** To increase the ageing characteristic of the latex compound.

(e) **Fillers:** To stiffen the product obtained from latex and also reduce the cost of final product.

(f) **Viscosity modifiers (thickeners):** To enhance the colloidal stability and modify the flow behaviors of latex compound.