Cross-linking and Degradation Studies of Polyolefin Elastomers

Studie síťování a degradace u polyolefinových elastomerů

Doctoral Dissertation

Submitted

by

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CONTENTS

CHAPTER 1: BACKGROUND…………………..………………….……………....

CHAPTER 2: EXPERIMENTAL..

CHAPTER 3……………………………………………………………………………..

ABSTRACT

Polyolefin elastomers are a special class of polymers. The most favorable property of polyolefin elastomers is their elasticity. Due to this, they find application in the field of foams, cushions, seals, automotive applications, footwear, cable insulation etc. Their field of application can be even widened through the process of cross-linking. Through cross-linking, the polymer chains are bonded together to form a cross-linked network. This will enhance their mechanical properties, especially, improved elastic properties. Simultaneously, their service temperature can also be increased through cross-linking. Cross-linking of saturated polymers can be carried out through a variety of techniques. Most commonly used techniques are peroxide cross-linking, silane-water cross-linking and irradiation cross-linking.

Being a member of thermoplastic elastomer (TPE) group and having excellent elastic properties, ethylene-octene copolymer (EOC) has been selected for our studies. In this research work, peroxide and irradiation cross-linking techniques have been utilized to cross-link EOCs. Peroxide cross-linking of ethylene-octene copolymers was carried out using dicumyl peroxide (DCP) at different temperatures. For irradiation technique, different dosages of electron beam were selected.

Effect of peroxide content (in range 0.2 - 0.7 wt. %) and temperature (in range 150-200 °C) on EOC cross-linking has been subjected to study. It has been observed that as the peroxide content increases, cross-linking increases while increase in temperature accelerates the chain scission process (degradation). Less susceptible to chain scission are temperatures in range 150-170 °C and peroxide levels 0.2-0.5 wt.%. Cross-linking of EOC using dicumyl peroxide was found to be a first order reaction. The highest cross-linking rate constant K was found for 0.6 wt. % of peroxide at 200 °C. The activation energy of cross-linking (E_A) obtained by Arrhenius plot had the maximum at 0.5-0.6 wt. % of peroxide level. At higher temperatures (190-200 °C) and peroxide level (especially, 0.6-0.7 wt. % range) cross-linking is competing with degradation. Increase in peroxide content resulted in increase in gel content – in other words, cross-link network – and thus improvement in high-temperature mechanical properties were also observed. Dynamic mechanical analysis (DMA) also confirmed the above results. Two ethylene-octene copolymers were compared to investigate the effect of octene content on cross-linking. Cross-linking efficiency of peroxide and degree of cross-linking were found to be increasing with decrease in octene content. EOC with high octene content was observed to be more vulnerable for degradation. Crystallinity of the cross-linked

EOCs was found to be decreasing with increasing octene content. Due to high extent of cross-linking, EOC with low octene content undergone lower creep compared to the high-octene one. Extent of cross-linking increases with radiation dosage also. This was confirmed through the high-temperature creep and elastic property analysis. Differential scanning calorimetry (DSC) analysis revealed the presence of high melting fraction formed during cross-linking. Tensile testing illustrates that the stress at break increases with radiation dosage while elongation at break decreases. Rheological property analysis showed that elastic property increases after irradiation cross-linking. Significant improvement in thermal stability was observed through thermogravimetric analysis. Both irradiation and peroxide cross-linking are efficient techniques for cross-linking ethylene-octene copolymers.

Key words:

Polyolefin elastomers, peroxide cross-linking, electron beam irradiation cross-linking, cross-linking kinetics, creep, dynamic mechanical analysis (DMA), elastic properties, thermal properties.

ABSTRAKT

Polyolefinové elastomery přispívají jako speciální třída polymerů. Nejvýhodnější vlastností polyolefinových elastomerů je jejich elasticita. Následkem toho najdou uplatnění v oblasti pěn, polštářů, těsnění, automobilových aplikací, obuvi, izolaci kabelů atd. Oblast jejich aplikací může být rozšířena procesem síťování. Prostřednictvím síťování jsou polymerní řetězce spojeny dohromady, čímž se vytvoří síť. Toto zlepší jejich mechanické vlastnosti, zvláště pak elastické vlastnosti. Současně může být síťováním zvýšena jejich maximální provozní teplota.

Síťování může být provedeno nejrůznějšími způsoby. Nejčastěji používané způsoby jsou peroxidové síťování, síťovaní silanem a vodou a radiační síťování.

Jakožto součást skupiny termoplastických elastomerů (TPE) a mající vynikající elastické vlastnosti etylen-oktenový kopolymer (EOC) byl vybrán pro naše studium. V této výzkumné práci bylo použito peroxidové a radiační síťování EOC. Peroxidové síťování etylen-oktenových kopolymerů bylo provedeno za použití dikumylperoxidu při různých teplotách. Pro metodu síťování ozařováním byly vybrány různé dávky elektronových paprsků.

Vliv obsahu peroxidu (v rozmezí 0,2-0,7 hm.%) a teploty (v rozmezí 150-200 °C) na síťování EOC byl podrobně zkoumán. Bylo pozorováno, že s rostoucím obsahem peroxidu se síťování zlepšuje, zatímco zvyšování teploty urychluje krácení řetězců (degradaci). Méně náchylná oblast ke krácení řetězců je teplota v rozmezí 150-170 °C a koncentrace peroxidu 0,2-0,5%. Bylo zjištěno, že síťování EOC za použití dikumylperoxidu probíhá jako reakce prvního řádu. Nejvyšší rychlostní konstanta síťování K byla zjištěna pro 0,6 hm.% peroxidu při 200 °C. Aktivační energie síťování (E_A) získaná za pomocí Arrheniovy rovnice měla maximum při 0,5-0,6 hm.% peroxidu. Při vyšších teplotách (190-200 °C) a vyšších úrovních peroxidu (zvláště 0,6-0,7 hm.%) síťování soutěží s degradací. Zvýšený obsah peroxidu způsobil nárůst v obsahu gelu, jinými slovy, nárůst v síťové hustotě, a proto bylo také pozorováno zlepšení vysokoteplotních mechanických vlastností. Dynamická mechanická analýza (DMA) také potvrdila výše uvedené výsledky. Dva etylen-oktenové kopolymery byly porovnány pro výzkum vlivu obsahu oktenu na síťování. Bylo zjištěno, že účinnost síťování peroxidem a stupeň zesíťování stoupají s klesajícím obsahem oktenu. Bylo pozorováno, že EOC s vyšším obsahem oktenu je náchylnější k degradaci. Bylo zjištěno, že krystalinitazesíťovaných EOC klesá se vzrůstajícím obsahem oktenu. Díky vysokému stupni zesíťování vykazoval EOC s nízkým obsahem oktenu menší tečení při krípovém testu ve srovnání s vysoko-oktenovým EOC.

Stupeň zesíťování roste také s rostoucí dávkou radiace. Toto bylo potvrzeno zkouškou vysokoteplotního krípu a analýzou elastických vlastností. Diferenciální skenovací kalorimetrie (DSC) odhalila přítomnost frakce s vyšším bodem tání, která byla vytvořena během síťování. Zkouška pevnosti v tahu ukazuje, že napětí při přetržení roste s úrovní radiace, zatímco tažnost při přetržení klesá. Analýza reologických vlastností ukázala, že elastické vlastnosti se zlepšují po radiačním zesíťování. Významné zlepšení tepelné stability bylo pozorováno termografickou analýzou (TGA). Obě metody síťování, ozářením i peroxidem, jsou účinné pro etylen-oktenové kopolymery.

Klíčová slova:
Polyolefinové elastomery, peroxidové síťování, síťování ozářením elektronovými paprsky, kinetika síťování, kríp, dynamická mechanická analýza (DMA), elastické vlastnosti, tepelné vlastnosti.

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TABLES AND FIGURES

TABLES:

***Chapter* 1**

Chapter 2

***Chapter* 3**

***Chapter* 4**

***Chapter* 5**

***Chapter* 6**

FIGURES:

***Chapter* 1**

***Chapter* 2**

***Chapter* 3**

<u>Chapter</u> 4

<u>Chapter</u> 5

<u>Chapter</u> 6

SYMBOLS AND ACRONYMS

A	Pre-exponential factor (in Arrhenius equation)
ASTM	American society for testing and materials
C	Carbon
CGCT	Constrained geometry catalyst technology
CPM	Cycles per minute
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTBPH	2,5-Dimethyl-2,5-di (tert-butylperoxy) hexane
DTBPHY	2,5-Dimethyl-2,5-di (tert-butylperoxy) hexyne-3
DTBPIB	Di (tert-butylperoxyisopropyl) benzene
E_A	Activation energy in J mol^{-1}
EB	Electron beam
E' or G'	Storage modulus or elastic modulus
EOC	Ethylene-octene copolymer
EPDM	Ethylene-propylene diene monomer
H	Hydrogen
HDPE	High density polyethylene
ISO	International organization for Standardization
K	Reaction rate constant
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MFI	Melt flow index

NVH	Noise vibration harshness
O	Oxygen
PE	Polyethylene
PP	Polypropylene
R	Universal gas constant (8.314 J mol^{-1} K^{-1})
RPA	Rubber process analyzer
rpm	Revolutions per minute
SBR	Styrene butadiene rubber
Si	Silicone
s’	Elastic torque
s'_{max}	Maximum elastic torque
s'_{min}	Minimum elastic torque
T	Absolute temperature in K
t	Time
t_{90}	Time in min required for the 90% of cross-linking reaction to be completed
tanδ	Loss factor
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
T_m	Melting temperature
TPE	Thermoplastic elastomer
UV	Ultraviolet
VTMS	Vinyl trimethoxy silane
VTES	Vinyl triethoxy silane
wt. %	weight percentage

X	Percentage of achieved cross-linking or conversion ratio
X_c	Percentage crystallinity
α	Alpha transition (in DMA)
β	Beta transition (in DMA)
β	Beta irradiation
γ	Gamma irradiation
$\Delta s'$	$s'_{max}-s'_{min}$
η^*	Viscosity
ε_r	Residual strain

LIST OF PUBLICATIONS

The following articles are published/submitted in peer-reviewed journals and the content of these articles are explained in this dissertation chapter wise as an outcome of the research work during my doctoral study period.

Publication I:

Cross-linking of ethylene-octene copolymer (EOC) by dicumyl peroxide (DCP)

Petr Svoboda, Sameepa Poongavalappil, Rajesh Theravalappil, Dagmar Svobodova, Pavel Mokrejs, Karel Kolomaznik, Toshiaki Ougizawa, Takashi Inoue
Journal of Applied Polymer Science 2011, vol. 121(1), p. 521-530,
DOI 10.1002/app.33655
Impact Factor: 1.240 reported in 2011.

Publication II:

Cross-linking kinetics study and high temperature mechanical properties of ethylene–octene copolymer (EOC)/dicumyl peroxide (DCP) system

Sameepa Poongavalappil, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Vladimir Vasek, Kittisak Jantanasakulwong, Toshiaki Ougizawa
European Polymer Journal 2011, vol. 47 (10), p. 1949-1955,
DOI: 10.1016/j.eurpolymj.2011.07.006
Impact Factor: 2.517 reported in 2011.

Publication III:

Comparison of peroxide cross-linked ethylene-octene copolymers

Sameepa Poongavalappil, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Tomas Sedlacek
Polymer Bulletin (Manuscript ID: PB-11-0746). Submitted in December 2011.

Publication IV:

Study on the influence of electron beam irradiation on the thermal, mechanical and rheological properties of ethylene-octene copolymer with high comonomer content

Sameepa Poongavalappil, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Michal Danek, Martin Zatloukal
European Polymer Journal (Manuscript ID: EUROPOL-D-11-01336). Submitted in December 2011.

CHAPTER 1

BACKGROUND

1.1 Polymers, Polyolefins, Copolymers

Polymers are substances composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of constitutional units [1]. Polyolefin are polymers produced from a simple olefin as a monomer and are the largest volume family of commercially important high-tonnage thermoplastic polymers [2]. Polyethylene, polypropylene, polybutene, polyisobutylenes are some of the common polyolefins.

A copolymer is a polymer formed when two (or more) different types of monomers are linked in the same polymer chain. Since a copolymer consists of at least two types of repeating units, copolymers can be classified based on how these units are arranged along the chain. These classifications include:

a) Alternating copolymer

–A–B–A–B–A–B–A–B–A–B–A–B–A–B–A–B–A–B–

b) Random copolymer (statistical copolymer)

–A–A–B–A–B–B–A–B–A–A–B–B–B–A–B–A–A–

c) Block copolymer

–A–A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B–B–

d) Graft copolymer

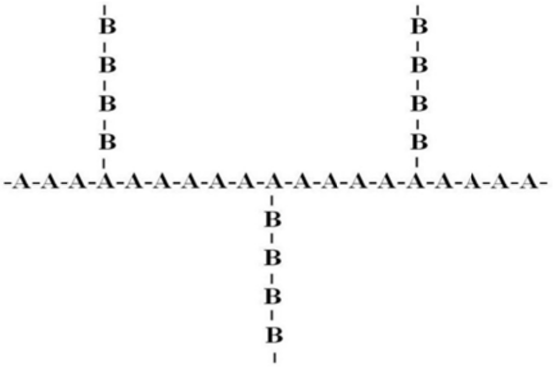


Figure 1.1 *Different types of copolymers* [3].

1.2 Thermoplastic elastomers (TPEs)

The thermoplastic elastomers (TPEs) concern large industrial and commercial fields, as well as academic and applied research. The real era of TPEs began with the advent of block and grafted copolymers. They are characterized by a set of properties inherent to block and graft copolymers, different blends, and some vulcanized materials [4]. Phase structure of TPEs is shown in Figure 1.2

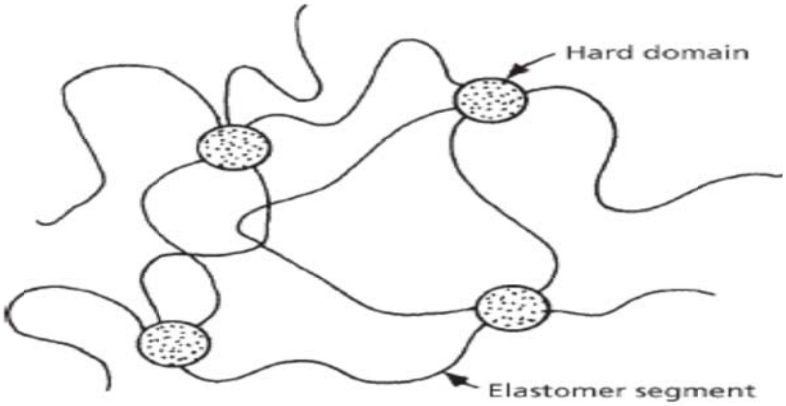


Figure 1.2 *Phase structure of thermoplastic elastomers [5].*

The introduction of thermoplastic elastomers in the 1950s provided a new direction to the field of polymers [6]. They are a class of polymeric materials which possess the physical characteristics of elastomers (high elastic behavior at ambient temperature) with easy processability associated with thermoplastics, simultaneously. There are mainly two different methods for the preparation of TPEs. They are,

i) synthesis of block copolymers having blocks of different chemical natures and possessing dissimilar physical characteristics, and
ii) compounding in order to obtain elastoplastic materials starting from polymers having thermoplastic and elastic properties.

A considerable growth in the production and use of TPEs has been observed during the last decades. Novel materials with improved properties which are different from those of the starting materials, with a wide range of applications, can be developed by blending rubbers with resins and thermoplastics. A good balance of properties of the resultant blends that the individual polymers do not possess can be achieved by varying the types of constituent polymers. For many years, such materials have been obtained by traditional technology used in rubber processing and their properties are well known [7].

Physical and chemical properties of TPEs can be controlled by varying the ratio of the monomers and the length of the hard and soft segments. These TPEs are normally phase separated systems which still retain unique features of its components such as good ultraviolet and ozone resistance, solvent resistance and high deformation temperature. Furthermore, they can be processed very easily to provide commercially attractive products that show the softness, extensibility and resilience of conventional thermoset rubbers [8].

TPEs have both advantages and disadvantages in comparison with conventional vulcanized rubbers [9],

Advantages:

- They are suitable for methods of thermoplastic processing, such as injection moldings, blow molding, thermoforming, and heat welding

- Scrap can be recycled and reused without significant deterioration in performance

- Properties can very easily be manipulated for different requirements by just a change in the blend ratio.

Disadvantages:

- TPEs soften or melt at an elevated temperature, above which they lose their rubbery character that means article looses shape.

- On extended use, TPEs show creep behavior.

There are different types of TPEs;

- Block copolymers
- Blends and elastomeric alloys
- Crystalline–amorphous block copolymers
- Ionomers and
- Miscellaneous

Polyethylene/poly (α-olefin) copolymers belong to the class of crystalline-amorphous block copolymers [10]. Polyolefin-based TPEs have received considerable attention due to their chemical inertness, low density, and low cost compared with other TPEs [11]. Since olefin copolymers became commercially available in the 1960s, a sizable effort has been expended to develop catalyst technology and structure-property relationships for very low crystallinity olefin copolymers.

The development of metallocene catalysts in the field of polyolefins permits the production of new ethylene copolymers with very low density that constitutes a unique class of thermoplastic elastomers. Ethylene-octene copolymer (EOC) with the trade name ENGAGE® is a special copolymer developed by Dow chemical co. through their INSITE™ constrained geometry catalyst technology (CGCT) [12]. A good control over polymer structure, molecular weight distribution and co-monomer composition helps ENGAGE® to have exceptional performance. EOC has several other advantages, including easy handling, better compound economy because of its reduced modifier levels and reduced weight via lower density products [13-15]. Table 1.1 shows their low density and wide range of physical/mechanical properties (using ASTM test methods).

Table 1.1 *Physical Properties of unfilled ENGAGE Polyolefin Elastomers [16].*

Property	Values
Specific gravity, g/cm^3	0.857–0.91
100% modulus, lb/in^2 (MPa)	145–725 (1–5)
Elongation, %	700+
Hardness, Shore A	50–95
Haze, %, 0.070 in (1.8 mm) injection-molded plaque	<10–20
Melt flow index, g/10 min	0.5–30
Melting point, °F (°C)	91–225 (33–107)

EOCs are having narrow molecular weight distribution, homogeneous comonomer distribution and homogeneous long chain branching structure [17]. This presents an opportunity to probe the limits imposed by branch concentration on miscibility of ethylene copolymer blends. Although solid state structure and properties change gradually with increasing comonomer content. EOCs have a saturated chain, providing inherent UV stability. Ethylene-octene copolymers are excellent materials for impact modification in hydrocarbon polymers such as polypropylene.

These polymers have a potentially wide range of applications and are of special interest for the automotive industry [16]. Typical applications are,

i) foams and cushioning components
ii) sandal and slipper bottoms
iii) swim fins, winter and work boots
iv) interior trim and rub strips
v) automotive interior air ducts, mats and liners
vi) extruded hose and tube
vii) NVH applications
viii) primary covering for wire and cable voltage insulation, appliance wires
ix) semi conductive shields
x) low smoke emission jackets and bedding compounds.

EOC is aimed at competing with conventional thermoplastic elastomers, such as ethylene propylene diene monomer (EPDM) in the automobile industry. Most of the uses in this field require a good balance of mechanical properties at high temperatures [18, 19]. Introduction of ethylene-octene copolymer in the commercial market gradually replaces the EPDM market in almost all fields of applications [20, 21].

EOC exhibits strong disadvantages which are low thermomechanical stability and a large permanent distortion, linked to the melting of crystallites. These disadvantages prevent applications involving temperatures higher than T_m of EOC, in particular many textile applications. Cross-linking technology represents a highly effective way for improving thermal and chemical resistance of polyolefins and then extends their applications [2, 22]. The cross-linking of polymers leads to an improvement in the thermal stability. Moreover, it can increase the tensile strength of polymers and thus, at a reasonable yield of cross-linking, improve their mechanical properties [23, 24]. Over the last few years a growing interest has developed regarding the process of cross-linking conventional polymers to meet the demands of specialty applications.

Now, we are going to discuss about cross-linking and various cross-linking techniques.

1.3 Cross-linking

Cross-linking is the intermolecular bond formation of polymer chains. Multidirectional chain extension of polymers leads to the formation of network structures. Cross-linking restricts chains from sliding past one another and generates elasticity in an amorphous polymer. In most cases, the cross-linking is irreversible [25].

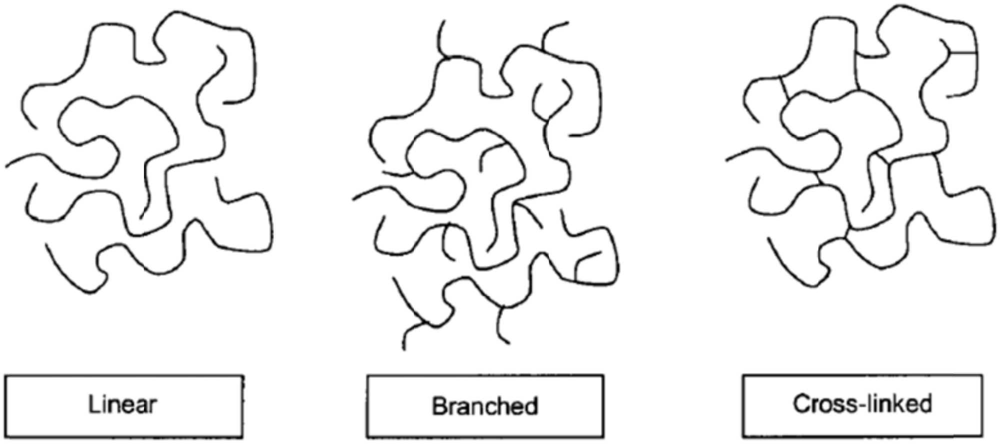


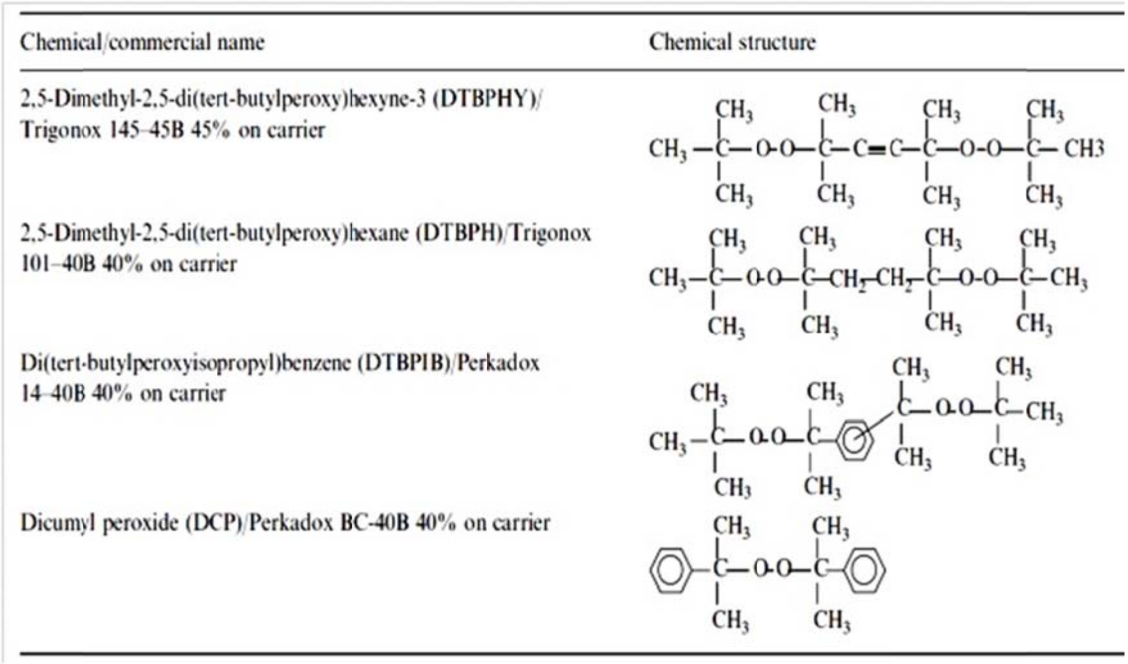
Figure 1.3 *Linear, branched, and cross-linked polymer structures [16].*

Cross-linked polymers when heated will not undergo melting and flowing. When the semi-crystalline polymers are cross-linked, they show the mechanical properties of a thermoplastic below its melting temperature (T_m); and exhibit the mechanical properties of a rubber above T_m. The cross-linking leads to an increase in the viscosity of the polymer melt, increased tensile strength, improvement of creep properties and an increase in the resistance to environmental stress cracking [26-28]. The effects of cross-linking on the physical properties of the polymers are primarily influenced by the degree of cross-linking, the regularity of the network formed, and the presence and absence of crystallinity in the polymer. A molten polymer undergoing a chemical cross-linking process is converted from a viscoelastic liquid into a viscoelastic solid. Changes in properties are more marked near the liquid-gel transition. Generally, chemical modifications in reactive polymer processing may cause important changes in the rheological behavior, leading to important consequences in the flowing behavior [29]. For example, mixing and shaping operations require sufficient molecular mobility, which vanishes when the chain motions slow down near the gel point [30]. Cross-linking enables a thermoplastic polymer like PE to exhibit a viscoelastic behavior, characteristic of an elastomer, at temperatures above the crystalline melting temperature of the thermoplastic. This valuable property is widely exploited commercially in the preparation of heat-shrinkable materials, wire and cable coating, hot water tubing and steam resistant food packaging, and so on [31-38].

Normally in rubber industry sulfur cross-linking is used for polymers with double bond. When the polymer does not have the double bond then one has to use other methods, such as irradiation [39-44], peroxides [45-48] and silane-water cross-linking [49-51].

1.3.1 Peroxide cross-linking

Cross-linking of elastomers using peroxide has been known for more than 50 years. The subject of peroxide curing has always been of interest to chemists and physicists working in the elastomer field because of its controlled decomposition rate, minimal side products, and economical process [52-56]. The more widely used vulcanization systems based upon sulfur or sulfur compounds are very much more complex in mechanism and produce more varied cross-links together with other chain modifications [52]. The activity of peroxide depends on the type of polymer and presence of other ingredients in the system [57]. The rate at which peroxide cross-linking takes place is dependent on the decomposition temperature of the selected peroxide, because the initial and rate determining step in the cross-linking process is the formation of free alkoxy radicals [58]. Cross-linking agents include ketone peroxides, peroxyketals, hyrdoperoxides, dialkyl peroxides, diacyl peroxides and so on. One advantage of peroxide cross-linking agents over sulfur compounds is that the former can be used to cross-link both saturated and unsaturated polymers. Some examples of unsaturated polymers that can be cross-linked using peroxides are unsaturated polyester resin, ethylene vinyl acetate copolymer, polystyrene, acrylonitrile-butadiene-styrene copolymer, and most rubbers [59]. The formation of strong C-C bonds provides substantial heat resistance and good compression set property without any discoloration. Peroxides which are generally being used for cross-linking are shown on Figure1.4.



Chemical/commercial name	Chemical structure
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (DTBPHY)/ Trigonox 145–45B 45% on carrier	$CH_3-C(CH_3)_2-O-O-C(CH_3)_2-C{\equiv}C-C(CH_3)_2-O-O-C(CH_3)_2-CH3$
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH)/Trigonox 101–40B 40% on carrier	$CH_3-C(CH_3)_2-O-O-C(CH_3)_2-CH_2-CH_2-C(CH_3)_2-O-O-C(CH_3)_2-CH_3$
Di(tert-butylperoxyisopropyl)benzene (DTBPIB)/Perkadox 14–40B 40% on carrier	
Dicumyl peroxide (DCP)/Perkadox BC-40B 40% on carrier	

__Figure 1.4__ Chemical/commercial names and structures of the peroxides [58].

Anbarasan et. al [53] studied the effect of various organic peroxide on the cross-linking of high density polyethylene and reported that dicumyl peroxide is most efficient peroxide for cross-linking.

Peroxides can be incorporated into the polymer by extrusion or in the internal mixer below the activation temperature of the peroxide. The cross-linked polymer will be later formed by one of the processing methods and cured under pressure and temperature. In the case of peroxide cross-linking, peroxide is used as a heat-activated chemical that generates free radicals for cross-linking [48]. A suitable peroxide has to be selected to give fast cross-linking without pre-curing in the extruder, and dicumyl peroxide is widely used for this purpose [6, 26].

Peroxide cross-linking of elastomers is relatively simple having only 3 steps.

Step 1: Homolytic cleavage of the peroxide

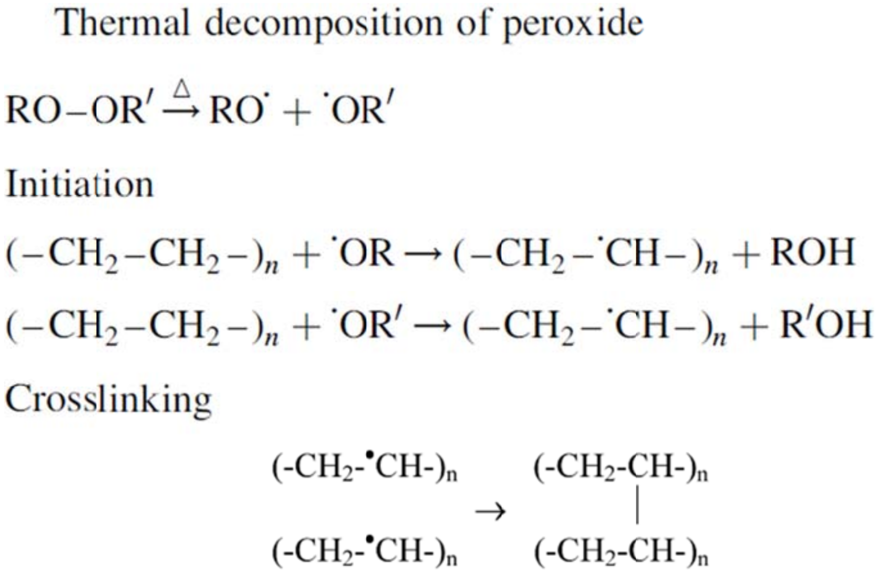
The first step in the cross-linking reaction is the homolytic cleavage of a peroxide molecule to form two free radicals. The cleavage rate of the peroxide molecule is proportional only to the concentration of the peroxide at any time. The rate is also controlled by the energy required for homolytic cleavage.

Step 2: Formation of polymer chain radical

The second step in peroxide vulcanization of elastomers is the abstraction of a hydrogen atom from a polymer chain by an alkoxy radical. The free radical site is then transferred to the polymer molecule. A large number of hydrogen atoms are available on the polymer chain, so the concentration of hydrogen atom is not significantly reduced as the reaction proceeds.

Step 3: Coupling of polymer chain radicals

The final step in peroxide vulcanization of elastomers is the coupling of two radicals on adjacent polymer chains to form a cross-link. The peroxide is not a part of the cross-link and does not affect polymer stability by introducing a foreign structure. The cross-link is a carbon-carbon bond between chains. The sulfur cross-link is more flexible than the carbon-carbon bond, but is less thermally stable. Therefore, a peroxide cross-link gives improved heat resistance, while the sulfur cross-link gives higher tear strength and abrasion resistance [60]. Peroxide cross-linking reaction of polyethylene is illustrated in Figure 1.5



Thermal decomposition of peroxide

$$RO{-}OR' \xrightarrow{\Delta} RO^{\cdot} + {}^{\cdot}OR'$$

Initiation

$$(-CH_2-CH_2-)_n + {}^{\cdot}OR \rightarrow (-CH_2-{}^{\cdot}CH-)_n + ROH$$

$$(-CH_2-CH_2-)_n + {}^{\cdot}OR' \rightarrow (-CH_2-{}^{\cdot}CH-)_n + R'OH$$

Crosslinking

$$\begin{array}{c} (-CH_2-{}^{\bullet}CH-)_n \\ (-CH_2-{}^{\bullet}CH-)_n \end{array} \rightarrow \begin{array}{c} (-CH_2-CH-)_n \\ | \\ (-CH_2-CH-)_n \end{array}$$

***Figure 1.5** Peroxide cross-linking reaction of polyethylene [26].*

The general advantages of peroxide cross-linking systems can be summarized as follows [61],

1. Simple formulation.
2. Ability to store the peroxide containing compound over a long time without scorching.

3. Ability to cross-link saturated as well as unsaturated rubbers.
4. High temperature resistance of the vulcanizates.
5. Good compression set properties of the vulcanizates (elastic recovery) at elevated temperature.
6. No moisture uptake, and
7. No staining or discoloration of the finished products.

One of the main disadvantages of DCP is rather strong odor.

1.3.2 Radiation cross-linking

Radiation cross-linking of rubbers has a number of technical advantages over thermal curing such as absence of various noxious chemical additives, high speed of curing process, effective penetration of radiation inside the sample and uniformity and ease of curing [43, 62, 63]. Radiation cross-linking is a well-established industrial process. Irradiation is usually applied to finished parts at room temperature [19, 64]. Irradiation is a very powerful form of energy treatment and produces deep effects on materials. Two of the most common industrial irradiation types used is gamma irradiation (γ) and electron beam (EB) irradiation. EB irradiation has limited penetration compared with gamma-rays; however, it is very energy-efficient because the entire amount of energy is deposited on the sample. As EB irradiation contains no radioactive isotope, it provides a significant advantage from a public acceptance point of view [65]. The degree of cross-linking is proportional to radiation dose. It does not require unsaturated or other more reactive groups. The mechanism of cross-linking generally varies with polymers.

The universally accepted mechanism involves the cleavage of a C-H bond on one polymer chain to form a hydrogen atom, followed by abstraction of a second hydrogen atom from a neighboring chain to produce molecular hydrogen. Then, the two adjacent polymeric radicals combine to form a cross-link, leading to branched chains until ultimately a three-dimensional polymer network is formed when each polymer chain is linked to another chain. Cross-linking during electron irradiation occurs by a free radical process is probably very similar to that of peroxide cross-linking [52].

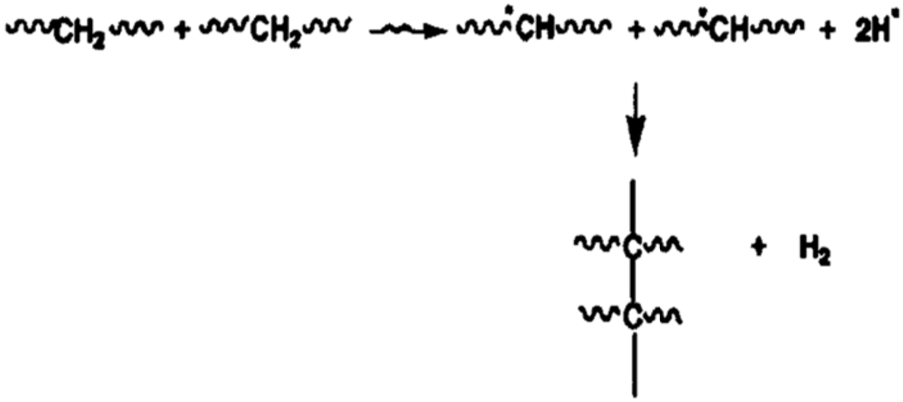


Figure 1.6 *Radiation cross-linking mechanism in polyethylene [66].*

1.3.3 Silane- water cross-linking

In addition to the typical peroxide cross-linking or irradiation cross-linking, the utilization of silane–water cross-linking has gained considerable attention in recent years not only for industrial applications such as cable insulation and water heating pipes, but also in fundamental research. Major advantages of silane-water cross-linking are easy processing, low capital investment and favorable properties in the cross-linked materials [29, 67-69].

This process is based on the preparation of a silane-grafted polymer using peroxides and vinyl alkoxy silane in either solution or melt. Generally used silanes are unsaturated alkoxy silanes, such as vinyl trimethoxy silane (VTMS) and vinyl triethoxy silane (VTES). Cross-linking via silane is a thermo chemical reaction in which the peroxide first decomposes at an elevated temperature; this results in the formation of oxy radicals. These highly active oxy radicals abstract hydrogen from the polymer molecule and can attack the vinyl group of a molecule and convert it into free radicals. These free radicals either combine with one another or attack another molecule in a similar fashion to propagate the free-radical reaction. This process results in the grafting of vinyl silane onto polymer chains, and this is first step for the cross-linked material [70, 71]. After shaping into products, the silane grafted polymer is cross-linked by exposure to a humid environment. The cross-linking reaction involves hydrolyzation of the hydrolysable alkoxy groups with moisture, followed by condensation of the formed hydroxyl groups to form stable siloxane linkages (Si– O–Si) [72]. Silane-water cross-linking is explained in Figure 1.7 using polyethylene as an example.

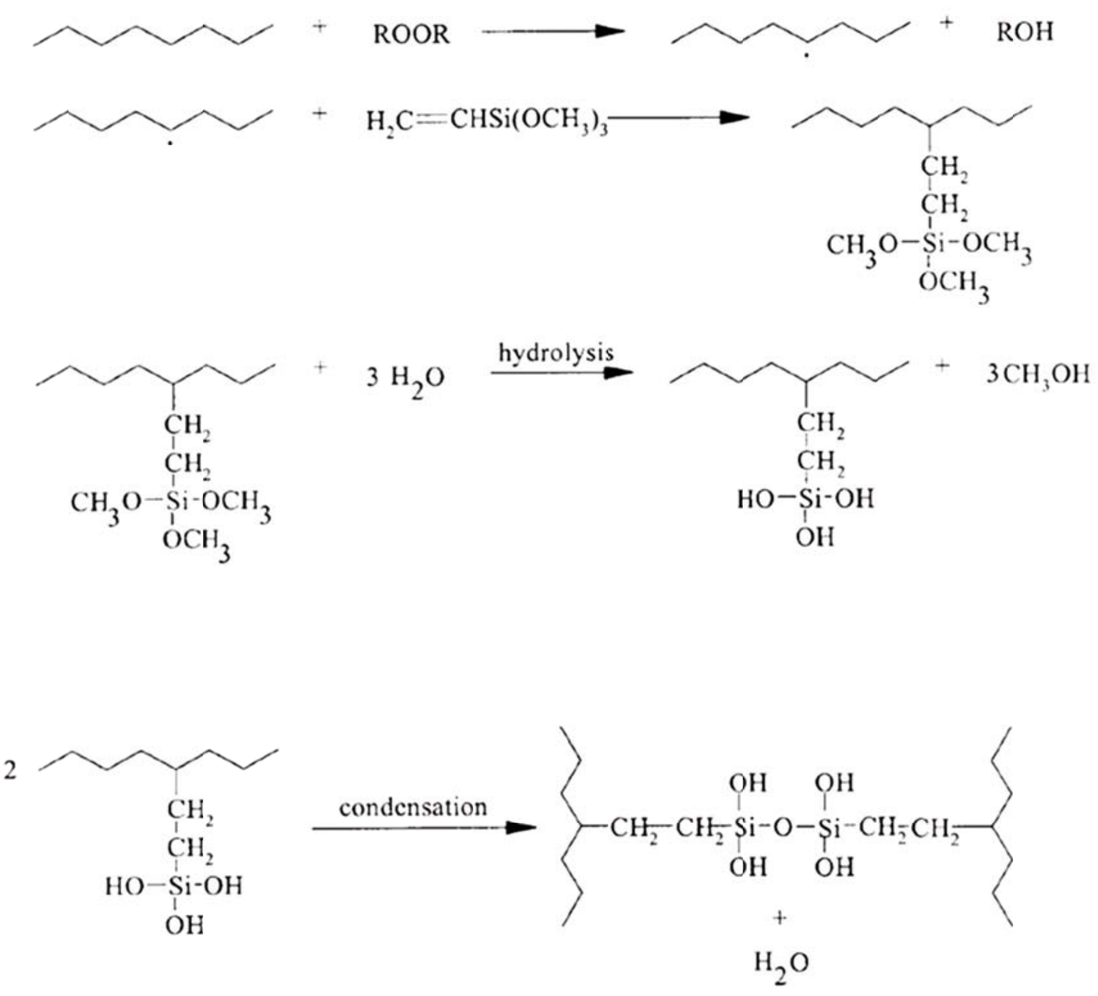


Figure 1.7 *Scheme of silane-water cross-linking of polyethylene [73].*

1.4 Chain scission and Degradation

It is well known that the polymer degradation is a natural or/and an accelerated process, that in the most cases, takes place in oxygen atmosphere during synthesis, processing and / or service life, under the action of the ageing factors (temperature, UV radiations, γ-irradiation, atmospheric pollutants and so). Because of degradation, the polymer chemical and morphological structure and so its physical and mechanical properties are changed. For this reason, the degradation can be also used for tailoring the polymer chemical structure, and so the obtaining of goods with desired utilization properties [74].

The two main phenomena that occur in radiation and peroxide initiated reaction is cross-linking and chain scission. Scission is the opposite of cross-linking reaction. Both these processes occur simultaneously but generally one of them dominates. Presence of many chain branches in the polymer molecule at high temperatures leads to lower thermal stability and has been shown to affect scission probability. Temperature is an important factor determining the ratio between cross-linking and chain scission, other influencing factors are type and concentration of peroxide, radiation dose and also the oxygen concentration. Low oxygen access favors cross-linking, whereas an excess of oxygen at high melt temperatures (such as during mixing) can induce chain scission [75, 76]. Irradiation and peroxide involves the formation of radicals, in the presence of oxygen these radical tend to react more rapidly with oxygen than with molecular chains [77]. The scission reaction leads to the degradation of polymers by rupture of covalent bond inducing a decrease of molecular weight and intrinsic viscosity. In contrast, cross-linking reactions lead to the formation of inter- and intra-molecular bonds, which increases molecular weight and intrinsic viscosity [78, 79].

Oxidation is generally considered as the main degradation mechanism of saturated polymers like polyolefins and elastomers. In presence of oxygen, the carbon radicals of the polymer chains, as formed by heat or shear are first converted to peroxy-radicals, which can further react with labile hydrogens of the polymer, to form unstable hydroperoxides, commencing auto-catalytic reactions. Stabilizers, for instance antioxidants, are used to prevent the degradation of polymers due to the detrimental effects of oxygen. Commonly used antioxidants are hindered phenols and amines (primary antioxidants), which neutralize alkoxy and peroxy-radicals prior to their harmful actions, by donating hydrogen atoms.

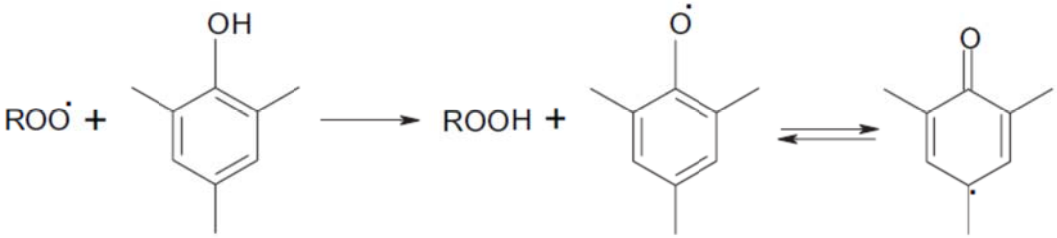


Figure 1.8 *Mechanism of action of a primary phenolic antioxidant.*

The selection and use of the antioxidants in a peroxide-cure system needs special care, because these materials compete with the polymer for the radicals formed after the decomposition of the peroxide. Reactions between antioxidants and peroxy and/or polymer-radicals take place, resulting in a reduced cross-linking efficiency of the peroxide. The most effective antioxidants are also the most effective inhibitors of peroxide cross-linking. The antioxidants contain easily abstractable hydrogen atoms and can neutralize oxy or polymer-radicals by donating a hydrogen atom. As a result, the radical is transferred to the antioxidant molecule and the cross-linking is hampered. Therefore the selection of antioxidant for peroxide cross-linking depends on following points [80],

(a) the interaction and utilization of peroxide-radicals by the stabilizer during the production stage and

(b) the effectiveness of the antioxidant in stabilizing the polymers against oxidation during the process of ageing.

The type of reaction observed in a given polymer obviously depends upon on the nature of the hydrogen atom most easily abstractable and the polymer structure around this radical. In the case of linear polyethylene and poly (ethylene oxide) only one type of hydrogen atom exists and the polymer radicals formed can most easily react by combination to give cross-links [81-83]. But, PP is degraded, due to chain scission in β position to the macroradical site [84-87]. The chain scission proceeds very fast at high temperatures because of the high instability of macro radicals. Both processes are usually undesired since short-chained PP exhibit inferior properties.

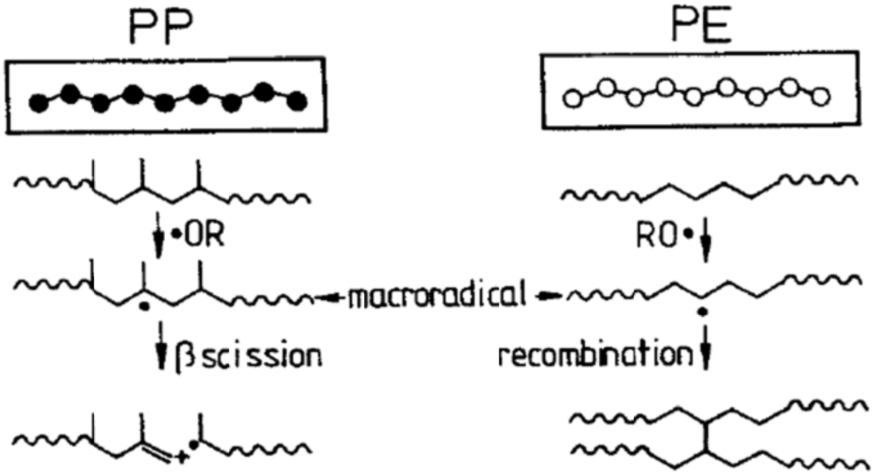


***Figure 1.9** Possible chemical reactions during cross-linking in polyethylene and polypropylene [88].*

A much more interesting situation exists where both types of unit are present in a single polymer chain. This occurs in ethylene-propylene rubbers and as might be expected a mixture of cross-linking and scission reactions occurs. The propylene groups in ethylene-propylene rubbers are vulnerable to scission. The possible chain scission mechanism occurring in ethylene-propylene rubber is shown in Figure 1.10. There are three possibilities listed.

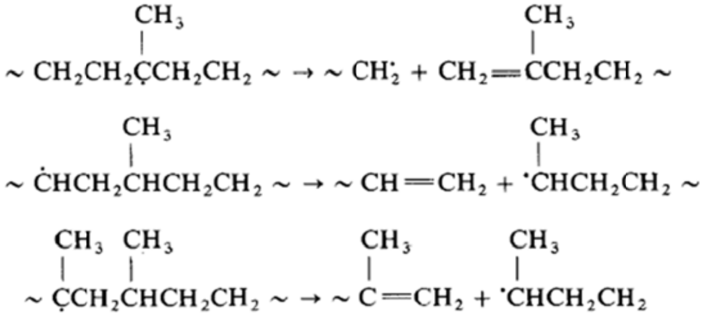


***Figure 1.10** Possible scission reactions in ethylene-propylene rubbers [52].*

EOC also has a structure somewhere in between these two (PE and PP), one could expect interplay between cross-linking and degradation during cross-linking. Sajkiewicz and Philips [89] reported that in the case of peroxide cross-linking of high branched LLDPEs tertiary carbon atoms are responsible for chain scission.

1.5 Aim of the Work and Brief Summary

The aim of the present work is to contribute towards the industrial applications of polyolefin elastomers. In the present work ethylene-octene copolymer is selected because of its excellent elastomeric properties. The main tasks of the doctoral thesis are as follows:

- Study the effect of peroxide content and temperature on cross-linking and degradation of EOC/DCP system.
- Peroxide cross-linking kinetics study and influence of peroxide content on high-temperature mechanical properties.
- Comparison of peroxide cross-linking of two different ethylene-octene copolymers.
- Apply electron beam irradiation technique to ethylene-octene copolymer and evaluate the effect of radiation dosage on thermal, mechanical and rheological properties.

Chapter 3 deals with the effect of temperature and peroxide content on cross-linking of ethylene-octene copolymer. ENGAGE 8842 (45 wt. % octene) was cross-linked by dicumyl peroxide (DCP) at various temperatures (150-200 °C). Six concentrations of DCP in range 0.2-0.7 wt. % were investigated. Cross-linking and degradation were studied by rubber process analyzer (RPA). From RPA data analysis real part of elastic torque s' and tanδ were investigated as a function of peroxide content and temperature. The highest s'_{max} and the lowest tanδ were found for 0.7 wt. % of DCP at 150 °C. Chain scission was analyzed by slope analysis of conversion ratio, X in times after reaching the maximum. Less susceptible to chain scission are temperatures in range 150-170 °C and peroxide levels 0.2-0.5 wt. %. Evaluation of scission/cross-linking ratio suggested to perform cross-linking in the 150-170 °C temperature range and 0.3-0.5 wt. % of peroxide level to avoid possible fast chain scission immediately following cross-linking.

Chapter 4 focuses on cross-linking kinetic study and high temperature mechanical properties of peroxide cross-linked ethylene-octene copolymer. Rate constant *K* for all EOC/DCP system (mentioned in chapter 3) was calculated from RPA data. The quantitative analysis confirmed that the DCP-EOC cross-linking was occurring as first order reaction. The highest cross-linking kinetics constant *K* was found for 0.6 wt. % of peroxide at 200 °C. The activation energy of cross-linking E_A obtained by Arrhenius plot had maximum at 0.5-0.6 wt. % of peroxide. While at 190-200 °C temperature range there was no detectable degradation for 0.2 wt. % of peroxide, for 0.4-0.7 wt. % of peroxide there was increasing level of degradation with increasing peroxide content. Generally, at low temperatures (150-180 °C) the increasing peroxide content caused increase in cross-linking kinetics. However at higher temperatures (190-200 °C) increase in kinetics (for 0.2-0.5 wt. % of peroxide) was followed by decrease. Especially in 0.6-0.7 wt. % peroxide level range the cross-linking is in competition with degradation which lowers the overall cross-linking kinetics. Gel content of the cross-linked EOC samples was found to be increasing with increase in peroxide content, which is caused by the increased cross-link network. Cross-linked samples were subjected to creep studies at elevated temperature (150 °C) and the result was found in agreement with the gel content and RPA results. Storage modulus and tanδ values obtained by dynamic mechanical analysis (DMA) also support the RPA results.

Chapter 5 deals with the comparison of two different peroxide cross-linked ethylene-octene copolymers (ENGAGE 8450 and ENGAGE 8452). EOC with two different octene contents (20 and 35 wt. %) and the same melt flow index (3 g/10 min) were cross-linked using various levels (0.3, 0.5 and 0.7 wt. %) of dicumyl peroxide (DCP) at different temperatures (150-200 °C). The highest s'_{max} and the lowest tanδ were found for EN8450 with low octene content (20 wt. %) at all cross-linking temperatures. Lower cross-linking efficiency of peroxide was observed in the case of high-octene copolymer (35 wt. %). EOC with high octene content was found to be more vulnerable to degradation when compared to the low-octene one. From dynamic mechanical analysis, storage modulus (M') and glass transition temperature (T_g) obtained from tanδ peaks were found decreasing with increasing octene content. Differential scanning calorimetry (DSC) results show that increasing octene content has an inverse effect on crystallinity and melting point T_m due to the reduction in average number of consecutive ethylene units. Finally, mechanical properties above T_m (at 150 °C) were analyzed by high temperature creep measurement. The creep results confirmed the cross-linkability results obtained by RPA and the gel content analyses.

Chapter 6 concerned with the effect of electron beam irradiation on thermal, mechanical and rheological properties of ethylene-octene copolymer. EOC was irradiated using electron beam irradiation at different dosages (30, 60, 90 and 120 kGy). Gel content analysis revealed that degree of cross-linking increases with radiation dosage. This was reflected in the improvement of high-temperature creep and elastic properties. Effect of irradiation on melting temperature (T_m) was analyzed by DSC. As the extent of cross-linking increases, stress at break showed an increasing trend whereas irradiation dosage has an inverse effect on elongation at break. It was proved from the rheological analysis that elastic modulus (G') and viscosity (η^*) increases with irradiation dosage while tanδ showed a decreasing trend. Radiation dosage has positive effect on thermal stability.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

2.1.1 Ethylene-octene copolymer (EOC)

ENGAGE is a special copolymer developed by Dow Chemical Co. through INSITE^{TM} technology. We have carried out our experiments using EOCs with the physical properties given below:

Table 2.1 *Physical properties of ethylene-octene copolymers used.*

Material	wt. % of Octene[a]	MFI (g/10 min) (at 190 °C/2.16 kg)[a]	Density (g/cm^3)[a]
ENGAGE 8450	20	3.0	0.902
ENGAGE 8452	35	3.0	0.875
ENGAGE 8842	45	1.0	0.857

[a] Provided by the manufacturer.

2.1.2 Dicumyl Peroxide (DCP)

Perkadox BC-40B-PD (also known as dicumyl peroxide) was the peroxide initiator we used in our studies. It was supplied by Akzo Nobel. DCP is having active peroxide content of 40%; temperature at which half-life time ($t_{1/2}$) is 1 h is 138 °C and specific gravity is 1.53 g cm^{-3} at 23 °C. Molecular structure of DCP is given in Figure 2.1.

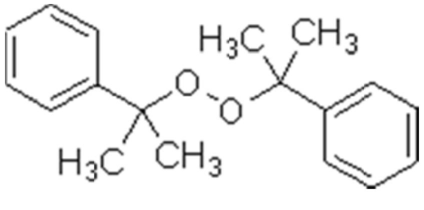


Figure 2.1*Molecular structure of DCP [90].*

2.1.3 Irganox 1010

Irganox 1010 having the chemical name tetrakis-(methylene-(3,5-di-(tert)-butyl-4-hydrocinnamate)) methane was used as the antioxidant to prevent oxidation. Irganox 1010 is having density 1.15 g cm^{-3} and it was supplied by Ciba, Switzerland. Amount of antioxidant was kept constant throughout the experiment as 0.40 wt. %. Molecular structure of Irganox 1010 is given in Figure 2.2.

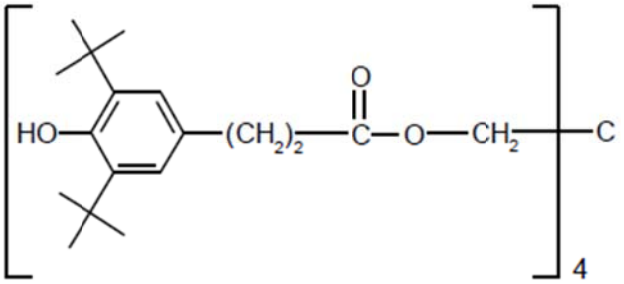


Figure 2.2 *Molecular structure of Irganox 1010 [91].*

2.2 Methodology

2.2.1 Mixing of EOC with DCP

EOC, peroxide and Irganox were mixed in a Brabender Plasti-corder PL2000 mixing machine with mixing volume of 50 cm^3 at 100 °C at mixing speed 50 rpm for 10 minutes**.** The influence of peroxide was investigated for concentrations 0.50, 0.75, 1.00, 1.25, 1.50 and 1.75 wt. %. The active peroxide content was then 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 wt. % respectively. Compounded batches were stored in deep-freeze at -18 °C to avoid unwanted cross-linking during storage.

Figure 2.3 *Brabender PL-2000 Plasti-Corder [92].*

2.2.2 Peroxide Cross-linking and Degradation studies

Cross-linking of EOC samples pre-mixed with DCP was carried out in a rubber process analyzer, RPA-2000 (Alpha Technologies) at different temperatures in the range 150-200 °C. The rubber process analyzer is an advanced (dynamic mechanical rheological) test instrument, designed to measure the viscoelastic properties of polymers and rubber compounds before, during and after cure.

Figure 2.4 *Rubber Process Analyzer, RPA-2000 and its die configuration [93].*

Crosslinking and degradation (during cross-linking) of EOC-DCP compounds has been analyzed using RPA at different temperatures and times. Testing conditions were maintained at an angle of 0.5° and a frequency of 100 CPM (1.667 Hz)

Theoretical Background

Burhin HG [94] suggested a way of cross-linking kinetics analysis. For first order reaction, Eq. (1) can be used

$$ln(1 - X) = f(t) \qquad (1)$$

Where, t is the time in min and X is the percentage of achieved cross-linking (0.9 for 90%) or the conversion variable. This mathematical function is linear for first order reaction and was derived from the reaction kinetics formula for any chemical process shown by Eq. (2).

$$\frac{dX}{dt} = K^{(n)}.(1 - X)^n(t > t_i) \qquad (2)$$

Where, t is the time in min, dX/dt is the reaction rate, $K^{(n)}$is the nth order conversion rate constant, n is the reaction order in respect of time, t_i is the incubation time in min or the predicted time for the start of vulcanization ($X=0$).

A linear regression of the Eq.(2) gives the slope K, the time value for a conversion variable (X) equal to zero or the time the vulcanization reaction starts, and the coefficient of regression.

Considering the cross-linking reaction as a normal chemical reaction, we can apply the law of Arrhenius [95] which expresses the relationship of the conversion rate constant K (or the rate of reaction) with the temperature according to Eq. (3) and (4).

$$K = A.e^{-\frac{E_A}{RT}} \qquad (3)$$

or

$$ln\,K = lnA - \frac{E_A}{RT} \qquad (4)$$

Where E_A is the activation energy in J mol^{-1}, R is the universal gas constant, 8.314 J mol^{-1} K^{-1}, T is the absolute temperature in K, A is the pre-exponential factor.

By carrying out a series of tests at various temperatures, the E_A value can be calculated from the slope of the Eq.(5).

$$ln(K) = f(\frac{1}{T}) \qquad (5)$$

The linear regression of Eq.(5) gives $E_{A.}$

2.2.3 Irradiation Cross-linking

Ethylene-octene copolymer sheets (sample size was 12x6x0.2 mm) for beta (electron beam) irradiation were prepared using a compression molding machine at 110 °C for 10 min. Beta irradiation was performed in normal air at room temperature, in Beta-Gamma-Service (BGS) GmbH, Germany. It was made sure that the temperature did not exceed 50 °C. Source of radiation was toroid electron accelerator Rhodotron (10 MeV, 200 kW). The irradiation was carried out in a tunnel on a continuously moving conveyer with the irradiation dosage ranging from 30-120 kGy; in steps of 30 kGy per pass.

2.2.4 Gel Content Analysis

Gel content is the direct measure of extent of cross-linking. The gel content of the cross-linked EOC was evaluated by determination of the content of insoluble fraction of cross-linked material after solvent extraction according to ASTM D2765-01. About 0.3 g of cross-linked sample was wrapped in a 120 mesh stainless steel cage and extracted in refluxing xylene which contained 1% of antioxidant (Irganox 1010) for 6 h. Sample was then dried in vacuum at 55 °C and weighed. % gel content was calculated according to Eq. (6):

$$\text{Gel content} = \frac{\text{Final weight of sample}}{\text{Initial weight of sample}} \times 100 \qquad (6)$$

2.2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a tool that helps us to study the thermal transitions, melting and crystallization behaviors of a polymer during their heating or cooling or during isothermal annealing. Percentage crystallinity (X_c) of polymers also can be measured using DSC [96].

Figure 2.5 *Differential Scanning Calorimeter [97]***.**

The DSC analysis of cross-linked samples was performed in a Pyris-1 instrument. Nitrogen atmosphere was employed during the experiment at heat flow rate being 20 mL min^{-1}. The instrument was also attached to a cooling unit capable of cooling upto -130 °C. Heating and cooling rates were 20 and 50 °C/min. The temperature and heat flow of the apparatus was calibrated on indium standard. Percentage crystallinity (X_c) of EOC was calculated using the heat of fusion value of perfectly crystalline polyethylene which is 290 J g^{-1} [98].

2.2.6 Dynamic Mechanical Analyzer (DMA)

DMA measures stiffness and damping, these are reported as modulus and tanδ. Because we are applying a sinusoidal force, we can express the modulus as an in-phase component, the storage modulus, and an out of phase component, the loss modulus, see Figure 2.6. The storage modulus, either E' or G', is the measure of the sample's elastic behavior. The ratio of the loss to the storage modulus is the tanδ and is often called damping. It is a measure of the energy dissipation of a material.

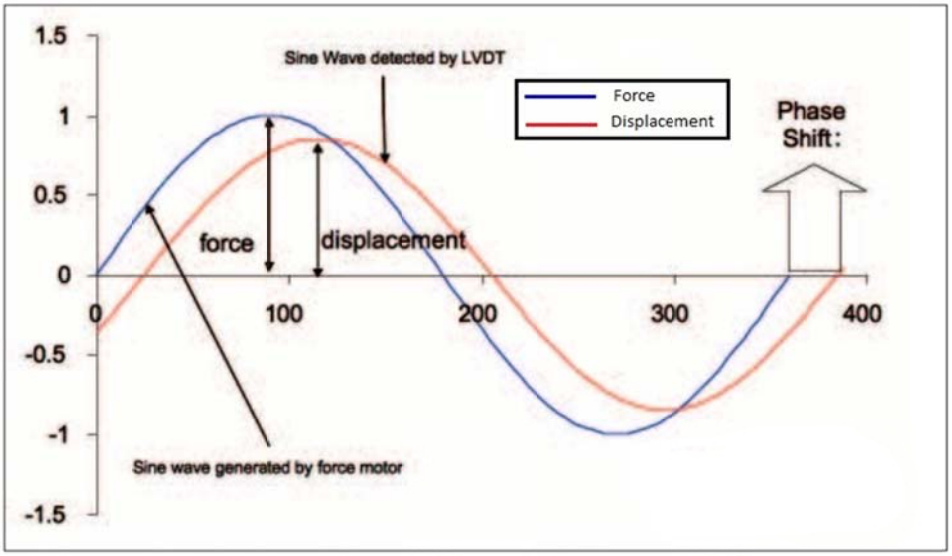


Figure 2.6 *The relationship of the applied sinusoidal stress to strain is shown, with the resultant phase lag and deformation [99].*

DMA analysis was carried out using two different instruments. Effect of peroxide content on cross-linked EOC samples was analysed in an IT Keisoku-seigyo (DVA-200S) machine in the temperature range 0- 200 °C at a heating rate of 5 °C /min. The analysis was carried out in cyclic tensile strain mode with the frequency of 10 Hz. Storage modulus (E’) and tanδ of the samples were noted.

Influence of octene content on cross-linking was tested employing the DMA instrument - DMA/SDTA 861e (Mettler Toledo, Switzerland) – in tensile mode with a frequency of 5 Hz. The specimens were heated at rate of 3 °C/min in the temperature range from -60 to 150 °C.

2.2.7 Evaluation of Mechanical Properties

When a plastic material is subjected to a constant load, it undergoes a continuous deformation. The material will continue to deform slowly with time indefinitely or until rupture or yielding causes failure. This phenomenon of deformation under load with time is called creep. The degree of creep depends on several factors, such as type of plastic, magnitude of load, temperature and time.

Creep study reveals the usability of a polymer in long term application. Creep behavior has been subjected to considerable number of researches due to its practical importance. Tensile samples were cut out of the cross-linked sheets and used for the tensile creep experiments according to ISO 899 standard. Creep test was carried out at different temperatures in a Memmert UFE 400 oven with digital temperature control. Creep of the samples was recorded through using a SONY SLT-A33 camera capable of HD 1920x1080 video (25 frames/sec). This video was later analyzed at proper time intervals. Effect of peroxide content, octene content, temperature and radiation dosage (at stress levels of 0.05 and 0.1 MPa) on creep behavior of cross-linked EOCs was studied.

In the case of peroxide cross-linking system sheets for dynamic mechanical analysis (25x3x0.7 mm) and creep measurements were prepared by cross-linking during compression molding at 170 °C for 15 min in a compression molding machine.

Elastic properties of irradiated samples were measured by residual strain experiments conducted using an Alpha Tensometer 2000 instrument. Microtensile samples with dimensions according to ISO 12086 were used for tensile experiments. Hysteresis experiments for the residual strain evaluation were carried out at a cross-head speed of 10 mm min^{-1}, where the cross-head was allowed to return to the original position after reaching to a pre-set strain of 100%. Tensile experiments till rupture were carried out at a different cross-head speed of 100 mm min^{-1} and tensile modulus, stress at break and elongation at break was noted.

To study the effect of irradiation cross-linking on elastic properties, residual strain experiments were also carried out above the melting temperature of the virgin copolymer. For this, the samples were stretched to 100% elongation for 5 min and kept in a hot air oven (Memmert UFE 400) maintained at 70 °C. The samples were then cooled to room temperature and the residual strain values were noted.

2.2.8 Rheological Properties

Advanced Rheometric Expansion System ARES 2000 (Rheometrics Scientific, USA) equipped with 25 mm parallel plates geometry was used to determine storage modulus G’, tanδ and complex viscosity (η^*) of irradiation cross-linked EOC samples in the frequency range 0.1 - 100 rad s^{-1} at constant temperature (150 °C) and strain (1%).

2.2.9 Thermogravimetric Analysis (TGA)

Thermal stability of cross-linked ENGAGE 8842 samples was studied using a TGA Q500 instrument (TA Instruments). Thermogravimetric analysis (TGA) experiments were carried out in nitrogen atmosphere at a heating rate of 20 °C min^{-1} in the selected temperature range of 25-600 °C.

CHAPTER 3

Effect of peroxide content and temperature on cross-linking and degradation of EOC/DCP system

3.1 Introduction

In this chapter we have focused on peroxide cross-linking of ethylene-octene copolymer using various peroxide levels at various temperatures. For this study, we selected ethylene-octene copolymer with high octene content (45 wt. %) with trade name ENGAGE 8842. EOC was cross-linked by dicumyl peroxide at different temperatures in range 150-200 °C. The influence of peroxide was investigated for concentrations 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 wt. %. Cross-linking and degradation was studied by rubber process analyzer. From RPA data analysis elastic torque s' and tanδ were investigated as a function of peroxide content and temperature. Here, we also calculated t_{90} value (time in min required for the 90% of cross-linking reaction to be completed) for all samples at all temperature. We have compared the effect of storage time on s' during cross-linking at two temperatures also.

3.2 Influence of Peroxide Level and Temperature on Cross-linking

The raw data out of the RPA, more specifically real part of the elastic torque, s' is shown in Figure 3.1. From this graph one can notice that with increasing peroxide content the s' elastic torque increases to higher levels. That would support the idea of cross-linking rather than chain scission. Both the minimum and maximum values of s' are growing with increasing peroxide content. The minimum of the s' value represents processability and the maximum of the s' contains information about mechanical properties after cross-linking. The peroxide was mixed into EOC carefully at low temperature (100 °C) to avoid premature cross-linking. Apparently even at 100 °C some cross-linking happened. The minimum of s' is quite peroxide level dependent. Figure 3.1 shows data just for one temperature: 180 °C.

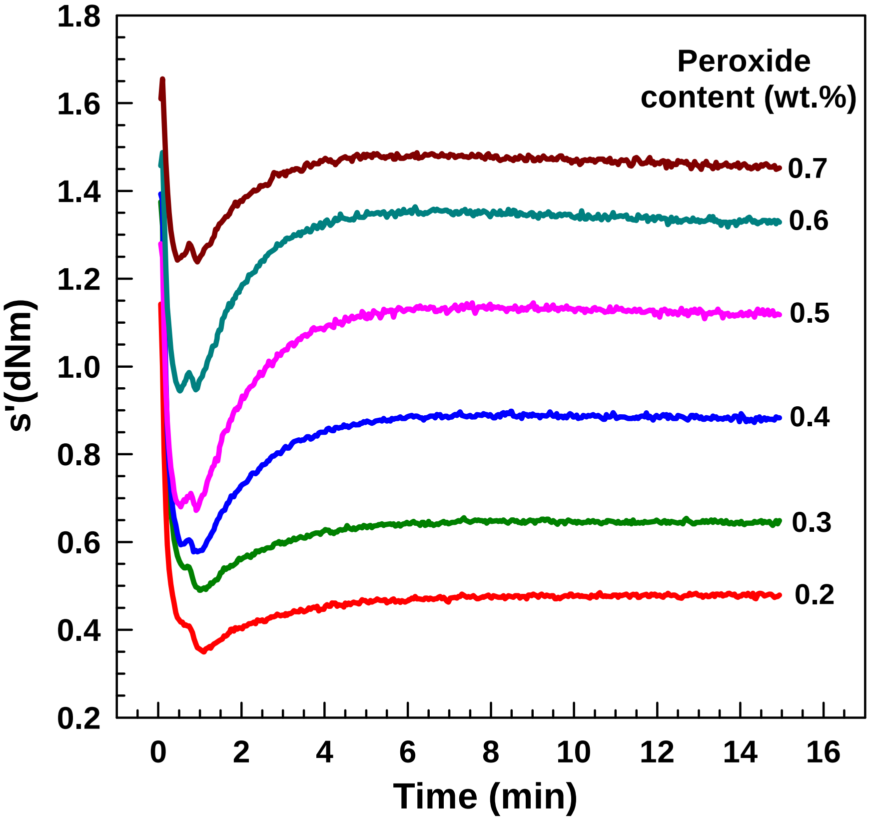


Figure 3.1 *Plot of elastic torque (s') vs. time at 180 °C for various peroxide contents.*

Figure 3.2 is mapping the maximum s' (s'$_{max}$) value as a function of peroxide level and temperature altogether in 3D plot. For all cross-linking temperatures, the s'$_{max}$ value increases with increasing peroxide content. On the other hand, with increasing temperature the s'$_{max}$ values decrease for all peroxide levels. To obtain the maximum s'$_{max}$, one has to use the highest peroxide level (0.7 wt. %) together with the lowest cross-linking temperature (150 °C). The lowest s'$_{max}$ value was found for the lowest peroxide level (0.2 wt. %) and the highest cross-linking temperature (200 °C). The numerical values of s'$_{max}$ are summarized in Table 3.1.

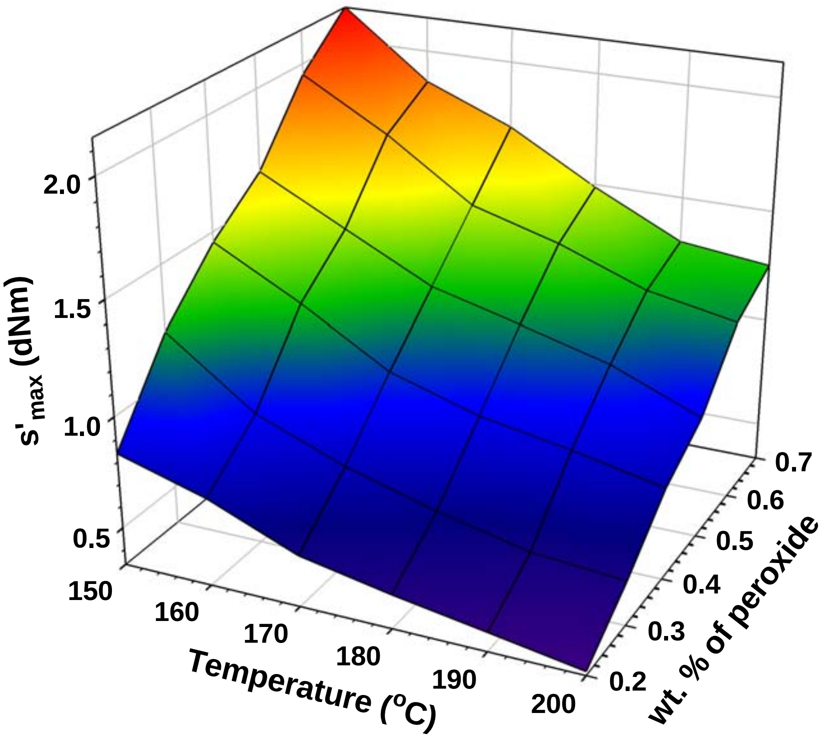


Figure 3.2 *3D plot of s'$_{max}$ as a function of temperature and peroxide content.*

Table 3.1 *s'$_{max}$ (dNm) values for various peroxide content at different temperatures.*

wt.% of peroxide	**Temperature (°C)**					
	150	**160**	**170**	**180**	**190**	**200**
0.2	0.84	0.76	0.56	0.48	0.42	0.35
0.3	1.21	0.92	0.77	0.65	0.56	0.53
0.4	1.45	1.25	1.02	0.90	0.83	0.74
0.5	1.63	1.44	1.25	1.15	1.04	0.88
0.6	1.95	1.78	1.47	1.36	1.22	1.14
0.7	2.15	1.79	1.71	1.49	1.30	1.25

Another useful and important value is tanδ (tanδ=s''/s'). The lower the tanδ value the better elasticity one can expect. For example, in tire industry the lower tanδ value is connected with lower rolling resistance and lower consumption of gasoline by the car. So the companies are trying to develop new formulations to get lower tanδ or even new polymers such as solution type of butadiene-styrene rubber (SBR).

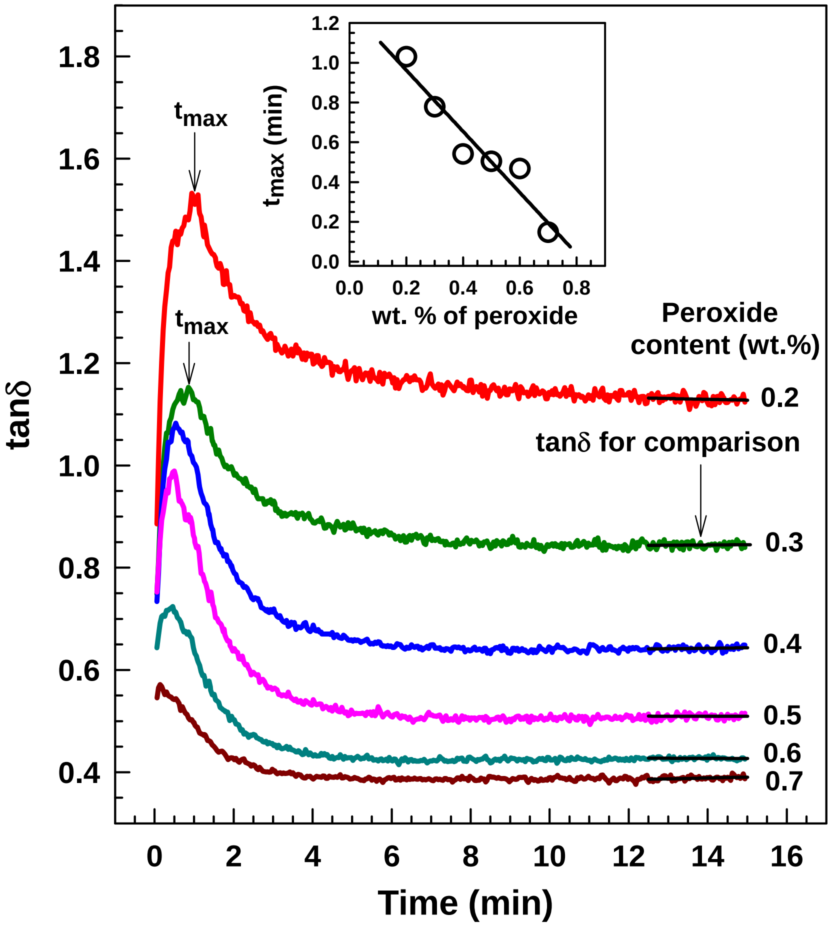


Figure 3.3 *tanδ vs. time at180 °C.*

The raw graphs with tanδ curves from RPA are shown in Figure 3.3. The highest values of tanδ were found for 0.2 wt. % of peroxide and the lowest ones for 0.7 wt. % of peroxide. Initially, tanδ increases as the sample is melting and getting viscous. Then tanδ starts to decrease with progressing cross-linking. Finally it reaches certain equilibrium value (shown by line) that will be compared in the following Figure 3.4. It is important to notice also the time to reach the maximum. It is getting shorter with increasing peroxide content. While t_{max} is about 1 min for 0.2 wt. % of peroxide, it is only few seconds for 0.7 wt. % of peroxide. One could call that induction period of cross-linking and plot it as a function of peroxide content as shown in the inserted picture of Figure 3.3.

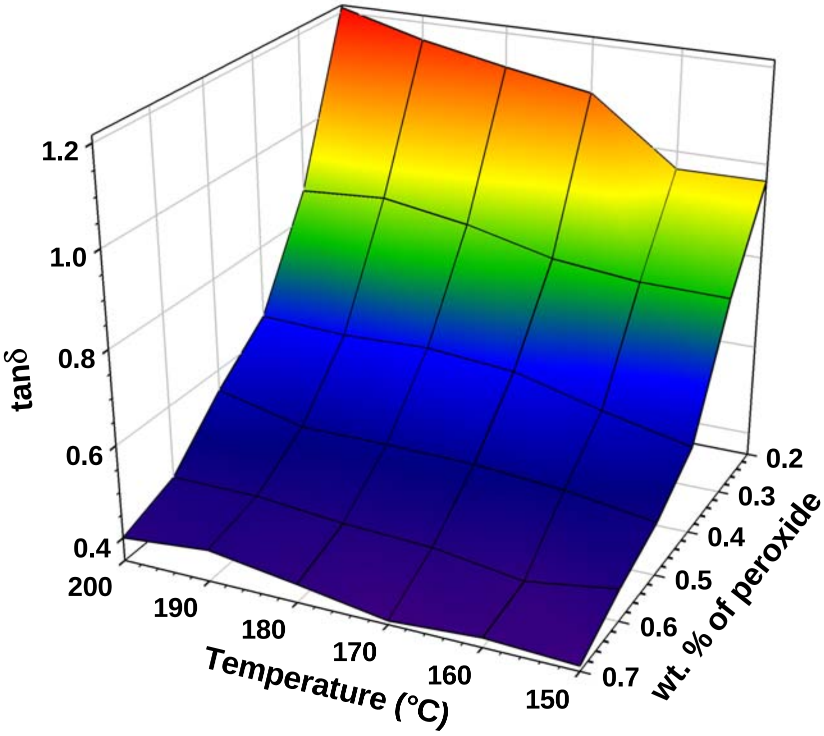


Figure 3.4 *3D plot of tanδ as a function of temperature and peroxide content.*

Figure 3.4 shows the equilibrium tanδ values as a function of peroxide content and temperature in the form of 3D plot. There is a tremendous decrease in tanδ values in peroxide range 0.2-0.5 wt. %. Then, in range 0.5-0.7 wt. % there is also a decrease but much more moderate. The difference in tanδ is quite small at higher peroxide levels (0.6-0.7 wt. %). The largest difference in tanδ values was found to be for the lowest peroxide level (0.2 wt. %). Concerning cross-linking temperature for the 0.2 wt. % of peroxide the tanδ values are the largest (the worst elasticity) and the dependence on temperature is also the largest. With increasing temperatures the tanδ value increases as well with exception to 150 and 160 °C when the tanδ values are almost the same. There is strong dependence on peroxide content and much smaller dependence on cross-linking temperature. The lowest tanδ values were found for 0.7 wt. % of peroxide cross-linked in 150-170 °C range, tanδ being in 0.3-0.4 range. The largest tanδ values were found for 0.2 wt. % of peroxide in 180-200 °C range, tanδ being in 1.1-1.2 range. The numerical values of tanδ are summarized in Table 3.2.

Table 3.2 *tanδ values for various peroxide content at different temperatures.*

wt.% of peroxide	**Temperature (°C)**					
	150	**160**	**170**	**180**	**190**	**200**
0.2	0.96	0.96	1.10	1.13	1.16	1.21
0.3	0.78	0.78	0.80	0.85	0.87	0.86
0.4	0.54	0.58	0.63	0.64	0.64	0.65
0.5	0.46	0.49	0.51	0.51	0.51	0.55
0.6	0.42	0.39	0.42	0.43	0.44	0.44
0.7	0.36	0.37	0.36	0.39	0.42	0.40

In rubber industry the t_{90} value is frequently evaluated to set the proper vulcanization time. The t_{90} value represents time in min required for the 90% of cross-linking reaction to be completed. All the t_{90} numerical values are listed in Table 3.3 and examples of the t_{90} values for three peroxide levels as a function of temperature are shown in Figure 3.5. The curves have exponential decay shape. In inserted picture of Figure 3.5 the natural logarithmic values of t_{90} are plotted as a function of temperature. There is a linear relationship in 150-190 °C temperature range confirming the exponential nature of this temperature dependent phenomenon.

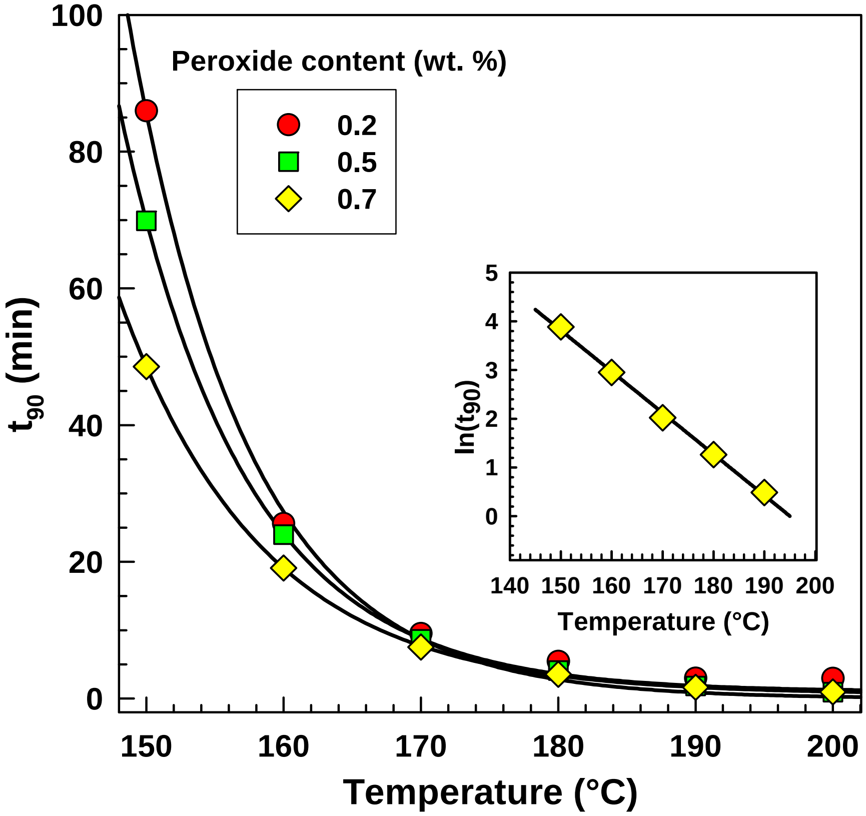


Figure 3.5 *t_{90} as a function of cross-linking temperature.*

Table 3.3 *t_{90} (min) values for various peroxide content at different temperatures.*

wt.% of peroxide	**Temperature (°C)**					
	150	**160**	**170**	**180**	**190**	**200**
0.2	86.0	25.6	9.47	5.43	2.98	2.95
0.3	66.4	25.4	9.34	5.28	2.28	1.17
0.4	77.3	25.4	8.50	4.45	2.01	0.97
0.5	69.9	24.0	8.69	4.10	1.84	0.94
0.6	68.0	22.0	7.73	3.88	1.61	0.90
0.7	48.6	19.1	7.54	3.54	1.63	0.95

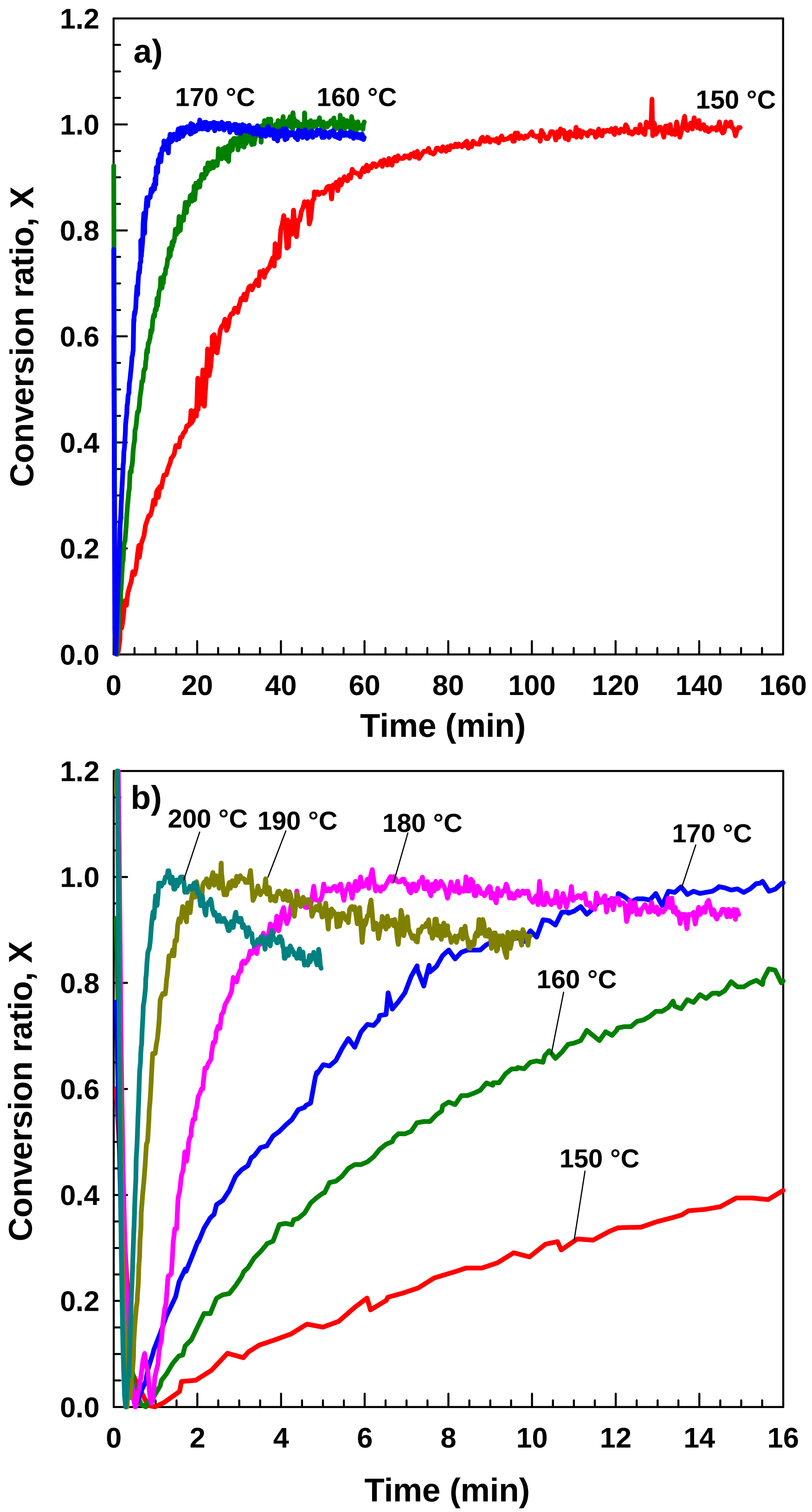


Figure 3.6 *Plot of conversion ratio, X vs. time for 0.6 wt. % of peroxide at various temperatures, a) 150 -170 °C and b)150-200 °C.*

The s' curve is recalculated so that it is in range 0.0-1.0 (or 0-100%). X is defined as the percentage of achieved cross-linking. The examples of such curves are shown in Figures 3.6 a-b. Figure 3.6a covers very long time period (150 min) that was required for very slow cross-linking at 150 °C. Figure 3.6b focuses on high temperature cross-linking (180-200 °C) that is finished in less than 15 min.

As it is shown in above figure, the conversion curves exhibit a maximum and then the *X* values decrease differently for different temperatures. The decrease in X value represents degradation. The network created by cross-linking is being damaged most likely by chain scission. Possible chemical reactions occurring in the system are shown on Figures 3.7 and 3.8. In the peroxide the O-O bond breaks first rendering two free radicals. Then this free radical RO• reacts with the hydrogen of EOC chain. Then two macro-radicals react together forming cross-linked and also a longer molecule. There are three possible sites from where hydrogen can be abstracted which are shown on Figure 3.7c. Numbers on hydrogen atoms are given according to the priority. Number one is hydrogen atom on the tertiary carbon atom which is called labile hydrogen. Number 2 and 3 have almost equal probability of reaction. There are 6 possible recombination listed in the bottom of Figure 3.7. Only (2-2) combination is shown in Figure 3.7b. This reaction repeats many times until a cross-linked network is formed. Macro-radicals can sometimes break by chain scission mechanism shown on Figure 3.8. There are two possibilities of chain scission. The bond energy of C-H bond in case of tertiary carbon is slightly lower than that of secondary carbon (96.5 vs. 98.6 kcal mol^{-1}, respectively) [100].

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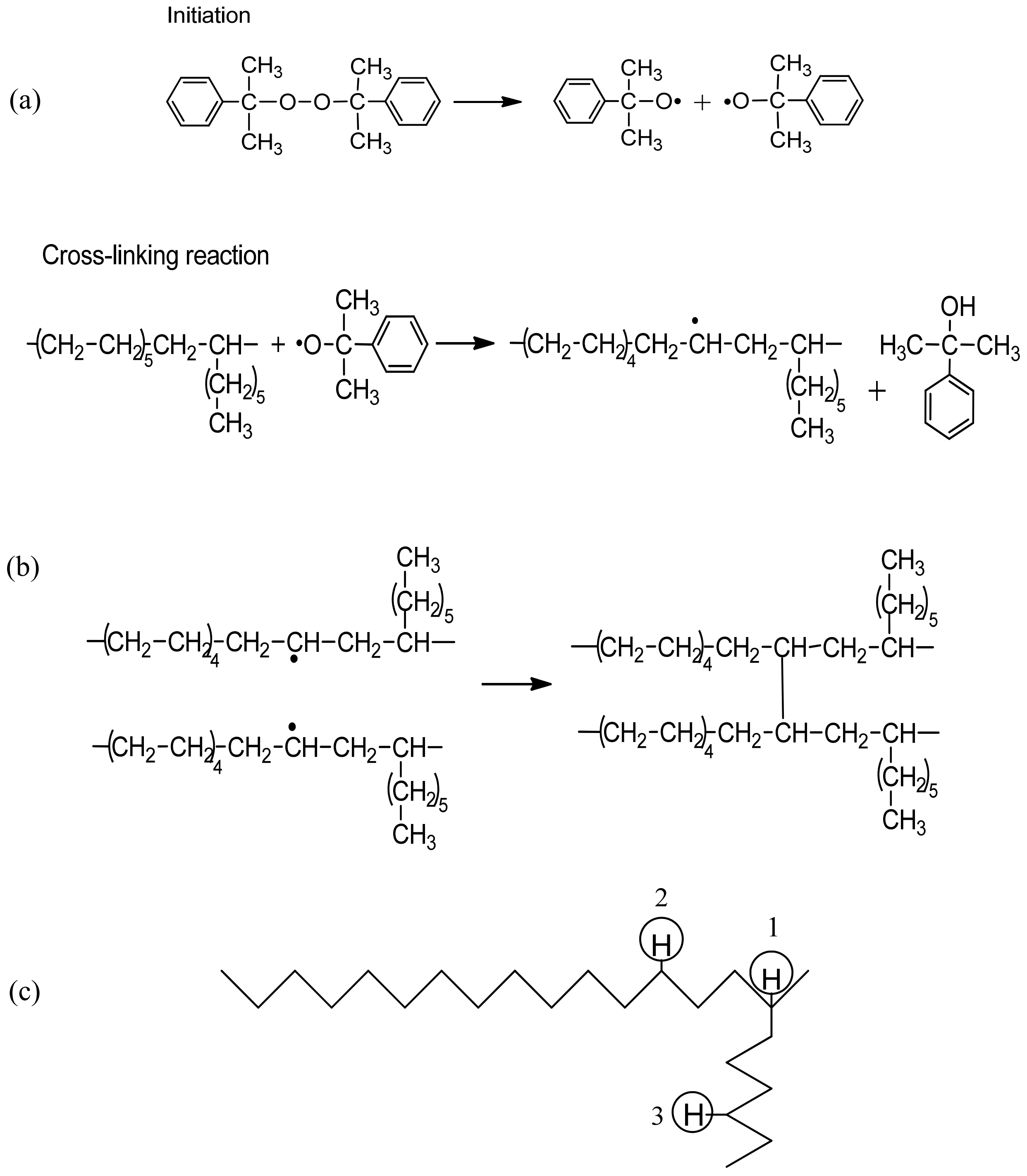


Cross-linking possibilities: (1-1), (1-2), (1-3), (2-2), (2-3) and (3-3).

Figure 3.7 *Peroxide initiation and cross-linking of EOC by DCP.*

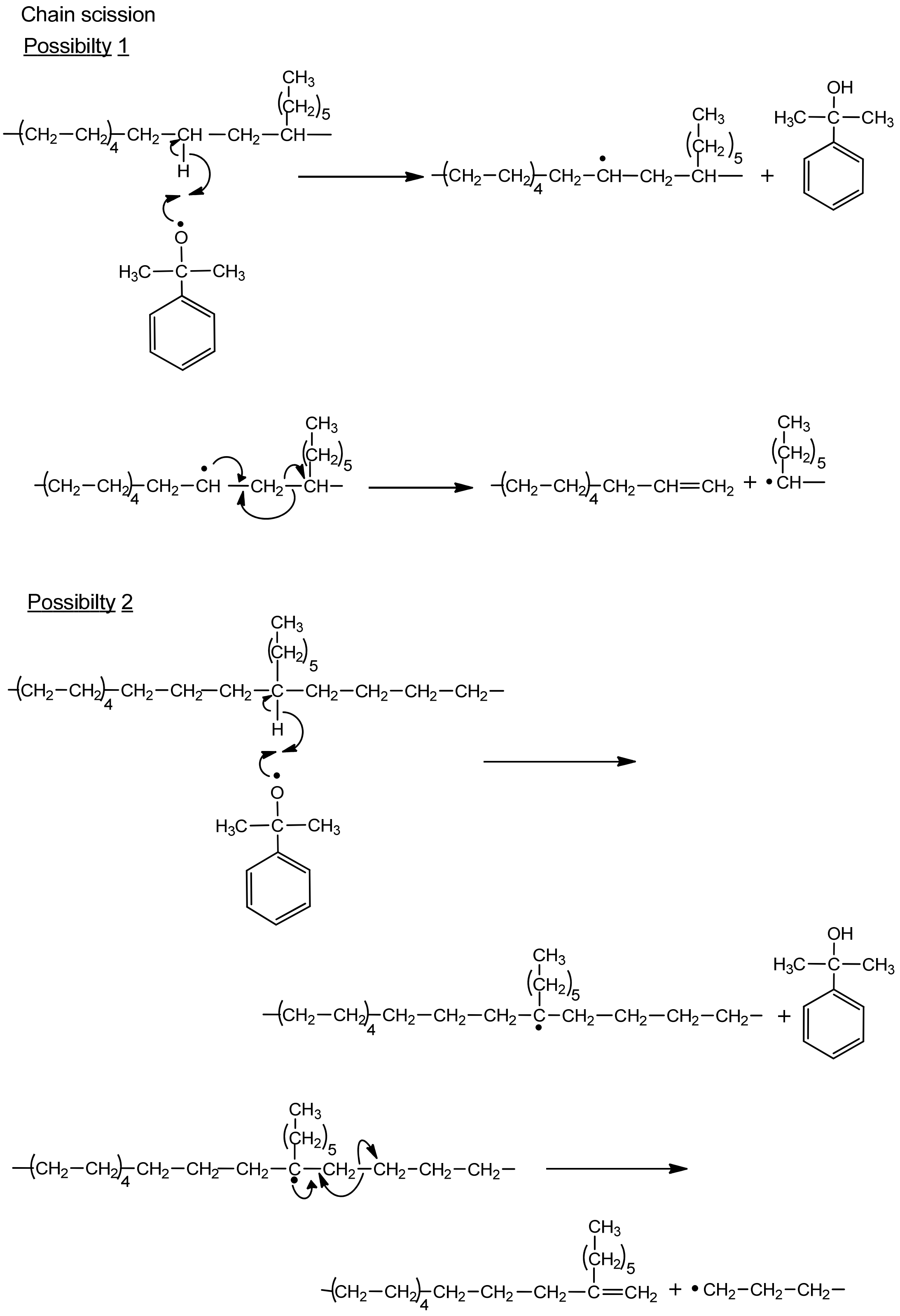


Figure 3.8 *Two possible chain scission reactions.*

One can practically evaluate the chain scission by slope analysis shown on Figure 3.9. Initially the X curve increases in time rapidly that indicates the progress of cross-linking reaction. After reaching the maximum, the X value decreases. This decrease slope (chain scission) can be analyzed for various temperatures as indicated in Figure 3.10a where the cross-linking slope is also shown. One can plot the scission/cross-linking ratio as a function of temperature (see Figure 3.10b). This ratio has very small value in 150-170 °C temperature range; one could assign this temperature range as "safe for cross-linking". However in 180-200 °C this scission/cross-linking ratio has much higher value and scission starts seriously compete with cross-linking. The inserted picture in Figure 3.10a shows an Arrhenius plot for evaluation of activation energy of degradation. In our case the E_A value was calculated to be 210 kJ mol^{-1} which is greater than that of cross-linking.

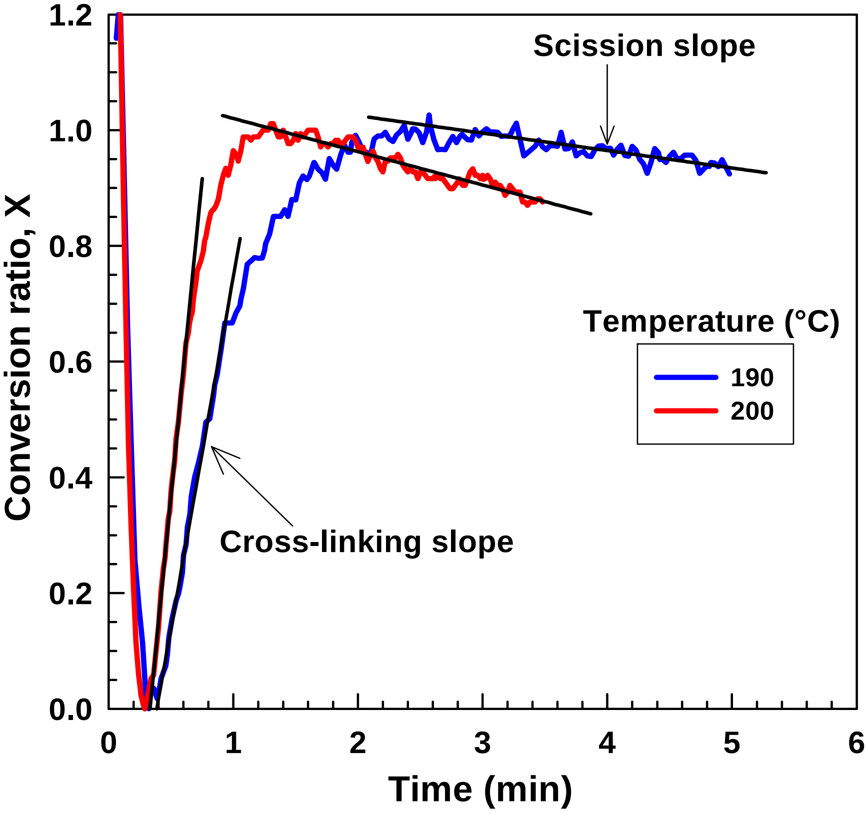
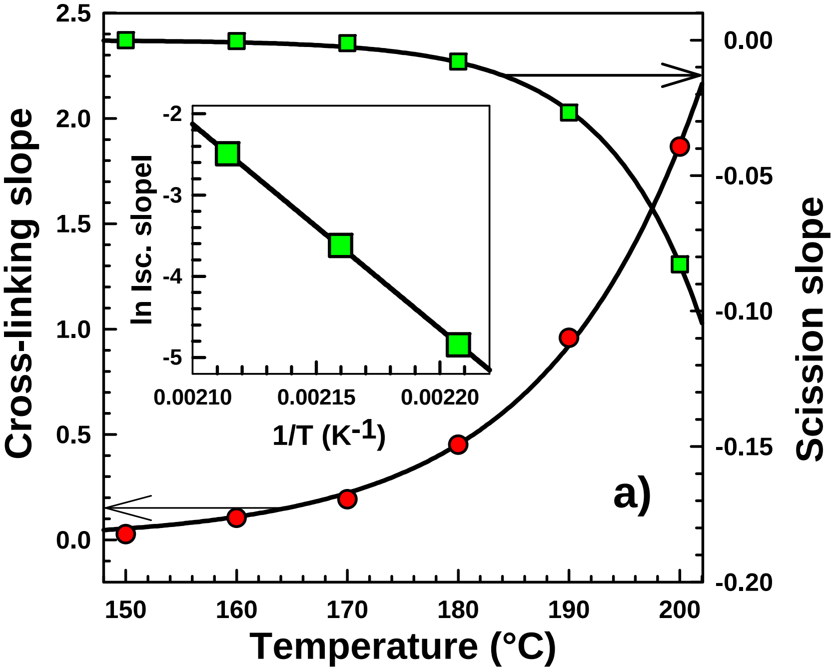


Figure 3.9 *Cross-linking and scission slope analysis in EOC with 0.6 wt. % of DCP.*



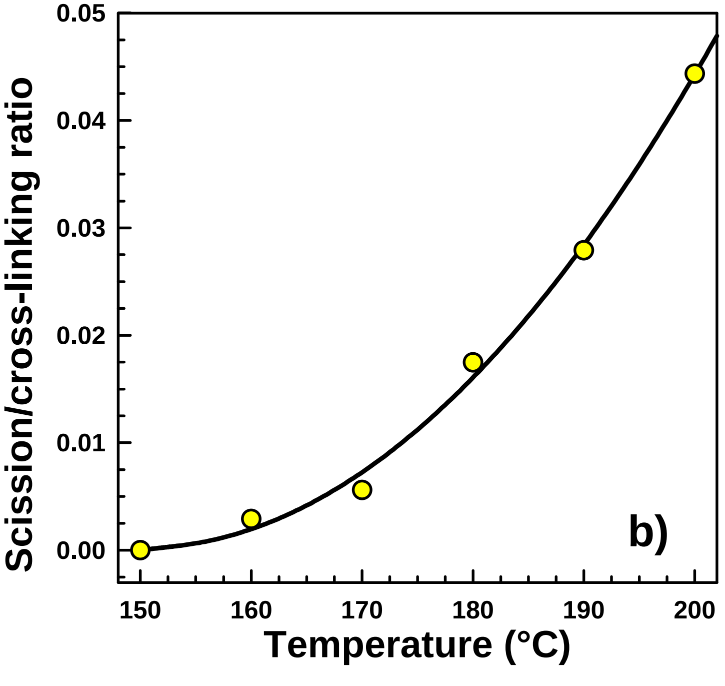


Figure 3.10 *a) Cross-linking and scission slopes as a function of temperature and b) Scission/cross-linking ratio as a function of temperature.*

The chain scission depends not only on temperature but also on peroxide level as it is shown on Figures 3.11 and 3.12. Figure 3.11 shows the conversion curves at 180 °C and various peroxide levels. The degradation slopes were analyzed and plotted in Figure 3.12.

In Figure 3.12, we have not seen any degradation for the 0.2 wt. % of peroxide in the 15 min time frame. However, for all other peroxide levels there was degradation. The degradation kinetics increases with the increasing peroxide level. These data show the danger of losing mechanical properties when the time of cross-linking is not kept precise. This risk of mechanical properties loss is greater for higher peroxide levels. For thick rubber articles, one has to count with very low thermal conductivity of EOC and thus very slow cooling rate. During this slow cooling, chemical reaction still proceeds and there is always risk of degradation and mechanical properties loss.

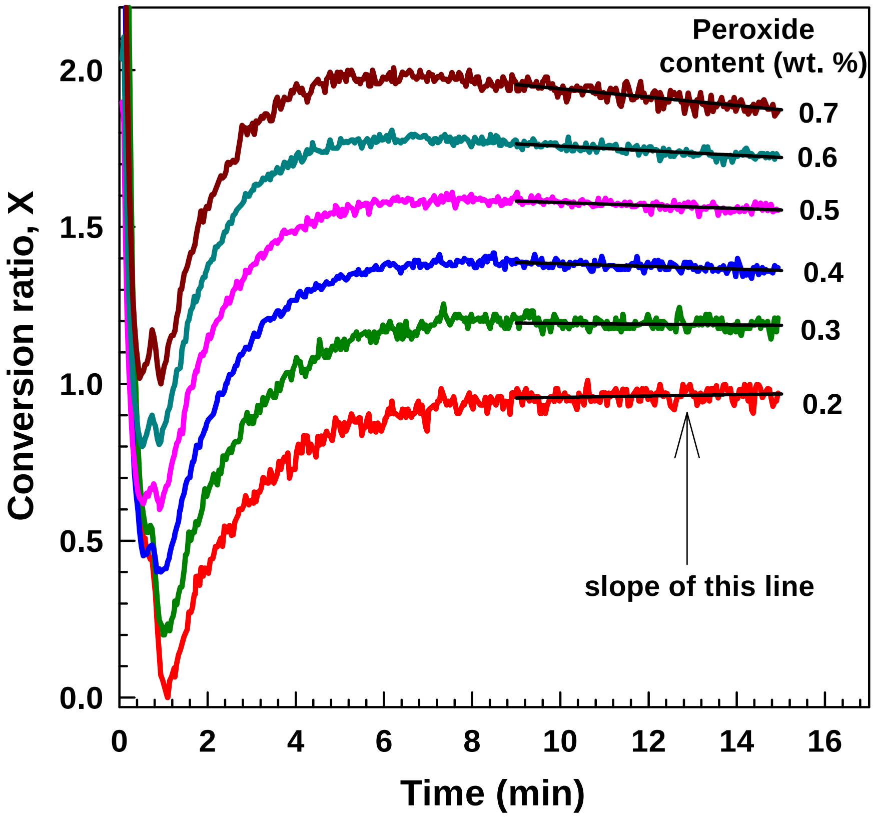


Figure 3.11 *Plot of conversion ratio X vs. time for different peroxide content at 180 °C.*

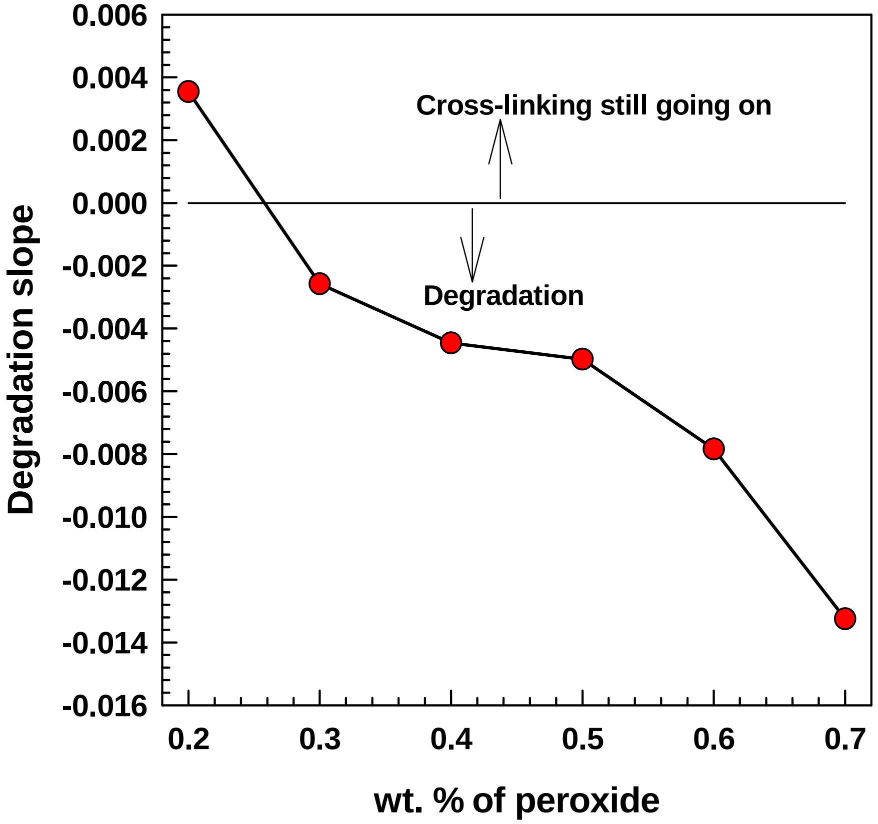


Figure 3.12 *Degradation slope as a function of peroxide content at 180 °C.*

In Figure 3.2 the elastic torque s' has the highest value at lower temperatures. However the situation is not completely clear. The temperature of s' measurement was also the cross-linking temperature in case of Figure 3.2. It is interesting to compare the s' values of samples cross-linked at different temperatures but measured at the same temperatures. This is shown in Figure 3.13. First experiment indicates very long cross-linking at low temperature (150 min at 150 °C). Then the s' values were immediately measured at 170 and 200 °C. In contrast the second experiment shows very fast cross-linking at high temperature (3 min at 200 °C). Then the s' values were immediately measured at 190, 180, 170, 160 and 150 °C. Clearly the s' values are higher in case of low temperature cross-linking. The difference is about 0.22 dNm. In industry the productivity of work pushes to lower times but one has to be careful about the mechanical properties loss in case of high temperature cross-linking.

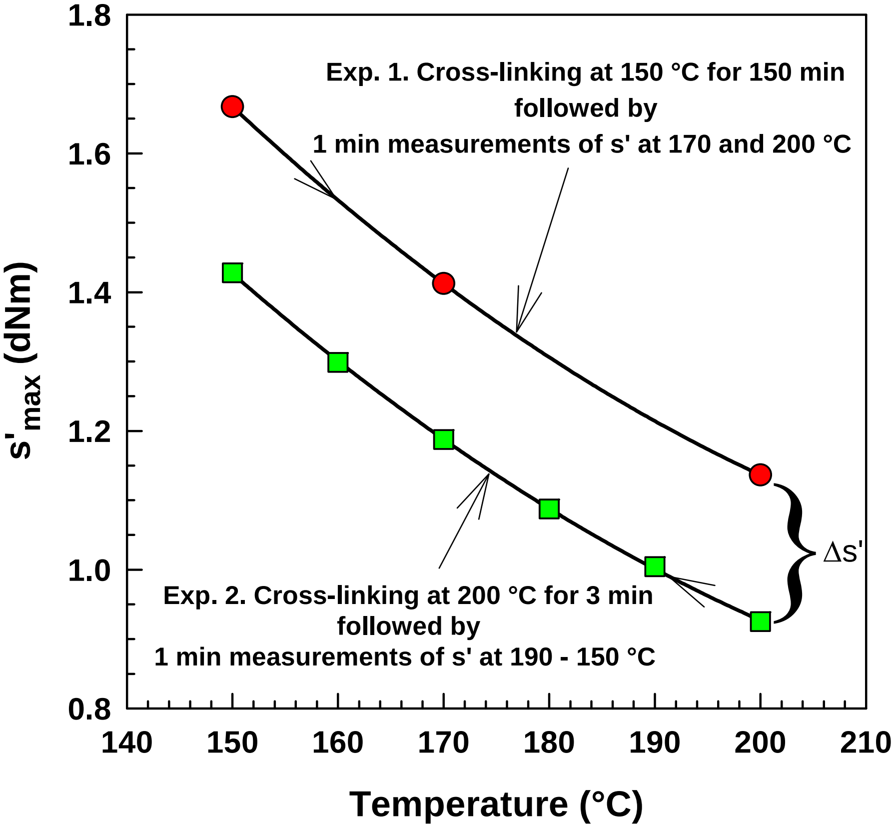


Figure 3.13 *Comparison of s', elastic torque for two cross-linking temperatures: 150 and 200 °C.*

The samples were stored in a freezer at -18 °C to prevent unwanted cross-linking and preserve good processability so that final article can be molded before cross-linking. Is something happening in the freezer? How long is the shelf life of the EOC/DCP mixture? We have compared the s' values of samples having different storage history, shorter, 10 or 20 days and longer, 90 days. The measurements were carried out at 150 and 200 °C as shown in Figure 3.14. In both cases the s' values at maximum were higher for longer storage time while the minimum s' values were not almost changed. Thus after longer storage time we can expect better mechanical properties without losing good processability. This is good news.

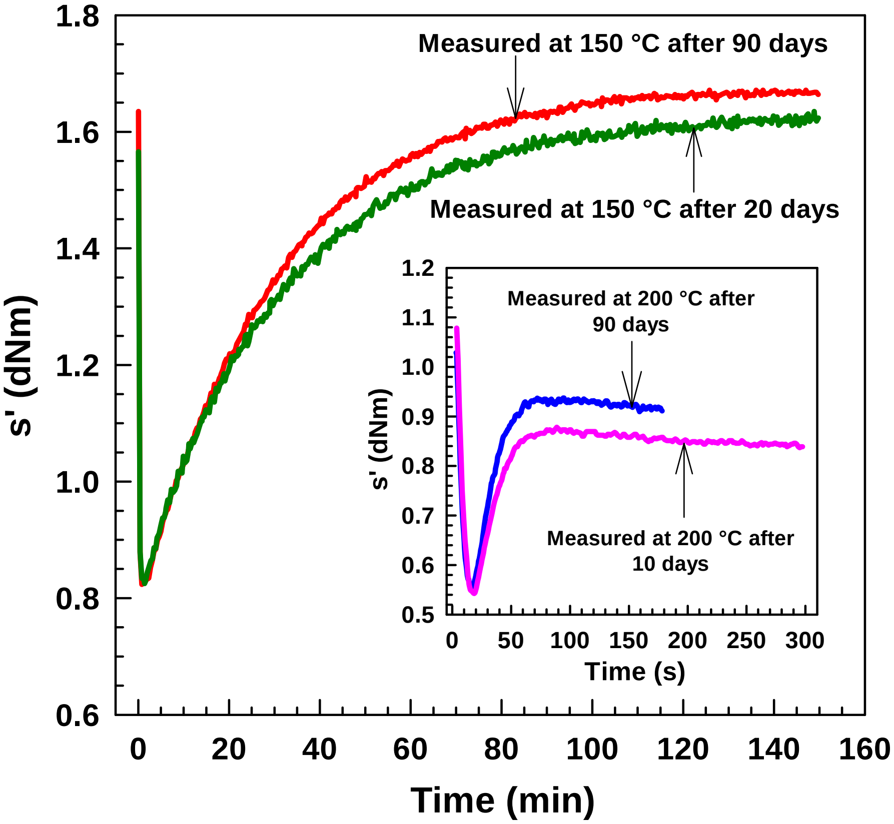


Figure 3.14 *Effect of storage time on s' evolution during cross-linking at two temperatures: 150 and 200 °C.*

3.3 Conclusions

EOC can be effectively cross-linked by dicumyl peroxide. The maximum modulus values were found for 0.7 wt. % peroxide content cross-linked at 150 °C for 150 min. Higher temperatures speed up the process at the cost of lower modulus. The lowest tanδ values were found also for this 0.7 wt. % peroxide content cross-linked in 150-170 °C temperature range. The scission/cross-linking ratio study suggested to perform cross-linking in the 150-170 °C temperature range and 0.3-0.5 wt. % of peroxide level to avoid possible fast chain scission immediately following cross-linking.

CHAPTER 4

Cross-linking kinetics study and high-temperature mechanical properties of ethylene-octene copolymer (EOC)/dicumyl peroxide (DCP) system

4.1 Introduction

This chapter deals with kinetic study and high temperature mechanical properties of ethylene octene copolymer cross-linked using dicumyl peroxide. Effect of peroxide content and temperature on cross-linking has been examined more elaborately by studying cross-linking kinetics. From RPA data analysis rate constant *K* and activation energy, E_A were investigated. Influence of peroxide level on gel content and mechanical properties was also analyzed. The extent of cross-linking has been obtained through gel content analysis. Storage modulus and $\tan\delta$ values also measured by DMA to support the RPA results. The usability of cross-linked polymer in long term applications was studied by creep analysis.

4.2 Cross-linking Kinetics Analysis

The manufacturer of RPA 2000 instrument recommends cross-linking kinetics analysis as following. The times necessary for the conversions in range 20-80 % (20, 25, 30, 35….75, 80) were calculated by the RPA software. We have plotted the points according to Eq. (1), see Figure 4.1. There are straight lines for all temperatures. The linearity confirms that the DCP-EOC cross-linking is occurring as first order reaction. Figure 4.1 represents cross-linking kinetics analysis for EOC with 0.4 wt. % of peroxide. Similar plots were performed for all peroxide levels. We have always observed straight lines confirming first order reaction. The slope of these lines gives us the reaction kinetics constant *K*.

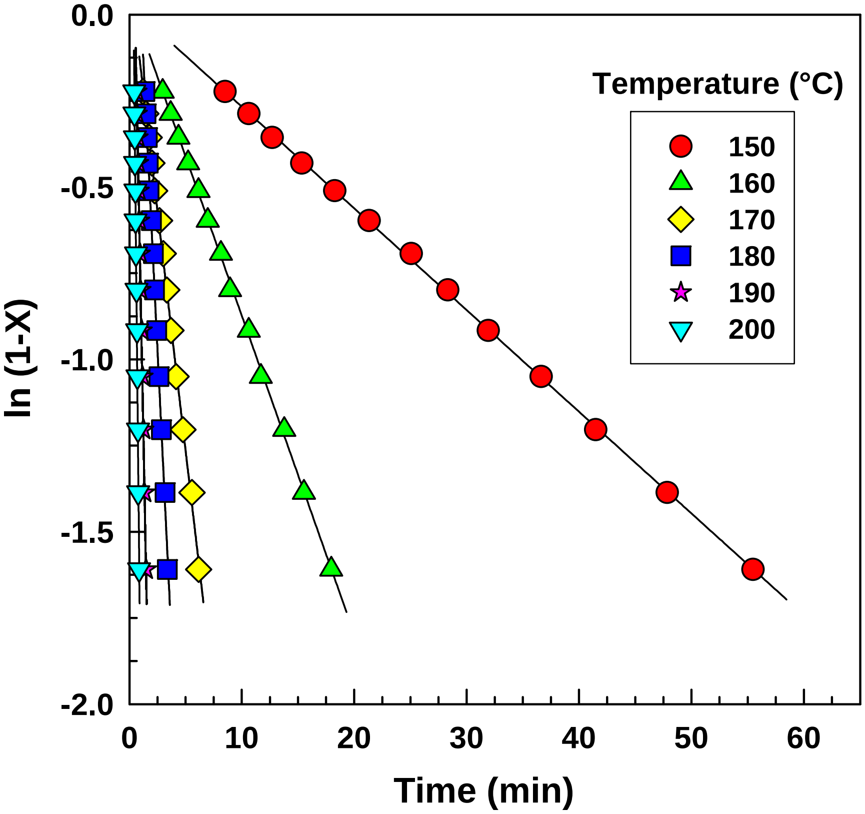


Figure 4.1 *ln(1-X) vs. time for 0.4 wt. % of peroxide at various temperatures.*

Figure 4.2 shows that with increasing peroxide level there is a steady increase in rate constant *K* up to 180 °C. At 190 °C, the values for 0.6 wt. % and 0.7 wt. % of peroxide are almost the same and at 200 °C there is even decrease in *K* value coming from 0.6 to 0.7 wt. % of peroxide. The curve at 200 °C has a maximum at 0.6 wt. % of peroxide.

The full map of rate constant as a function of temperature and peroxide content is shown by 3D plot in Figure 4.3. There is a strong exponential temperature dependence while the effect of peroxide level on rate constant is much smaller. The maximum value of rate constant for all temperatures and peroxide levels was found to be at 0.6 wt. % of peroxide and 200 °C. Apparently, the higher loading of peroxide (0.7 wt. %) does not speed up the cross-linking, most likely the other reactions (like chain scission) make the rate constant lower. The lowest rate constant value was found for 0.2 wt. % of peroxide at 150 °C, as summarized in Table 4.1.

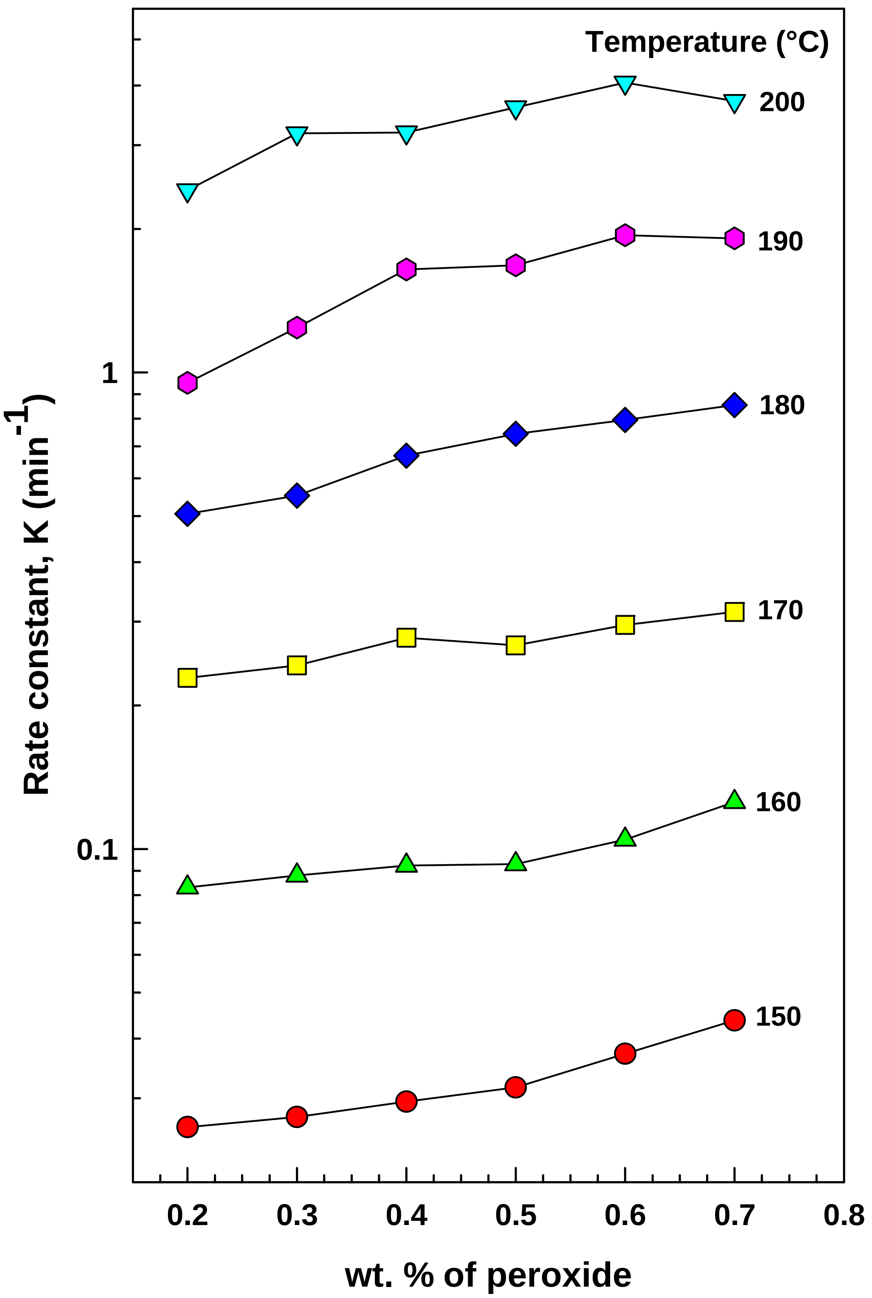


***Figure 4.2** Rate constant K as a function of peroxide content.*

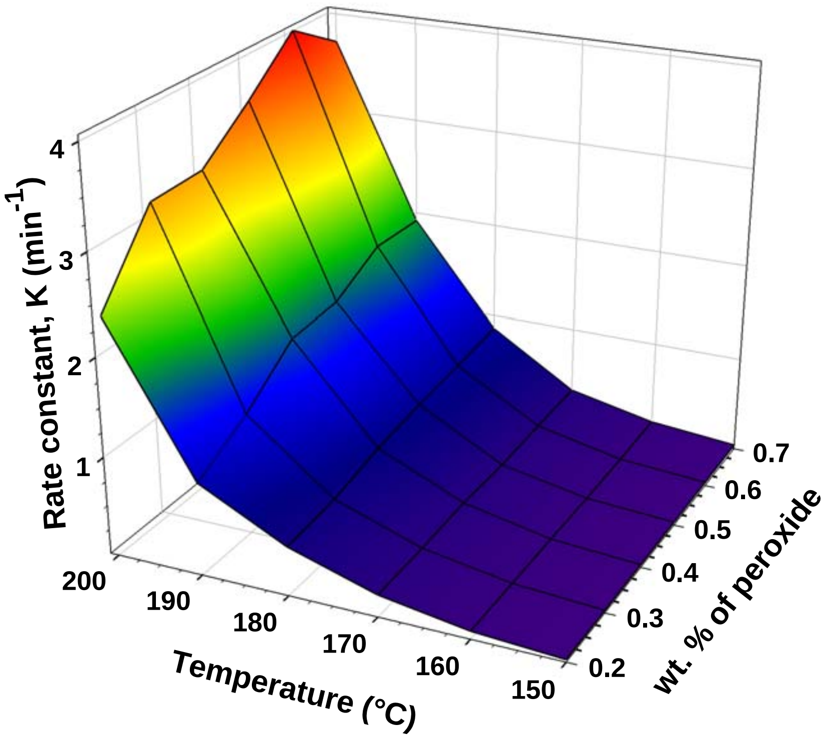


Figure 4.3 *3D plot of rate constant, K as a function of temperature and peroxide content.*

Table 4.1 *Rate constant, K values for various peroxide content at different temperatures.*

wt.% of Peroxide	**Temperature (°C)**					
	150	**160**	**170**	**180**	**190**	**200**
0.2	0.0261	0.083	0.229	0.505	0.95	2.41
0.3	0.0274	0.088	0.243	0.552	1.24	3.17
0.4	0.0295	0.092	0.278	0.669	1.64	3.19
0.5	0.0316	0.093	0.268	0.743	1.68	3.60
0.6	0.0372	0.105	0.295	0.795	1.94	4.06
0.7	0.0437	0.125	0.314	0.854	1.91	3.71

The inserted picture in Figure 4.4 shows the plots according to Arrhenius equation in logarithmic form (Eq. (5)) for 0.4 wt. % of peroxide. The linearity of these points was rather good, measured by R values being 0.9966 for 0.4 % of peroxide. In this way all of the activation energies shown in Figure 4.4 were obtained. There is a steady increase in E_A in range 0.2-0.5 wt. % of peroxide with the maximum being at around 0.52 wt. % and a decrease in range 0.55-0.7 wt. % of peroxide. When the peroxide level is lower, mainly cross-linking is taking place. But with higher amount of peroxide the probability of chain scission increases.

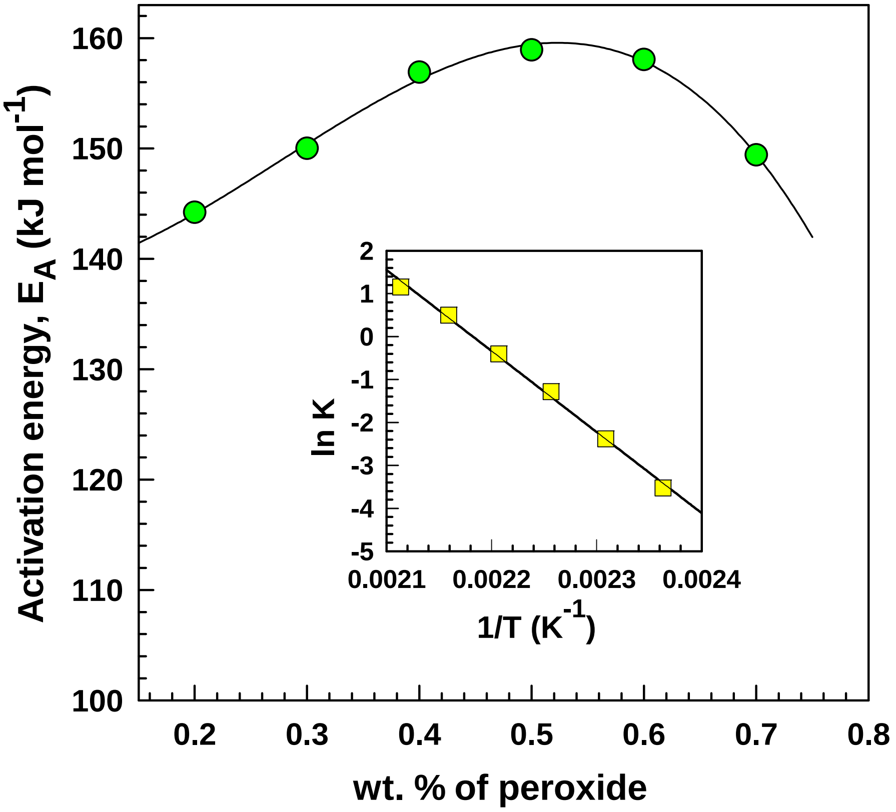


Figure 4.4 *Activation energies of cross-linking E_A as a function of peroxide content. The inserted picture is ln K vs. 1/T for 0.4 wt. % peroxide.*

4.3 Evaluation of high-temperature mechanical properties

Gel content of peroxide cross-linked samples are shown in Figure 4.5. It can be seen that as the peroxide content increases, gel content also increases with an exception in the case of 0.2 and 0.3 wt. % of peroxide. In the case of 0.2 and 0.3, there was no insoluble fraction left out after extracting with xylene, which implies that the cross-linking reaction lead only to longer molecules but the network was not created. There is a sharp increase (0 to 54 %) in gel content from 0.3 to 0.4 wt. % of peroxide. Then, in the case of 0.5, 0.6 and 0.7, gel content gradually increases with increasing peroxide content. Increase in gel content is due to increase in cross-link network and thus cross-link density.

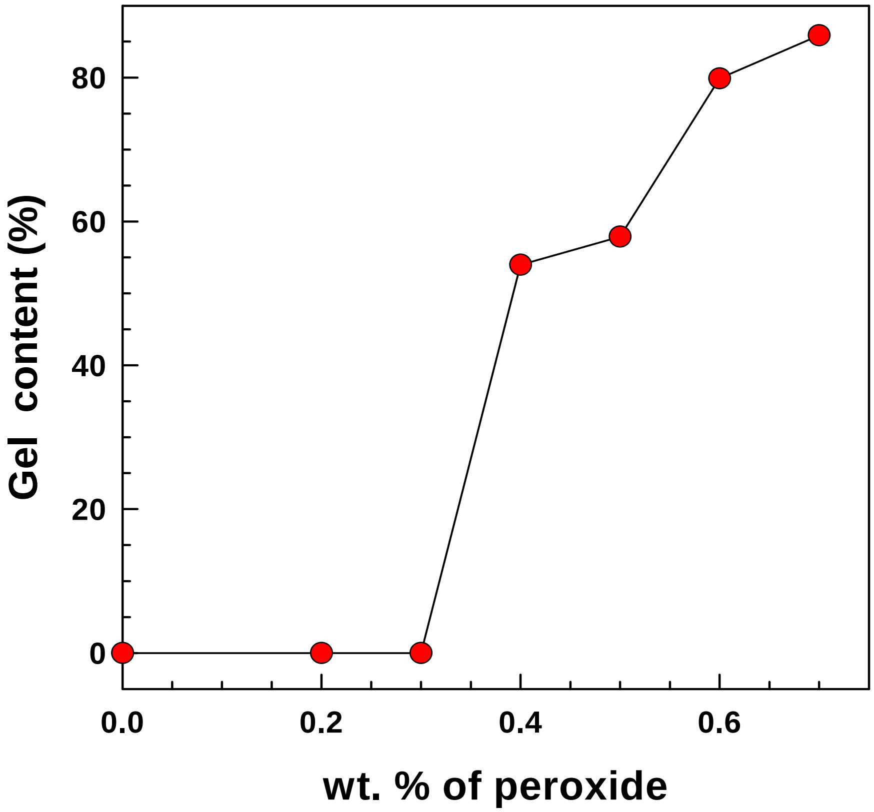


Figure 4.5 *Gel content of DCP cross-linked EOC samples at 150 °C.*

The results of DMA analysis are illustrated in Figures 4.6 and 4.7. Figure 4.6 shows storage modulus as a function of temperature. While for samples with 0.2 and 0.3 wt. % of peroxide the gel content was zero (no difference from pure EOC), the DMA analysis revealed big difference between pure EOC and samples with 0.2 and 0.3 wt. % of peroxide. While the pure EOC survived the DMA test only till 80 °C the sample with 0.3 wt. % of peroxide ran till 160 °C. Even though the network was not fully created there is a big change in the storage modulus curve. The 0.4-0.6 wt. % of peroxide curves have very similar trend and they are close to each other; just there is a small increase with increase in peroxide level. 0.7 curve has highest value of storage modulus till 180 °C, then it is rapidly decreasing and has lower value than the 0.6 curve. In the 180-200 °C temperature range the degradation of 0.7 samples is decreasing the mechanical properties.

In Figures 4.7, dependences of tanδ on peroxide content and temperature are shown. Increase in temperature causes an increase in tanδ value for all samples in the temperature range 30-200 °C. With increasing peroxide content the tanδ value decreases with exception 0.7 wt. % of peroxide. One can conclude that increasing peroxide content above 0.6 wt. % does not improve elastic properties.

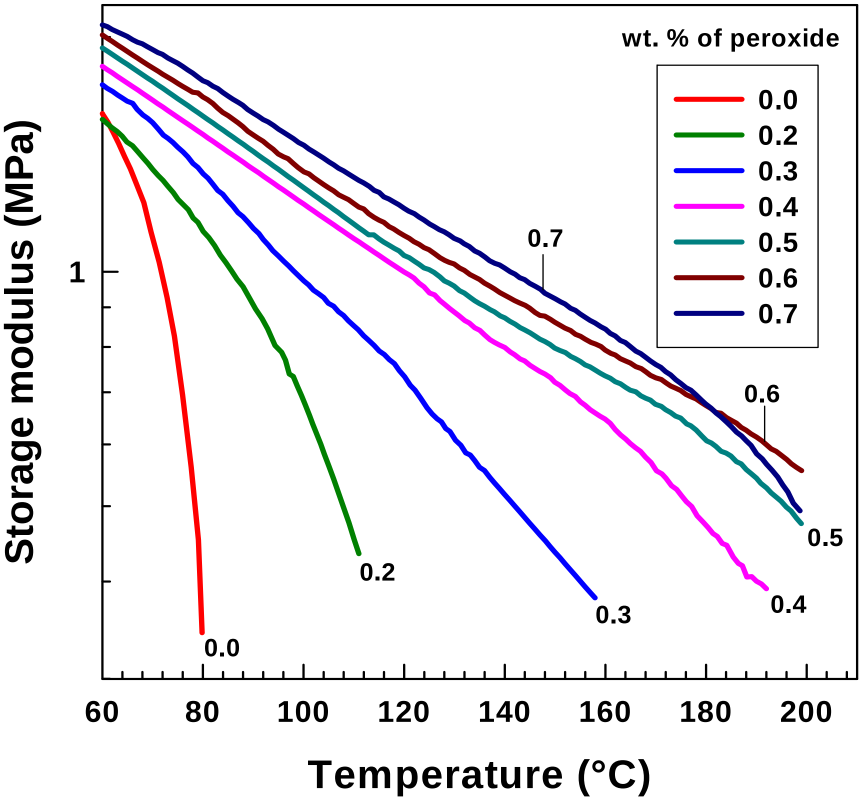


Figure 4.6 *Storage modulus from DMA as a function of temperature for EOC cross-linked with various levels of DCP.*

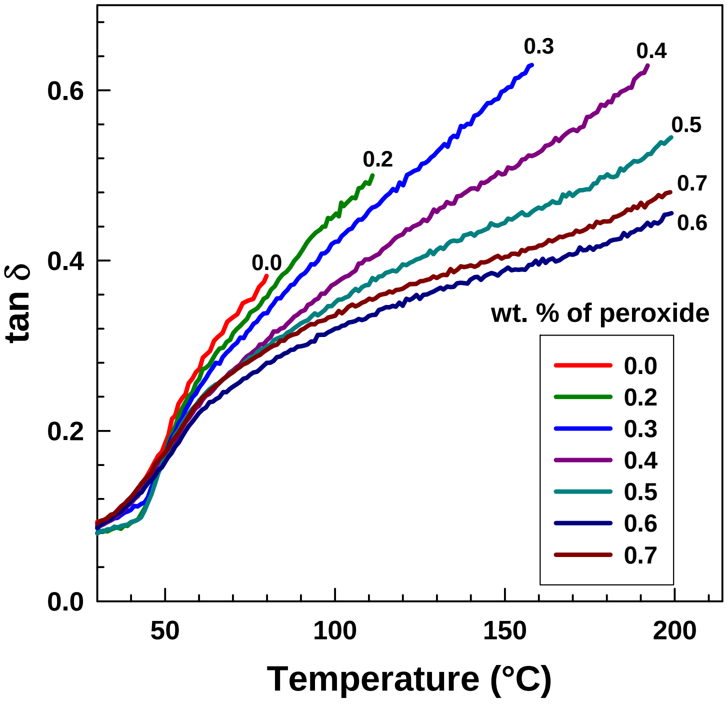


Figure 4.7 *tanδ as a function of temperature for EOC cross-linked with various levels of DCP from DMA analysis.*

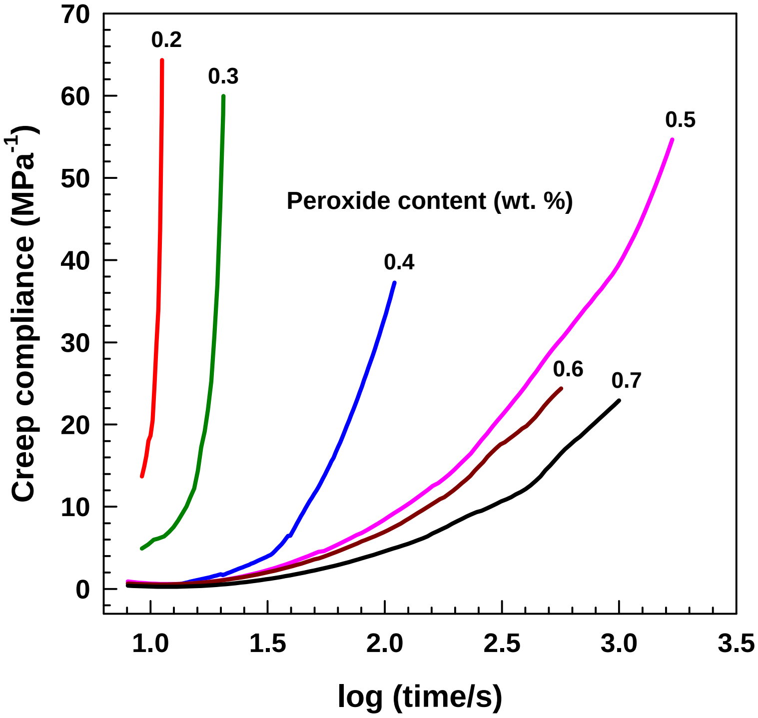


Figure 4.8 *Creep compliance curves at 150 ℃ and 0.05 MPa stress.*

Figure 4.8 depicts the creep compliance behavior of cross-linked EOC samples at 150 °C and 0.05 MPa stress level. As we can see from the figure, elongation and thus creep reduces as the peroxide content increases. Or, in other words cross-linking and thus strength of the samples increases when the peroxide level increases. This data are in good agreement with earlier shown RPA results.

4.4 Conclusions

Cross-linking study followed by Arrhenius equation treatment and activation energy evaluation suggested an optimum peroxide level being in 0.5-0.6 wt. % range. The highest cross-linking rate was found for 0.6 wt. % of peroxide at 200 °C. At higher peroxide levels (starting at 0.7 wt. %) the degradation affects seriously the crosslinking especially at higher temperatures (180-200 °C).This fact is again proven by the storage modulus and tanδ results obtained by the DMA. Gel content which has shown an increasing trend with increase in peroxide content is due to the increased cross-link network. Creep test results at 150 °C also support the claim that increase in modulus and gel content is caused by increase in peroxide level.

CHAPTER 5

Comparison of peroxide cross-linked ethylene-octene copolymers

5.1 Introduction

This chapter deals with comparison of two ethylene-octene copolymers cross-linked using DCP. Two ethylene-octene copolymers (ENGAGE 8450 with 20 wt. % and ENGAGE 8452 with 35 wt. % octene content) of same melt flow index (3 g/10 min) were cross-linked using various levels (0.3, 0.5 and 0.7 wt. %) of DCP at different temperatures (150-200 °C). Effect of octene content on cross-linking and degradation has been analyzed using RPA. Influence of octene content on thermal properties such as melting and crystallinity was studied by differential scanning calorimetry. Storage modulus (M’) and tanδ were also evaluated through dynamic mechanical analysis. Finally, mechanical properties above T_m (at 150 °C) were analyzed by high temperature creep measurement.

5.2 Studies on Two Different EOC/DCP Systems

In this chapter, these two ENGAGES are mentioned as EN 8450 and EN 8452, for the sake of simplicity.

Figure 5.1a and b show the raw data obtained from RPA, more specifically real part of elastic torque, s’ and tanδ for EN 8450 and 8452. From this graph, one can notice that EN 8452 with 35 wt. % of octene has lower elastic torque compared to EN8450 with a low octene content (20 wt. %). As we discussed in previous chapter, the minimum of the s’ value represents processability and the maximum of the s’ contains information about mechanical properties after cross-linking. tanδ after cross-linking is lower for low-octene EOC, which means better elasticity. Figure 5.1 shows data just for one temperature (180 °C) and one peroxide level (0.5 wt. %).

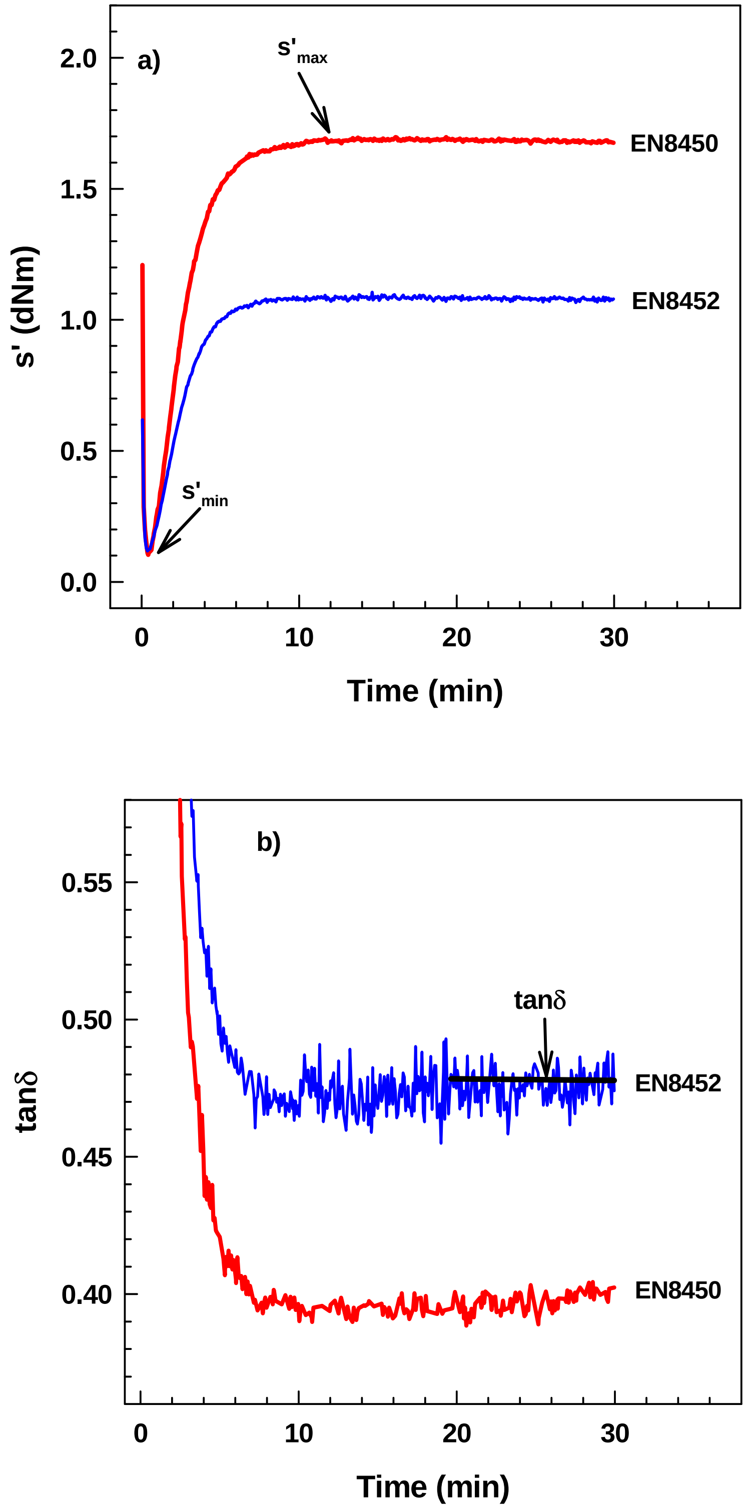


Figure 5.1 *Plots of elastic torque, s' (a) and tanδ (b) as a function of cross-linking time for EN 8450 and EN 8452 with 0.5 wt. % of peroxide at 180 °C.*

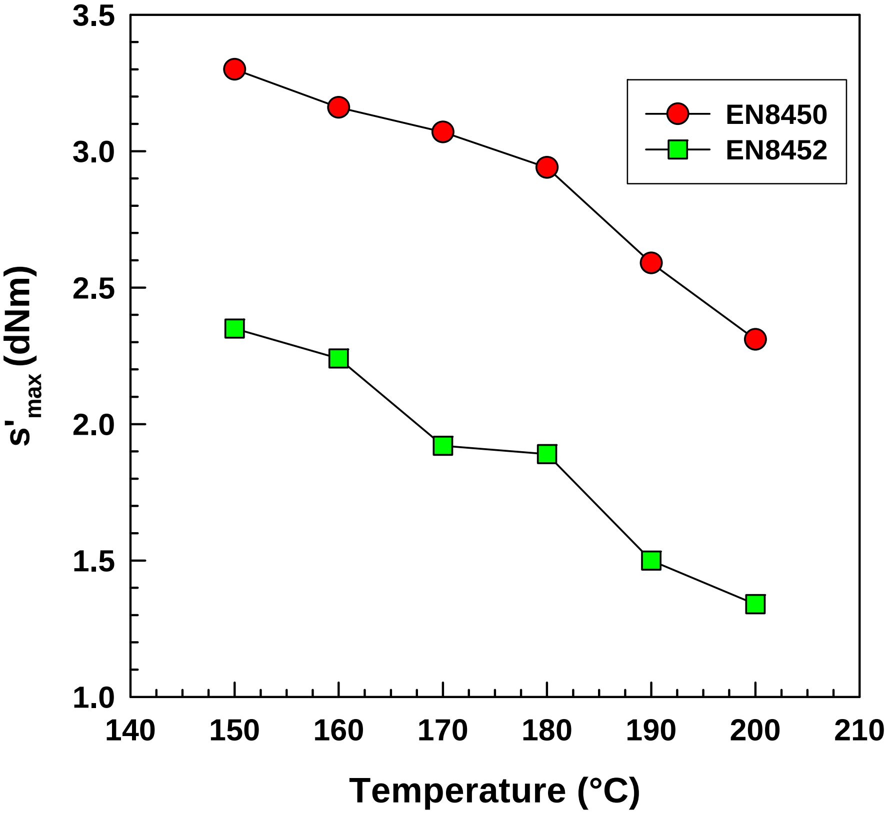


Figure 5.2 *Plot of s'$_{max}$ vs. temperature for EN 8450 and EN 8452 with 0.7 wt. % of peroxide.*

Figure 5.2 shows the plot of s'$_{max}$ as a function of cross-linking temperature for the two ENGAGEs. As one can see from the plot, s'$_{max}$ value is higher for EN 8450 (lower octene content). This decrease in s'$_{max}$ value with increase in octene content can be attributed to the increase in branch density. When branching increases, probability for β-scission during cross-linking increases and thus degradation too [101]. s'$_{max}$ decrease with cross-linking temperatures in both cases.

The Δs' value (s'$_{max}$-s'$_{min}$) represents the cross-linking efficiency of peroxide which is defined as the number of moles of chemical cross-links formed per mole of peroxide [9]. Figure 5.3 represents the Δs' value as a function of peroxide content for EN8450 and EN8452 cross-linked at 180°C. Efficiency of peroxide is higher for EOCs with lower octene content. The reason might be difficulty of peroxide free radicals to attack the main chains due to increased hindrance by octene side groups.

The same phenomenon was observed at all cross-linking temperatures. Increase in number of peroxide free radicals - in other words, increase in peroxide content - causes an increase in Δs' value (linear dependency).

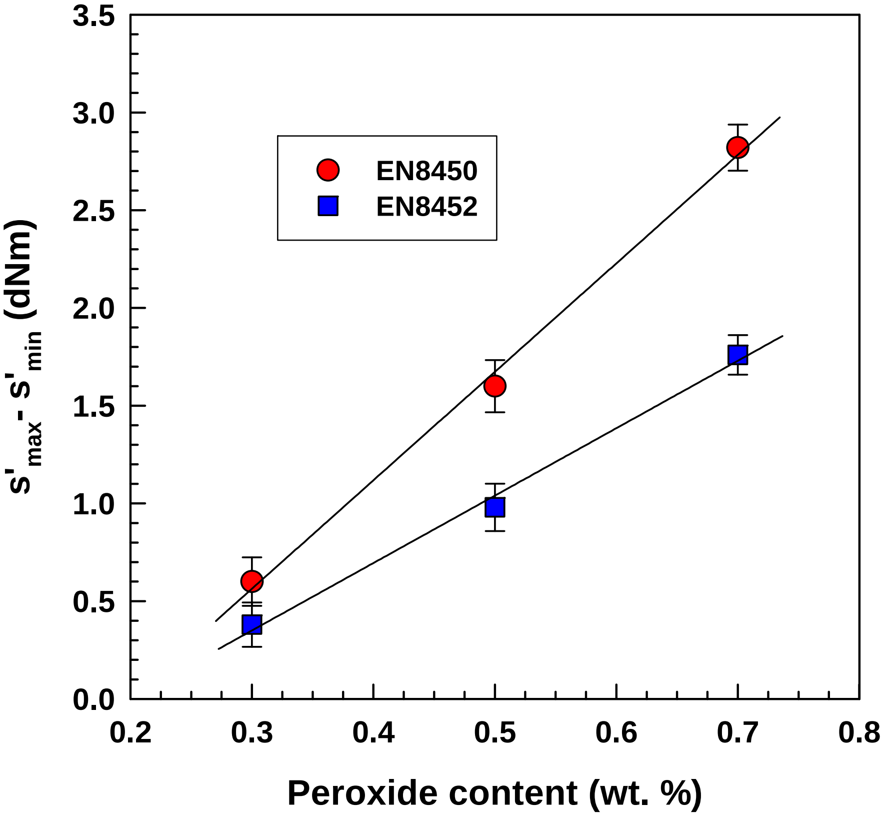


Figure 5.3 *Plot of* s'_{max}-s'_{min} *(Δs') vs. peroxide content at 180 °C for two different EOCs.*

tanδ values as a function of cross-linking temperature in the case of both ENGAGEs is shown in Figure 5.4. The lower tanδ value the better elasticity one can expect. tanδ values increase with increasing octene content and temperature. Overall, the best elasticity (lowest tanδ values) was found for EN8450 with lower octene content at 150 °C. This is pointing towards the conclusion that EN8450 has undergone a better cross-linking than EN8452.

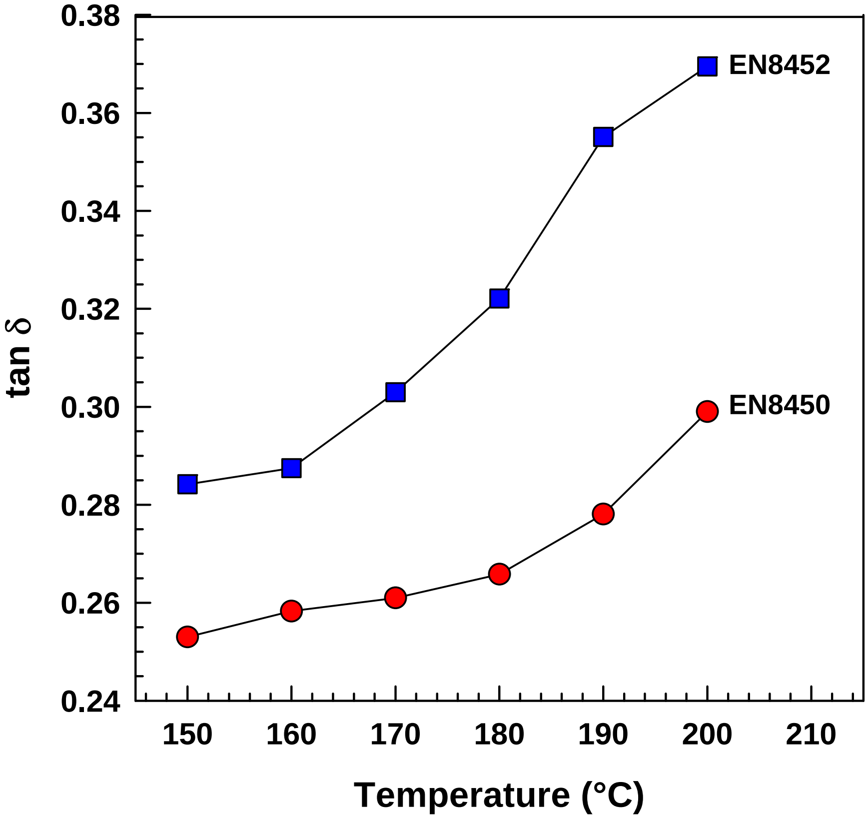


Figure 5.4 *Plot of tan δ vs. temperatures for two different EOCs with 0.7 wt. % peroxide.*

In Figure 5.5, s' curves for EN8450 cross-linking at 180 °C and 200 °C using 0.7 wt. % of DCP are shown. Rapid initial increase in the curves shows the progress of cross-linking reaction, then the curve reaches a maximum. After reaching the maximum, the curve shows a slight decreasing trend (quantitatively evaluated by degradation slope) caused by the possible chain scission at elevated temperature. Cross-linking and degradation slopes were calculated for the two copolymers at all temperatures (150-200 °C) and three peroxide levels.

From Figure 5.6, it can be observed that EN8450 with lower octene content is having higher cross-linking slope values which implies a faster cross-linking rate at all temperatures. However, this difference is smaller at lower temperature (150-170 °C) and it is increasing with temperature. The combined effect of β scission and temperature (above 170 °C) reduces cross-linking rate in the case of high-octene EOC.

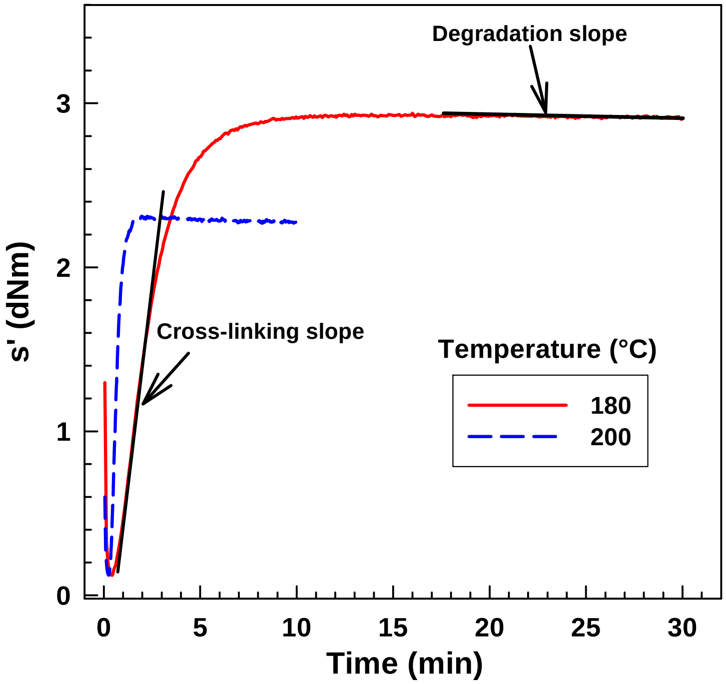


Figure 5.5 *s' as function of time for EN8450 cross-linked with 0.7 wt. % of DCP at 180 °C and 200 °C.*

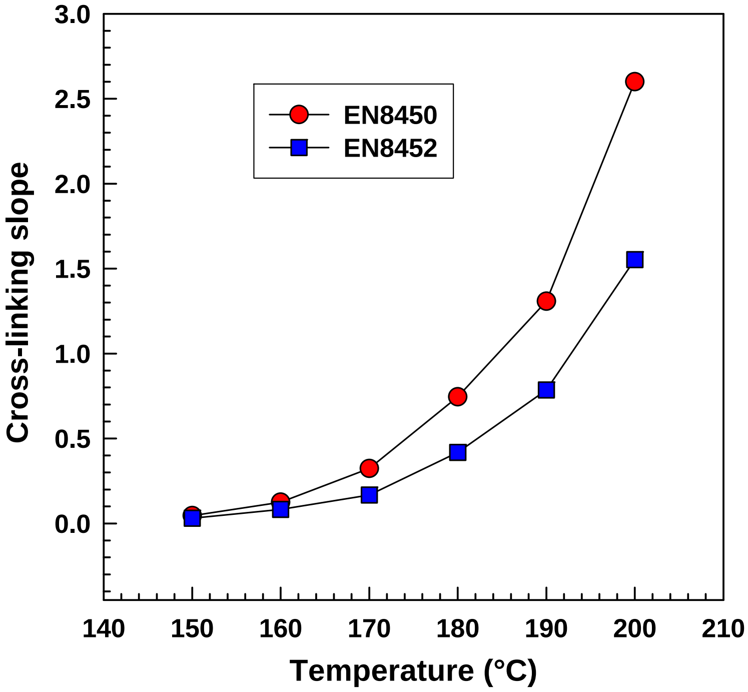


Figure 5.6 *Cross-linking slopes of two different ENGAGEs cross-linked by 0.7 wt. % of DCP.*

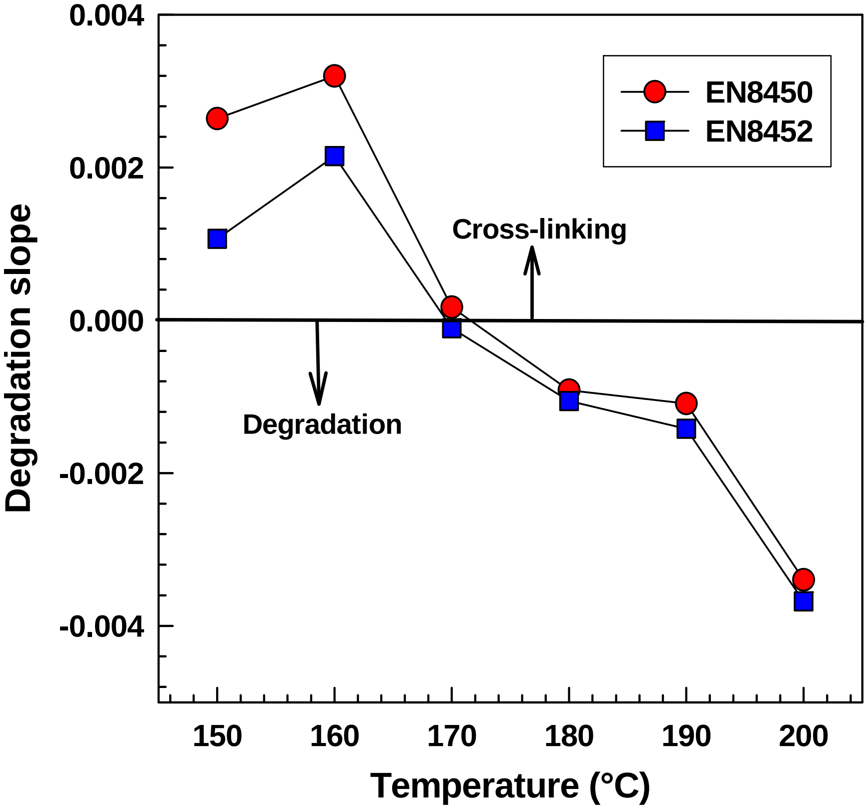


Figure 5.7 *Degradation slope as a function of cross-linking temperature for EOCs cross-linked with 0.7 wt. % of DCP.*

Dependence of degradation slope values on temperature is represented in Figure 5.7. It is clear from the figure that octene content has an influence on degradation slope value (i.e., degradation). As we discussed before, higher octene content results in a rise in chain branching which enhances the probability of degradation through β-scission. Another important factor which affects the degradation is cross-linking temperature. Up to 160 °C, a rise in temperature favors the cross-linking reaction and no or comparatively negligible scission was observed in the case of 170 °C. These can be considered as the "safe temperature range for cross-linking" as we have reported in previous chapter. This is pointing towards the possibility of losing favorable mechanical properties of high-octene EOC cross-linked at high temperatures.

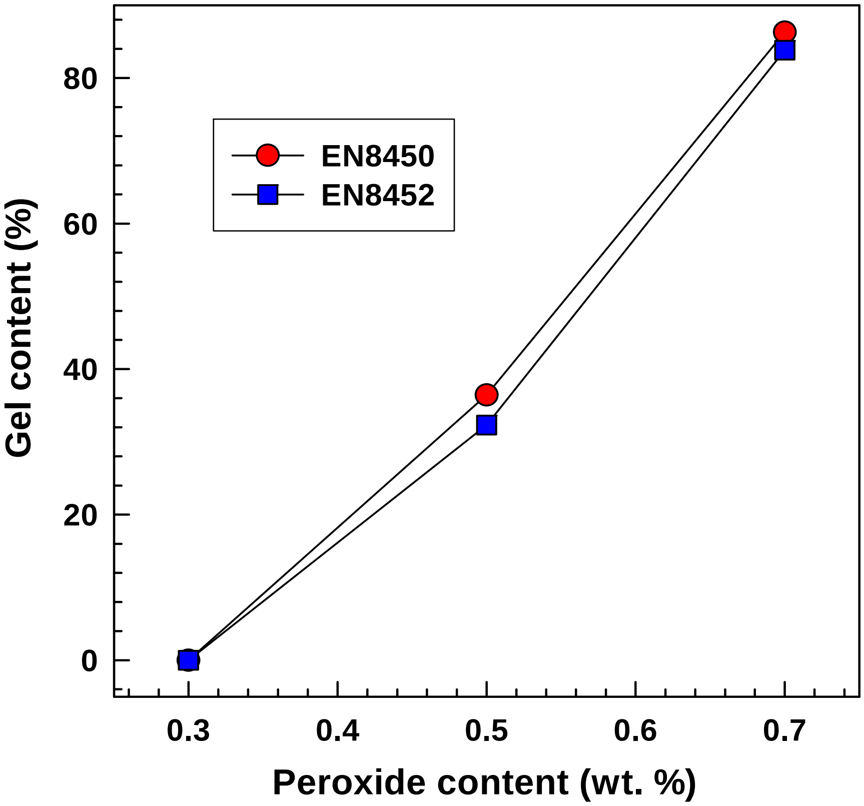


Figure 5.8 *Gel content analysis of cross-linked EOCs.*

Extent of cross-linking (or cross-linking density) of a polymer can be effectively studied using gel content analysis. Figure 5.8 represents the influence of peroxide levels on gel content in the case of two EOCs cross-linked at 150°C. With increasing peroxide content gel content also increases. Both samples with 0.3 wt. % of DCP dissolved in xylene completely. Another result from this analysis points out that for the ENGAGE with higher octene content the gel content was found to be slightly lower. The gel content data are in good agreement with the results obtained from RPA. From the gel content analysis, we can strengthen the statement that for higher-octene EOCs chain scission significantly influences the cross-linking reaction.

Mechanical properties were measured by dynamical mechanical analysis (DMA). The DMA data are very useful since we can obtain a temperature dependence of storage modulus and tanδ. Figure 5.9 shows the storage modulus (E') as function of temperature for EN8450 and EN8452 cross-linked with 0.7 wt. % of peroxide. The most important observation is that as the comonomer content increases, storage modulus decreases (the copolymer gets softer and more rubbery). EOC with lower octene content has higher modulus at all temperatures.

$\tan\delta$ results from DMA are shown in Figure 5.10. In this case, one can observe two transitions called α (+10 to +100 °C) and β (+10 to -70 °C). According to the literature, motion of CH_2 units of polyethylene within the crystal lattice results in α-transition while motion of branched structures in the amorphous phase causes the β-transition [66]. Comonomer content of EOC affects both of these transitions. In the case of high octene EOC (low crystallinity), α-transition is absent. At same time, it is more prominent for low octene EOC. Crystallinity decreases with increase in octene content which is proved by DSC result (see Table 5.1). Similar observations have been made by Simanke et al. for low octene content EOCs without any cross-linking. They reported that increase in comonomer content results in decrease in average number of consecutive ethylene units and thus crystallizable part of the copolymer reduces. This ultimately causes drop in crystallinity [102].

From the $\tan\delta$ curve, it is clear that, β-transition temperature shifted to lower temperature as the octene content increases. Peak position of β-transition corresponds to the T_g of the amorphous phase [103]. This decrease in T_g with octene content is due to an increase in amorphous portion.

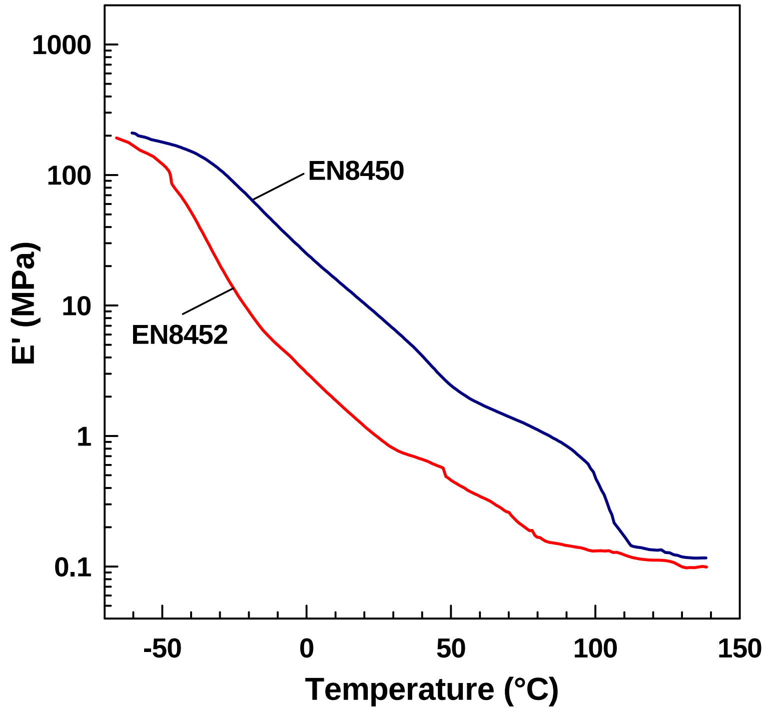


Figure 5.9 *DMA results: storage modulus of two EOCs cross-linked with 0.7 wt. % of DCP at 170 °C.*

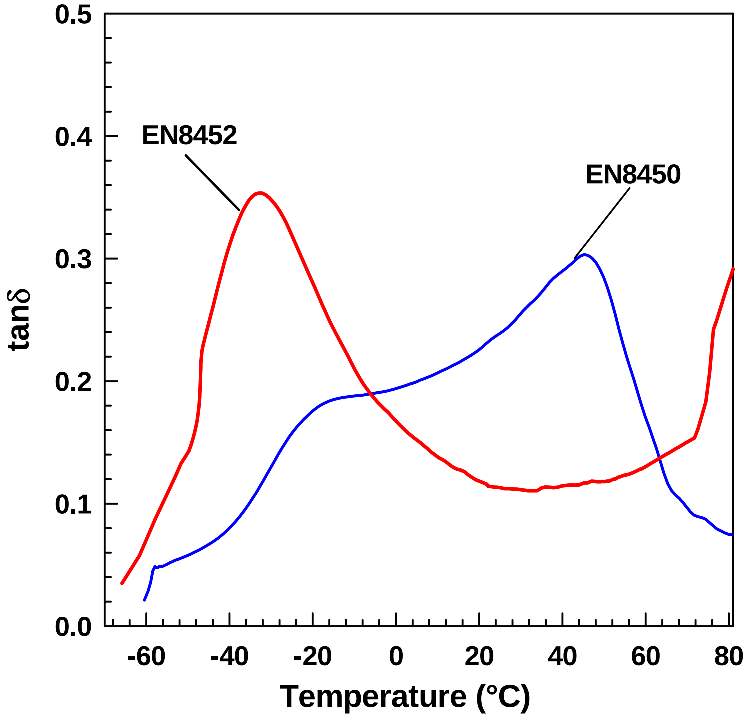


Figure 5.10 *DMA results: effect of octene content on tanδ.*

In order to support the above-claimed conclusions, we performed also measurement of mechanical properties above melting point of EOCs. Below T_m, the strength of cross-linked EOC comes from crystal lamellae that act as tie points for amorphous chains, and also from cross-linking. To see the influence of cross-linking only one has to measure mechanical properties above T_m of the semi-crystalline polymer.

In order to know the T_m of investigated EOCs, we carried out DSC experiments. The results are summarized in Table 5.1. With increasing octene content the melting point (T_m) and crystallinity (X_c) decrease. Based on this analysis, the temperature for high temperature creep testing was set to 150 °C when all the crystals are melted. The results are shown in Figures 5.11 and 5.12. From Figure 5.11, one can observe that EOC with lower octene content has lower creep compliance values than EOC with higher octene level. EN8452 has undergone a higher creep than EN8450 at all times during the measurement, due to the lower extent of cross-linking. Creep compliance values after different times were evaluated and plotted in Figure 5.12. The results are in good agreement with the RPA and gel content results which are discussed earlier.

Table 5.1 *DSC analysis of ENGAGEs*

Sample	T_m (°C)	ΔH (J/g)	Crystallinity (%)
EN8450	99.9	83.0	28.6
EN8452	71.0	37.8	13.0

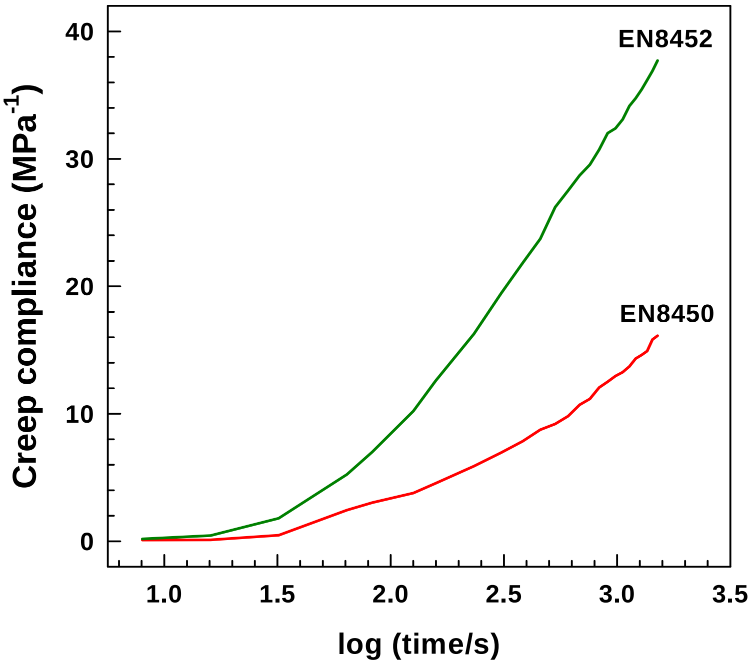


Figure 5.11 *Creep compliance curves at 150 ℃ and 0.1MPa stress for EOCs with 0.7 wt. % DCP.*

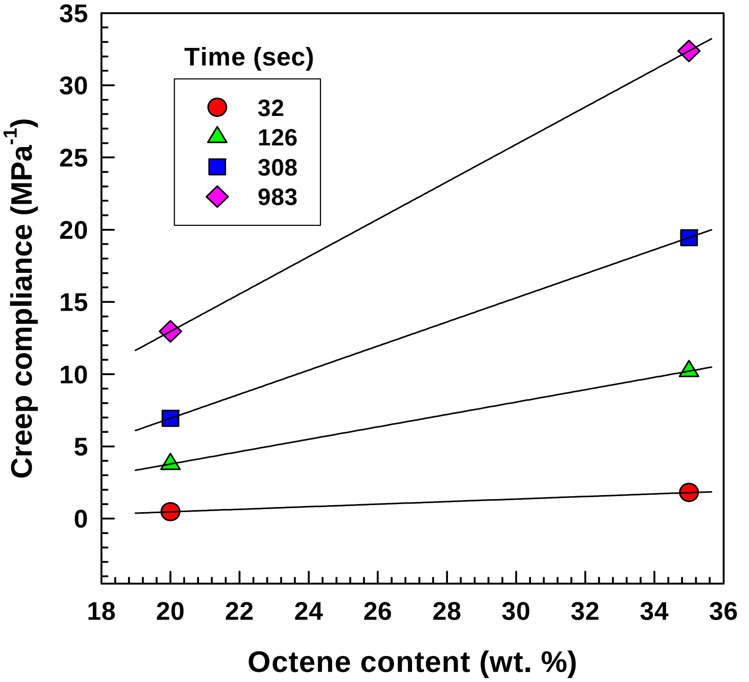


Figure 5.12 *Creep compliance as a function of octene content at 150 ℃ and 0.1MPa stress for EOCs cross-linked with 0.7 wt. % DCP.*

5.3 Conclusions

Two ethylene-octene copolymers with different octene content but the same initial MFI value were cross-linked using dicumyl peroxide at different temperatures. The influence of octene content, peroxide level and temperature on cross-linking, degradation and high temperature creep were studied. The cross-linking efficiency of etlylene-octene copolymers was greatly influenced by the octene content, peroxide level and cross-linking temperature. Better cross-linking was achieved for EOC with lower octene content. According to tanδ analysis, best elastic properties were observed for EN8450 (having 20 wt. % of octene) cross-linked at low temperature (150 °C). Increase in cross-linking temperature (above 170 °C) resulted in an increased degradation for both ENGAGEs. However, high-octene copolymer (EN8452) was more vulnerable to degradation compared to the low-octene one. Gel content and high temperature creep analyses confirm the conclusion that EN8450 with low octene content underwent better cross-linking. Crystallinity and melting point of EOCs decreases with increasing octene content, as it was illustrated by DSC analysis. DMA revealed lower T_g and lower modulus for higher octene copolymer.

CHAPTER 6

Influence of electron beam irradiation on the thermal, mechanical and rheological properties of ethylene-octene copolymer

6.1 Introduction

In this chapter we have focused on electron beam irradiation cross-linking of ethylene-octene copolymer with high comonomer content (45 wt. %). EOC was irradiated at different dosages (30, 60, 90 and 120 kGy). The effect of irradiation on thermal, mechanical and rheological properties of EOC has been analyzed. Melting and thermal degradation behavior was studied by DSC and TGA, respectively. The rheology study involves the effect of irradiation dose on elastic modulus (G'), viscosity (η*) and tanδ by Advanced rheometric expansion system (ARES 2000). Stress-strain behaviour of irradiation cross-linked EOC also discussed in detail. The effect of cross-linking was examined more elaborately by high temperature creep and elastic property measurements.

6.2 Study on irradiated ethylene-octene copolymer

Figure 6.1 shows the effect of irradiation dosage on gel content which denotes the extent of cross-linking. Structures with low molecular weight which are by-products of chain scission or chain branching may not contribute towards the insoluble fraction during analysis. As a result of increase in network formation (cross-linking extent), gel content increases. It is clear from the figure that samples irradiated with 30 kGy dose were completely dissolved due to low cross-linking degree. A gradual increase in gel content was observed thereafter. A maximum gel content of 87.84% was recorded for EOC irradiated with 120 kGy.

DSC thermograms of irradiated EOCs are shown in Figure 6.2. There is a clear difference in the position of melting peaks and peak areas. Only one melting peak around 43 °C is seen in the case of un-irradiated EOC sample while there is a second peak at around 56 °C in the case of EOCs irradiated with 90 and 120 kGy dosages. This may be ascribed to the formation of high-melting fraction (chains with high molecular mass) due to increased cross-linking. Peak area around 43 °C is getting decreased while at 56 °C is increased with irradiation.

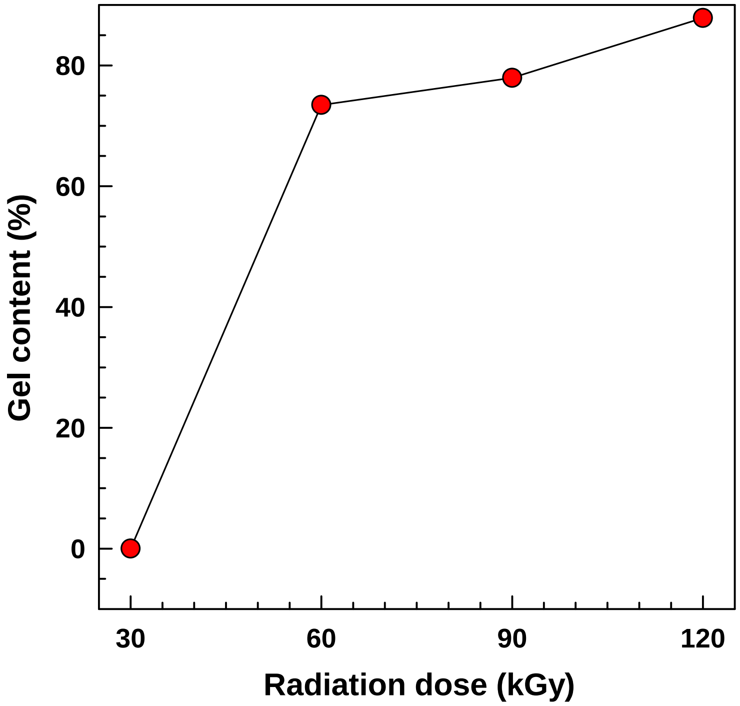


Figure 6.1 *Gel content analysis of irradiated samples.*

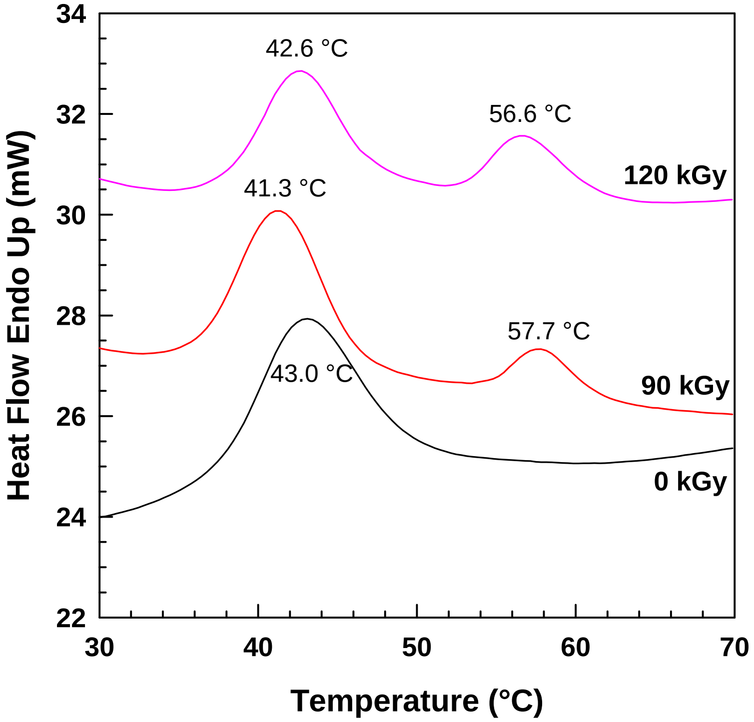


Figure 6.2 *DSC thermograms at 20 °C/min.*

The rheological properties of e-beam irradiation cross-linked ethylene-octene copolymer are shown in the following figures. Frequency dependence of elastic modulus, G’ of irradiated samples is illustrated in Figure 6.3. At low frequency, time is large enough to unfold the chains and relax slowly which reduces the modulus. But at higher frequency, the entangled chain had less time for reorientation and results in higher G’ values [104]. An increase in radiation dosage also increases the elastic modulus which implies that elasticity enhances with radiation dose. At low frequency range, longer chains are contributing more towards the elasticity of the polymer. As the radiation dosage increases, presence of shorter chains decreases i.e., longer and cross-linked chains are formed. This is obvious from the Figure 6.3 that, as the radiation dosage increases, G’ increases at lower frequency range. But at higher frequencies, shorter chains are responsible for the elasticity. This is the reason why G’ values are decreasing with the radiation dosage at higher frequencies when thenumber of shorter chains is relatively smaller.

The increase in elastic modulus with radiation dosage at lower frequency is very clearly explained in Figure 6.4.The increase in elastic modulus with radiation dosage is due to the increase in amount of large macromolecules that are formed by the cross-linking reactions as well as by the presence of the cross-linked chains.

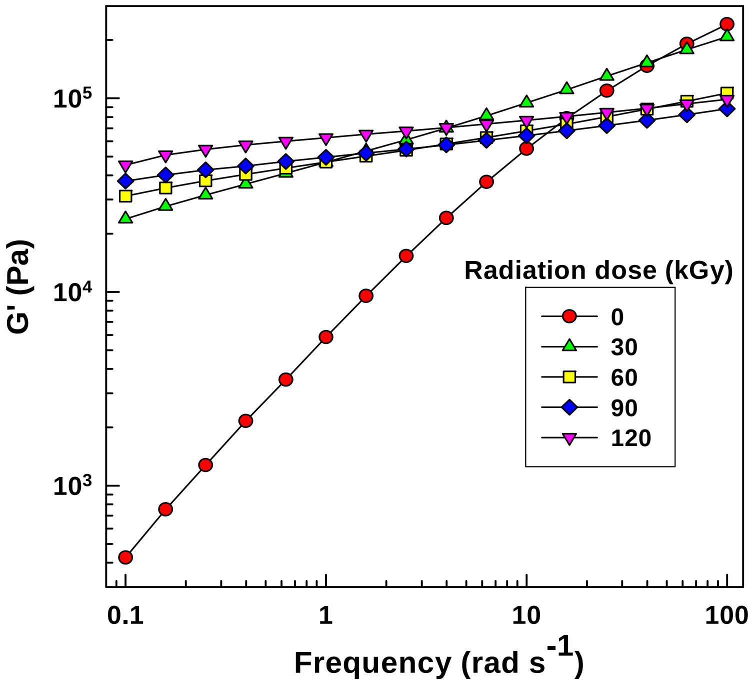


Figure 6.3 *Elastic modulus (G') vs. frequency for different radiation dose.*

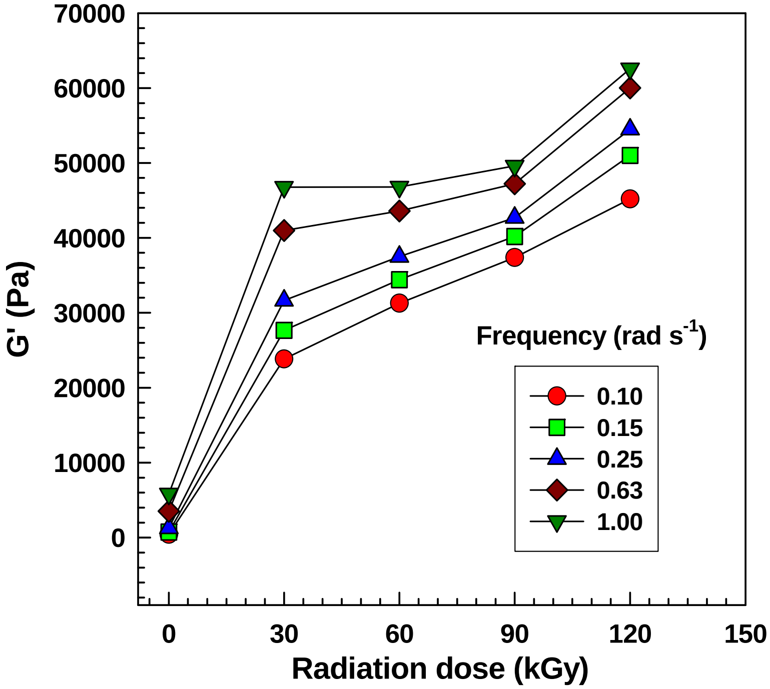


Figure 6.4 *Elastic modulus (G') as a function of radiation dose at different frequencies.*

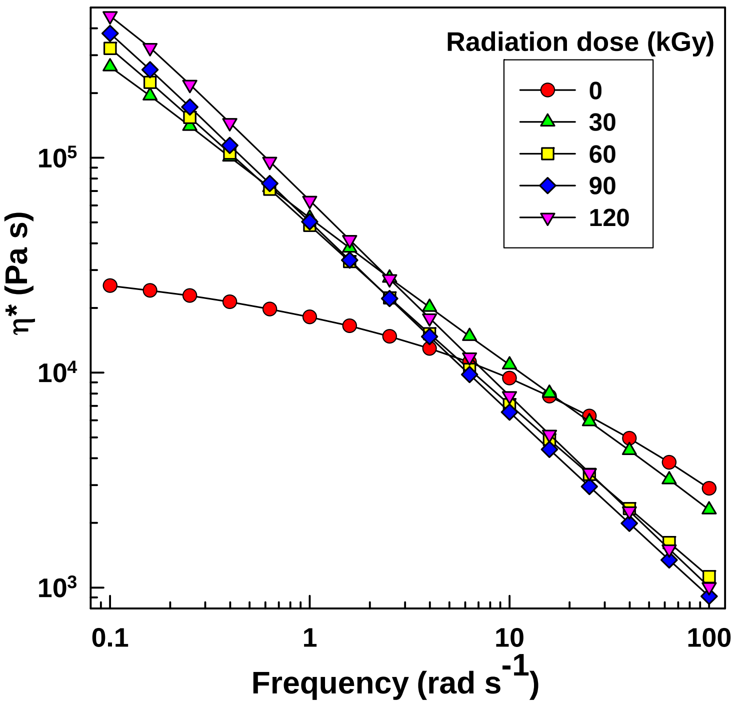


Figure 6.5 *Viscosity (η*) as a function of frequency for different radiation doses.*

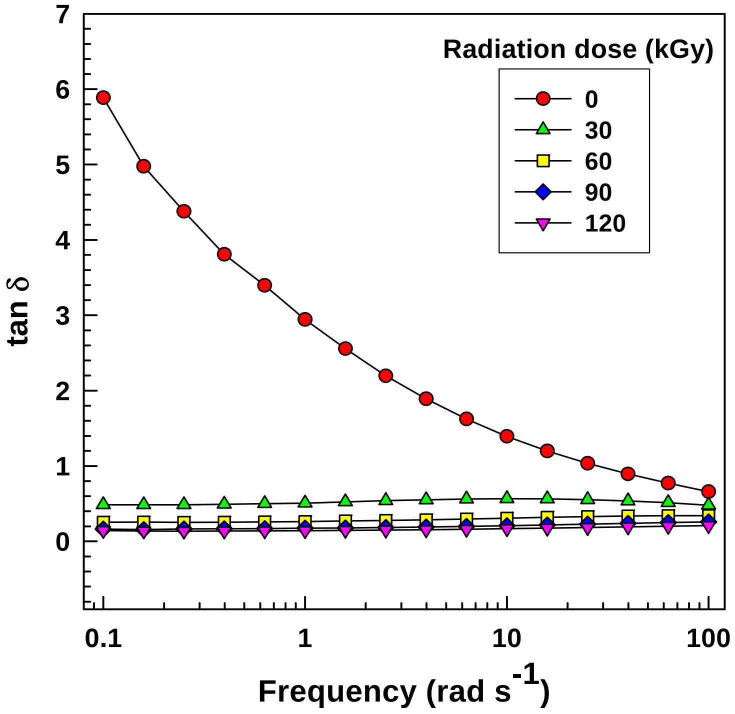


Figure 6.6 *tanδ as a function of frequency for different radiation doses.*

Figure 6.5 revealed that viscosity (η∗) decreased with increasing frequency and at low frequencies increased with increasing radiation dosage. This increase in viscosity indicates the formation of network structure by irradiation. As we discussed above, at higher frequency range shorter chains are contributing towards elastic modulus. The decrease in η∗ with radiation dosage at higher frequency is due to the reduction in number of shorter chains.

Figure 6.6 depicts the effect of radiation dosage and frequency on tanδ. There is a large decrease in tanδ with increasing frequency for 0 kGy. Then tanδ is almost independent of frequency level for the radiation above 30 kGy. As shows also in Figure 6.3 and 6.5, initially there is a large change in polymer structure (compare tanδ at 0.1 rad s^{-1} for 0 and 30 kGy, the values were about 6 and 0.5, respectively), then the change is rather moderate in range 30-120 kGy. The effect of radiation dose on tanδ at the frequency 0.1 rad s^{-1} for samples 30-120 kGy is illustrated in Figure 6.7. There is an exponential decrease of tanδ with radiation dosage. The decrease in tanδ means improvement in elasticity.

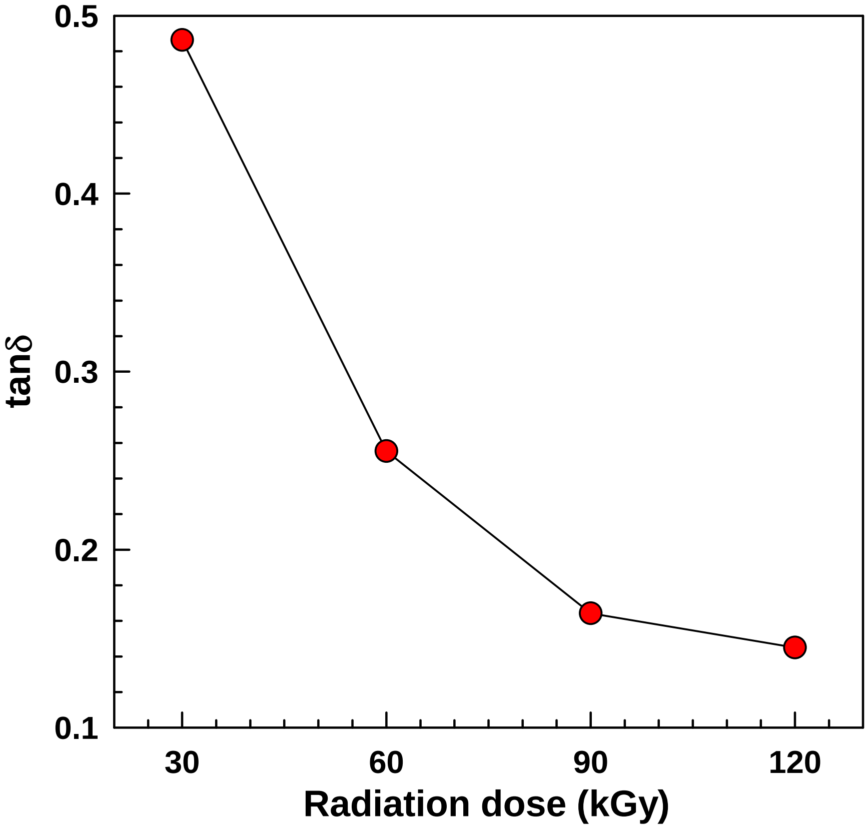


Figure 6.7 *Effect of radiation dose on tanδ at 0.1 rad* s^{-1}.

Tensile stress-strain curves of the pure and cross-linked EOCs are depicted in Figure 6.8. A gradual decrease in elongation at break has been observed while stress at break has shown an increase, except in the case of the highly irradiated (120 kGy) EOC. Increase in cross-linking is the reason for these two phenomena. For majority of the samples, elongation before failure has gone up to as high as 1000%. No yield points were noted in any of the measurements because of extremely low crystallinity. There was no significant effect of cross-linking observed in the case of tensile modulus. Perraud et al. have reported similar results for some other e-beam cross-linked poly (ethylene-co-octene) [105]. Tensile properties of irradiation cross-linked ENGAGE 8842 are summarized in Table 6.1.

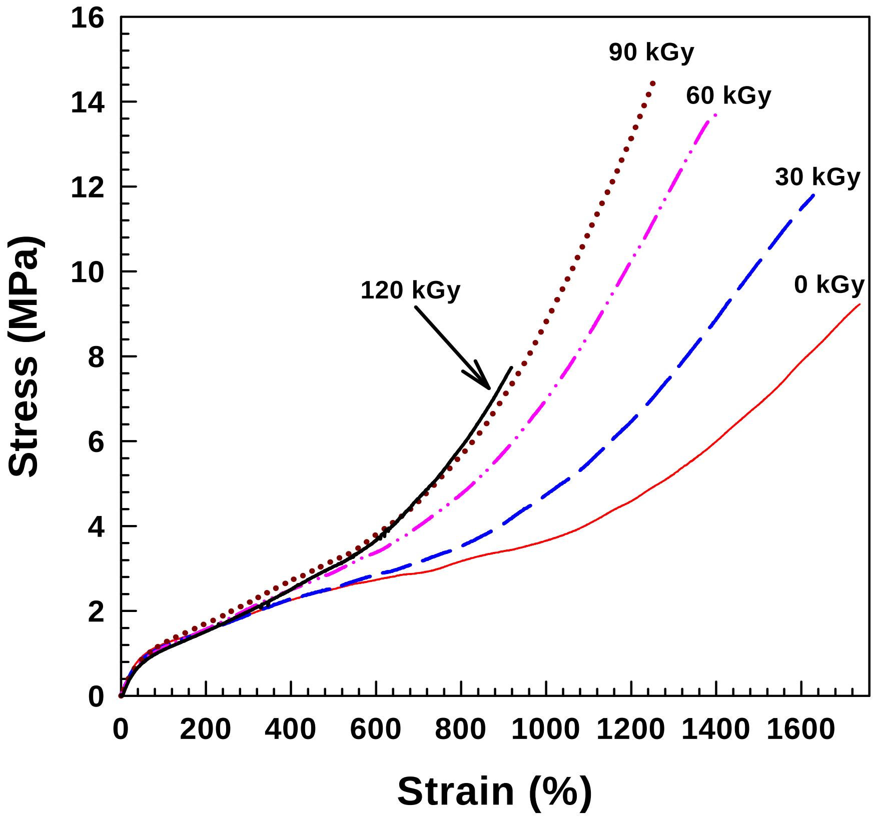


Figure 6.8 *Stress-strain curves at room temperature.*

Table 6.1 *Effect of irradiation dosage on tensile properties.*

Radiation dose (kGy)	Stress at break (MPa)	Elongation at break (%)
0	9.23	1737
30	11.79	1628
60	13.68	1397
90	14.65	1259
120	7.73	918

Influence of radiation dosage on elastic properties at room temperature is demonstrated in Figure 6.9. Residual strain (ε_r) values obtained from the hysteresis curves from the tensile instrument are being considered as the measure of elasticity. In this case, applied strain was 100%. Residual strain is found to be decreasing with increase in cross-linking via irradiation. In other words, elasticity of ENGAGE 8842 is getting improved by cross-linking. Just by the exposure to 30 kGy dosage irradiation, a significant drop of about 30% in the ε_r value has been observed. A gradual decrease in ε_r (or increase in elasticity) with further increase in irradiation dosage was found. Original stress-strain hysteresis curves of pure and the most cross-linked EOCs are shown in the inset of the Figure 6.9, where the position of ε_r is clearly marked.

Residual strain values above the T_m of the pure EOC (50 °C) were also measured and are shown on Figure 6.10. For this, a temperature of 70 °C was used, when there are no crystals present. At room temperature the crystals play the role of tie points for amorphous chains. Above T_m only cross-link chemical bonds are holding amorphous chains together during mechanical stretching. Then after 100% elongation at 70 °C one can clearly see a big difference among the samples (at room temperature the difference was much smaller). The residual strain values at 70 °C are much higher compared to room temperature. High temperature testing is common practice in industry and has a great importance for customers.

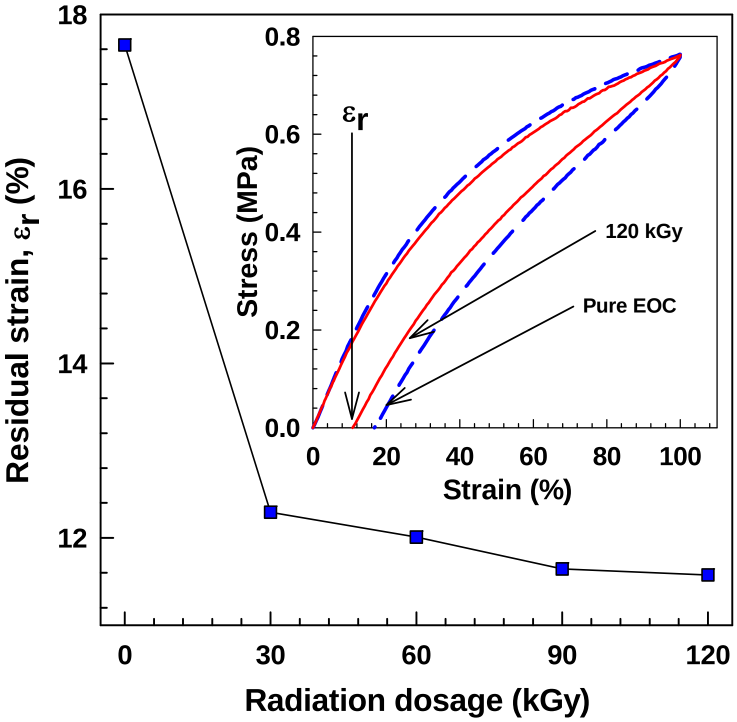


Figure 6.9 *Residual strain of irradiated EOCs at room temperature.*

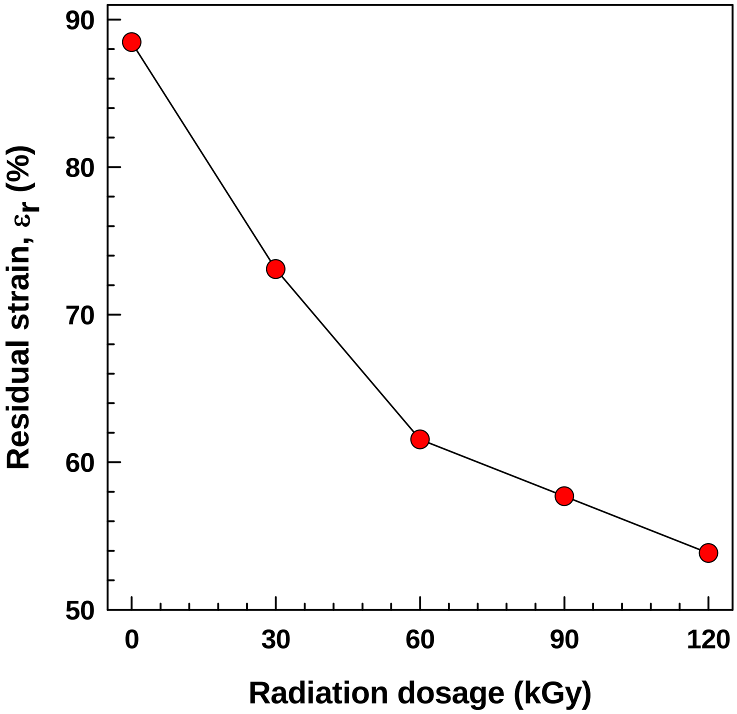


Figure 6.10 *Effect of radiation dosage on residual strain after 5 min exposure to 100% elongation at 70 °C.*

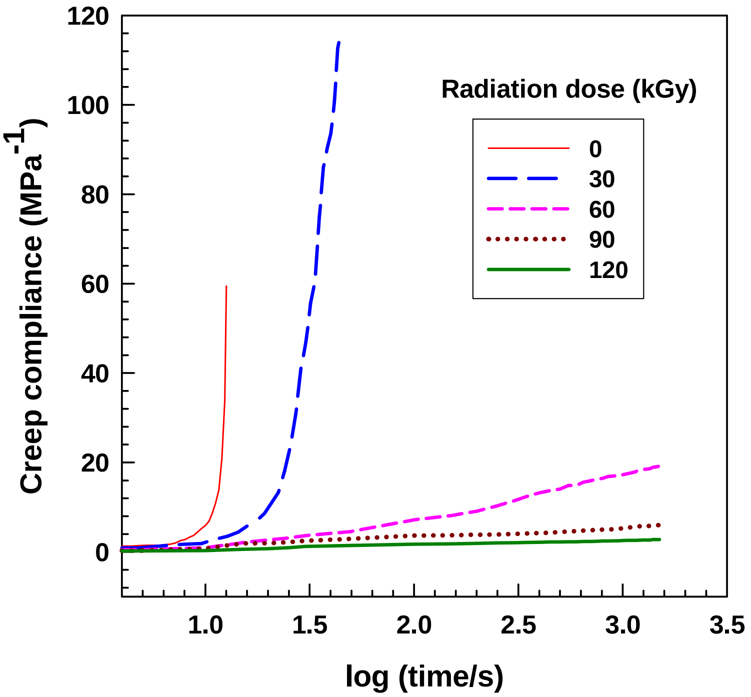


Figure 6.11 *Effect of radiation dose on creep compliance.*

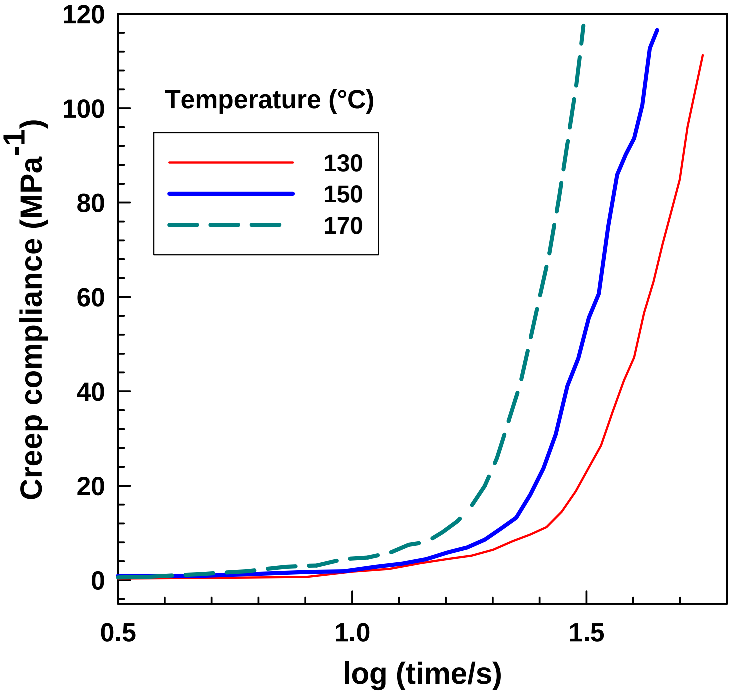


Figure 6.12 *Effect of temperature on creep compliance for irradiated EOC (30 kGy) at a stress level of 0.1 MPa.*

Creep is an important property for polymers that are being used under constant stress for a long duration of time such as pipes, storage tanks etc. Cross-linking can enhance the creep resistance of polymers. Effects of cross-linking and temperature on creep compliance of EOC are illustrated in Figures 6.11 to 6.13. Figure 6.11 shows the influence of irradiation dosage on creep behavior of ENGAGE 8842 at 150 °C under 0.1 MPa stress. Pure EOC and samples with low cross-linking undergoes a rapid and high creep behavior. As the cross-linking increases, the more the network is formed in the whole polymer system. These cross-links hold the polymer chains more firmly in the case of highly cross-linked EOC samples. Almost no creep was observed in the case of EOC irradiated with 120 kGy dosage. There is a transition from a high-creep to a low-creep which is noticeable between samples irradiated with 30 kGy and 60 kGy. Keeping in mind that there was no gel content found in the case of samples irradiated with 30 kGy dosage, this can be better understood. When the temperature increases, creep increases as well. This is demonstrated in Figure 6.12. Combined effect of radiation dose and temperature on creep compliance slope (from the later part of the curve) is illustrated in Figure 6.13. One can see from the figure the effect of radiation dose on creep is much higher than that of temperature.

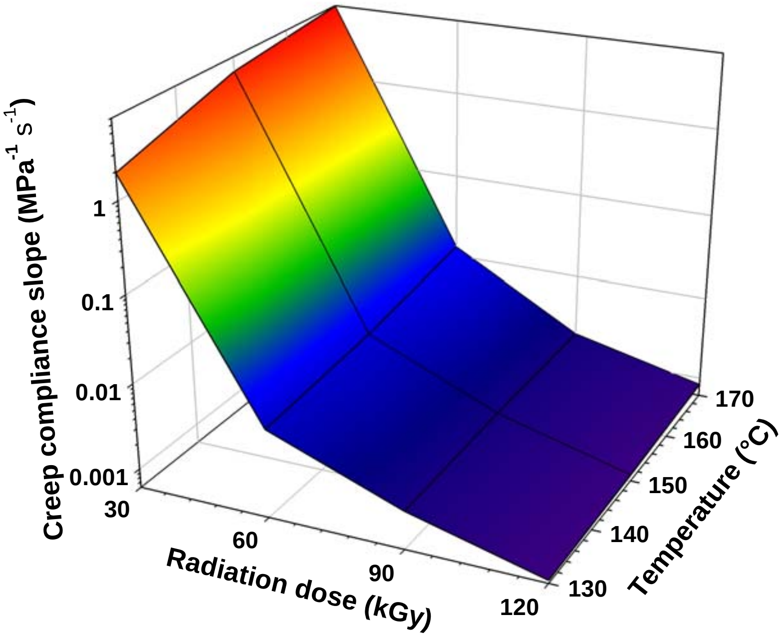


Figure 6.13 *Combined effect of radiation dose and temperature on creep compliance slope at a stress level of 0.1 MPa.*

Thermal stability of cross-linked and uncross-linked EOCs is shown in Figure 6.14. As we can see from the figure, thermal stability increases as the cross-linking increases. Virgin EOC starts to decompose rapidly at around 300 °C while EOC irradiated with 120 kGy dosage was thermally stable up to around 350 °C. For a comparison, we have evaluated the temperatures at which 50% of weight loss happened. These temperatures have been noted as 385, 391, 405, 407 and 409 °C respectively for the EOCs irradiated with 0, 30, 60, 90 and 120 kGy dosages.

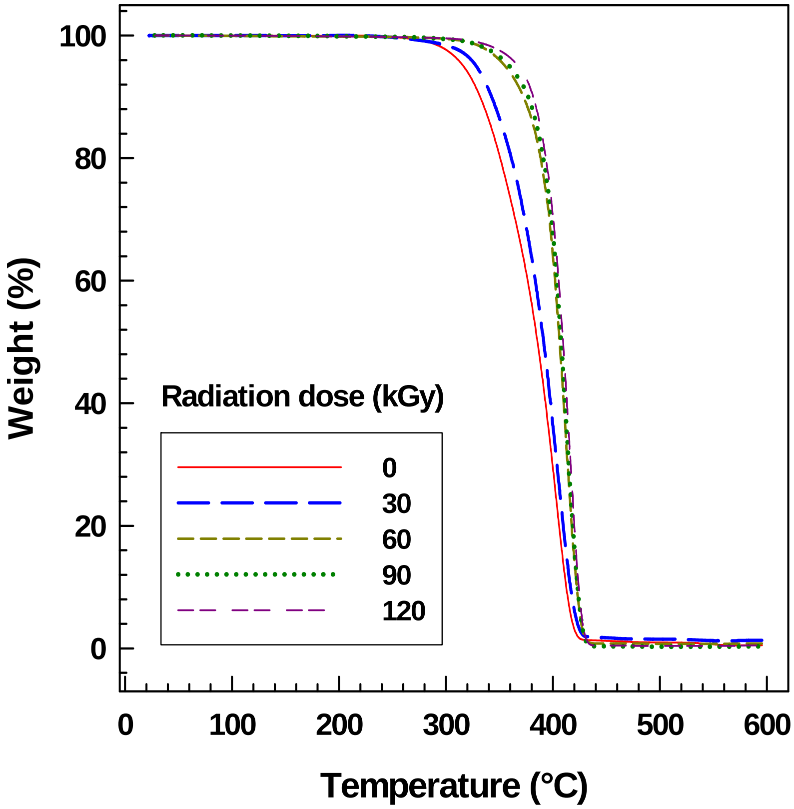


Figure 6.14 *Effect of radiation on thermal stability of ethylene-octene copolymer.*

6.3 Conclusions

Ethylene-octene copolymer has been irradiated using electron beam to investigate the effect of irradiation dose on thermal, rheological and high temperature elastic and creep properties. Extent of cross-linking increased with increase in radiation dose which was confirmed by gel content analysis. Rheological analysis showed that elastic modulus and viscosity increased with radiation dosage. Increase in radiation dosage resulted in a decrease in elongation at break and an increase in stress at break. The effect of cross-linking was proved by high temperature creep and elastic property measurements. Cross-linking through irradiation improved the thermal stability of ethylene-octene copolymer.

CHAPTER 7

CLOSING REMARKS

7.1 General Conclusions

This doctoral thesis demonstrates two different techniques for cross-linking ethylene-octene copolymers and their analysis which are aimed to extend their application. The main conclusions from this research work are,

- Peroxide cross-linking of ethylene-octene copolymer depends up on the cross-linking temperature and peroxide level. Up to certain level increase in amount of peroxide content favors cross-linking then chain scission comes into action. As temperature increases, competition between scission and cross-linking also increases and at high temperatures scission overrules cross-linking.
- Activation energy calculation suggested that optimum peroxide level for EOC cross-linking was in the range 0.5-0.6 wt. %. Increase in extent of cross-linking with peroxide content was reflected in high temperature mechanical properties.
- Comparison of two different EOC/DCP systems provided the information that octene content has a great influence on cross-linking. Better cross-linking was achieved for EOC with lower octene content which was confirmed through high temperature creep. High octene EOC was more vulnerable for degradation also.
- Electron beam irradiation also found to be an effective way to cross-link ethylene-octene copolymer. Considerable improvement in thermal stability and mechanical properties has been observed.

7.2 Contribution to Science and Practice

In this work attention is given to the cross-linking of polyolefin elastomers through different techniques. Ethylene-octene copolymer is able to cross-link properly with minimum degree of degradation to extend their useful temperature range to meet the demands of specialty applications. Cross-linked EOC possesses acceptable high temperature mechanical properties which have great value in automotive field. Optimization of the cross-linking parameters will help to carry out cross-linking easily, which has been discussed in detail in this work. This study will throw light on the factors causing degradation or chain scission during cross-linking and will be a useful reference in future.

7.3 Future works

- Silane-water cross-linking of ethylene-octene copolymers.
- Post irradiation degradation study at 160-250 °C.
- Comparison of different cross-linking techniques.

REFERENCES

[1] IUPAC. Basic Definitions of Terms Relating to Polymers. *Pure Appl Chem.* 1974, vol. 40, no. 3, p. 477 - 492.

[2] LIU, N.C., YAO, G.P., HUANG, H. Influences of Grafting Formulations and Processing Conditions on Properties of Silane Grafted Moisture Crosslinked Polypropylenes. *Polymer.* 2000, vol. 41, no. 12, p. 4537-4542.

[3] MCKEEN, L.W. *The Effect of Temperature and Other Factors on Plastics and Elastomers*, New York: William Andrew Inc., 2008. ISBN 978-0-8155-1568-5.

[4] FAKIROV, S. *Handbook of Condensation Thermoplastic Elastomer*, Weinheim: WILEY-VCH Verlag GmbH & Co., 2005. ISBN 978-3-527-30976-4.

[5] DE, S.K., WHITE, J.R. *Rubber Technologist's Handbook*, Shawbury: Rapra Technology Limited, 2001. ISBN 1-85957-262-6.

[6] NASKAR, K., NOORDERMEER, J.W.M. Dynamically Vulcanized PP/EPDM Blend : Multifunctional Peroxides as Crosslinking Agents-Part -1. *Rubber Chem Technol.* 2004, vol. 77, no. 5, p. 955-971.

[7] G.LVAN. Dynamic Vulcanization: An Accessible Way to Thermoplastic Elastomers. *Iran Polym J.* 1993, vol. 2, no. 1, p. 3-11.

[8] BASULI, U., CHAKI, T.K., NASKAR, K. Influence of Engage® Copolymer Type on the Properties of Engage®/Silicone Rubber-Based Thermoplastic Dynamic Vulcanizates. *eXPRESS Polym Lett.* 2008, vol. 2, no. 12, p. 846–854.

[9] BASULI, U., CHAKI, T.K., NASKAR, K. Mechanical Properties of Thermoplastic Elastomers Based on Silicone Rubber and an Ethylene–Octene Copolymer by Dynamic Vulcanization. *J Appl Polym Sci.* 2008, vol. 108, no. 2, p. 1079–1085.

[10] BHOWMICK, A.K. *Current Topics in Elastomers Research*, New York: Taylor & Francis Group, LLC, 2008. ISBN 978-0-8493-7317-6.

[11] DROBNY, J.G. *Handbook of Thermoplastic Elastomers*, New York: William Andrew Inc., 2007. ISBN 978-0-8155-1549-4.

[12] SEVERINI, F., GALLO, R., IPSALE, S., NISOLI, E., PARDI, M. Natural Weathering of Some New Ethylene Copolymers. *Polym Degrad Stabil.* 1999, vol. 65, no. 2, p. 329-335.

[13] BENSASON, S., MINICK, J., MOET, A., CHUM, S., HILTNER, A., BAER, E. Classification of Homogeneous Ethylene-Octene Copolymers Based on Comonomer Content. *J Polym Sci Pol Phys.* 1996, vol. 34, no. 7, p. 1301-1315.

[14] GUPTA, B., BANERJEE, D., GOSWAMI, L., BANDYOPADHYAY, A. Physicomechanical Studies and Solvent Resistance Analysis of Melt-Blended Novel Ethylene-1-Octene Elastomer and Ethylene-Co-Acrylic Acid Interpenetrating Network Hybrids. *J Appl Polym Sci.* 2011, vol. 120, no. 6, p. 3401-3409.

[15] BABU, R.R., SINGHA, N.K., NASKAR, K. Effects of Mixing Sequence on Peroxide Cured Polypropylene (PP)/Ethylene Octene Copolymer (EOC) Thermoplastic Vulcanizates (TPVs). Part. II. Viscoelastic Characteristics. *J Polym Res.* 2011, vol. 18, no. 1, p. 31-39.

[16] HARPER, C.A. *Handbook of Plastics, Elastomers, and Composites*, New York: McGraw-Hill, 2002. ISBN 0-07-138476-6.

[17] CHEN, X.L., WU, H., YU, J., GUO, S.Y., LUO, Z. Maleic Anhydride/Styrene Melt Grafting and Crosslinking onto Ethylene-Octene Copolymer. *Polym Eng Sci.* 2008, vol. 48, no. 12, p. 2289-2296.

[18] BENSASON, S., NAZARENKO, S., CHUM, S., HILTNER, A., BAER, E. Elastomeric Blends of Homogeneous Ethylene-Octene Copolymers. *Polymer.* 1997, vol. 38, no. 15, p. 3913-3919.

[19] NICOLÁS, J., RESSIA, J.A., VALLÉS, E.M., MERINO, J.C., PASTOR, J.M. Characterization of Metallocene Ethylene-1-Octene Copolymers with High Comonomer Content Cross-Linked by Dicumyl Peroxide or β-Radiation. *J Appl Polym Sci.* 2009, vol. 112, no. 5, p. 2691–2700.

[20] RAJESHBABU, R., GOHS, U., NASKAR, K., THAKUR, V., WAGENKNECHT, U., HEINRICH, G. Preparation of Polypropylene (PP)/Ethylene Octene Copolymer (EOC) Thermoplastic Vulcanizates (TPVs) by High Energy Electron Reactive Processing. *Radiat Phys Chem.* 2011, vol. 80, no. 12, p. 1398-1405.

[21] BABU, R.R., SINGHA, N.K., NASKAR, K. Phase Morphology and Melt Rheological Behavior of Uncrosslinked and Dynamically Crosslinked Polyolefin Blends: Role of Macromolecular Structure. *Polym Bull.* 2011, vol. 66, no. 1, p. 95-118.

[22] GARNIER, L., DUQUESNE, S., CASETTA, M., LEWANDOWSKI, M., BOURBIGOT, S. Melt Spinning of Silane-Water Cross-Linked Polyethylene-Octene through a Reactive Extrusion Process. *React Funct Polym.* 2010, vol. 70, no. 10, p. 775-783.

[23] BASFAR, A.A., MOSNÁCEK, J., SHUKRI, T.M., BAHATTAB, M.A., NOIREAUX, P., COURDREUSE, A. Mechanical and Thermal Properties of Blends of Low-Density Polyethylene and Ethylene Vinyl Acetate Crosslinked by Both Dicumyl Peroxide and Ionizing Radiation for Wire and Cable Applications. *J Appl Polym Sci.* 2008, vol. 107, no. 1, p. 642–649.

[24] WONG, W.K., VARRALL, D.C. Role of Molecular Structure on the Silane Crosslinking of Polyethylene: The Importance of Resin Molecular Structure Change During Silane Grafting. *Polymer* 1994, vol. 35, no. 25, p. 5447-5452.

[25] BHATTACHARYA, A., W.RAWLINS, J., RAY, P. *Polymer Grafting and Crosslinking*, New Jersey: John Wiley & Sons Inc., 2009. ISBN 978-0-470-40465-2.

[26] KHONAKDAR, H.A., MORSHEDIAN, J., WAGENKNECHT, U., JAFARI, S.H. An Investigation of Chemical Crosslinking Effect on Properties of High-Density Polyethylene. *Polymer.* 2003, vol. 44, no. 15, p. 4301–4309.

[27] HENNING, S.K., COSTIN, R. Fundamentals of Curing Elastomers with Peroxides and Coagents. *Rubber World.* 2006, vol. no., p. 28-35.

[28] MARCILLA, A., GARCIA-QUESADA, J.C., RUIZ-FEMENIA, R., BELTRAN, M.I. Crosslinking of Rotational Molding Foams of Polyethylene. *Polym Eng Sci.* 2007, vol. 47, no. 11, p. 1804-1812.

[29] MORSHEDIAN, J., HOSEINPOUR, P.M., AZIZI, H., PARVIZZAD, R. Effect of Polymer Structure and Additives on Silane Grafting of Polyethylene. *eXPRESS Polym Lett.* 2009, vol. 3, no. 2, p. 105–115.

[30] MSAKNI, A., CHAUMONT, P., CASSAGNAU, P. Crosslinking of Ethylene–Octene Copolymers under Dynamic Conditions: A New Way to Access Polymeric Hyperbranched Structure. *Polym Eng Sci.* 2006, vol. 46, no. 11, p. 1530-1540.

[31] KHONAKDAR, H.A., JAFARI, S.H., TAHERI, M., WAGENKNECHT, U., JEHNICHEN, D., HAUSSLER, L. Thermal and Wide Angle X-Ray Analysis of Chemically and Radiation-Crosslinked Low and High Density Polyethylenes. *J Appl Polym Sci.* 2006, vol. 100, no. 4, p. 3264–3271.

[32] SMEDBERG, A., HJERTBERG, T., GUSTAFSSON, B. Effect of Molecular Structure and Topology on Network Formation in Peroxide Crosslinked Polyethylene. *Polymer.* 2003, vol. 44, no. 11, p. 3395–3405.

[33] YAMAZAKI, T., SEGUCHI, T. Electron Spin Resonance Study on Chemical Crosslinking Reaction Mechanisms of Polyethylene Using a Chemical Agent. V. Comparison with Polypropylene and Ethylene-Propylene Copolymer. *J Polym Sci A.* 2000, vol. 38, no. 18, p. 3383–3389.

[34] YAMAGUCHI, M., SUZUKI, K.-I., MAEDA, S. Enhanced Strain Hardening in Elongational Viscosity for HDPE/Crosslinked HDPE Blend. I. Characteristics of Crosslinked HDPE. *J Appl Polym Sci.* 2002, vol. 86, no. 1, p. 73–78.

[35] ZHOU, W., ZHU, S. Esr Study of Peroxide-Induced Cross-Linking of High Density Polyethylene. *Macromolecules.* 1998, vol. 31, no. 13, p. 4335-4341.

[36] YAMAZAKI, T., SEGUCHI, T. ESR Study on Chemical Crosslinking Reaction Mechanisms of Polyethylene Using a Chemical Agent. *J Polym Sci A.* 1997, vol. 35, no. 2, p. 279–284.

[37] LAI, S.-M., LIU, J.-L., HU, S.-H., HUANG, C.-H., WANG, S.-J., CHIEN, S.-C. Fracture Behaviors of Metallocene Catalyzed Polyethylene Elastomer Via Peroxide Crosslinking. *J Appl Polym Sci.* 2009, vol. 113, no. 6, p. 3791–3798.

[38] ANBARASAN, R., BABOUT, O., DEQUIEL, M., MAILLARD, B. Functionalization and Cross-Linking of High-Density Polyethylene in the Presence of Dicumyl Peroxide - an FTIR Study. *J Appl Polym Sci.* 2005, vol. 97, no. 3, p. 766-774.

[39] BENSON, R.S., MOORE, E.A., MARTINEZ-PARDO, M.E., ZARAGOZA, D.L. Effect of Gamma Irradiation on Ethylene-Octene Copolymers Produced by Constrained Geometry Catalyst. *Nucl Instrum Meth B.* 1999, vol. 151, no. 1-4, p. 174-180.

[40] LI, J., PENG, J., QIAO, J., JIN, D., WEI, G. Effect of Gamma Irradiation on Ethylene–Octene Copolymers. *Radiat Phys Chem.* 2002, vol. 63, no. 3-6, p. 501–504.

[41] VACHON, C., GENDRON, R. Effect of Gamma-Irradiation on the Foaming Behavior of Ethylene-Co-Octene Polymers. *Radiat Phys Chem.* 2003, vol. 66, no. 6, p. 415-425.

[42] CARDOSO, E.C.L., LUGAO, A.B., ANDRADE, L. Crosslinked Polyethylene Foams, Via EB Radiation. *Radiat Phys Chem.* 1998, vol. 52, no. 1-6, p. 197-200.

[43] SHEN, F.W., MCKELLOP, H.A., SALOVEY, R. Irradiation of Chemically Crosslinked Ultrahigh Molecular Weight Polyethylene. *J Polym Sci Pol Phys.* 1996, vol. 34, no. 6, p. 1063-1077.

[44] SLOUF, M., SYNKOVA, H., BALDRIAN, J., MAREK, A., KOVAROVA, J., SCHMIDT, P., DORSCHNER, H., STEPHAN, M., GOHS, U. Structural Changes of UHMWPE after E-Beam Irradiation and Thermal Treatment. *J Biomed Maters Res.* 2008, vol. 85B, no. 1, p. 240-251.

[45] BABU, R.R., SINGHA, N.K., NASKAR, K. Melt Viscoelastic Properties of Peroxide Cured Polypropylene-Ethylene Octene Copolymer Thermoplastic Vulcanizates. *Polym Eng Sci.* 2010, vol. 50, no. 3, p. 455–467.

[46] RATNER, S., WEINBERG, A., MAROM, G. Morphology and Mechanical Properties of Crosslinked PE/PE Composite Materials. *Polym Composite.* 2003, vol. 24, no. 3, p. 422-427.

[47] SHEN, F.-W., MCKELLOP, H.A., SALOVEY, R. Morphology of Chemically Crosslinked Ultrahigh Molecular Weight Polyethylene. *J Biomed Maters Res.* 1998, vol. 41, no. 1, p. 71-78.

[48] SIRISINHA, K., MEKSAWAT, D. Comparison in Processability and Mechanical and Thermal Properties of Ethylene–Octene Copolymer Crosslinked by Different Techniques. *J Appl Polym Sci.* 2004, vol. 93, no. 3, p. 1179–1185.

[49] BARZIN, J., AZIZI, H., MORSHEDIAN, J. Preparation of Silane-Grafted and Moisture Cross-Linked Low Density Polyethylene: Part I: Factors Affecting Performance of Grafting and Cross-Linking. *Polym-Plast Technol.* 2006, vol. 45, no. 8, p. 979-983.

[50] KUAN, H.-C., KUAN, J.-F., MA, C.-C.M., HUANG, J.-M. Thermal and Mechanical Properties of Silane- Grafted Water Crosslinked Polyethylene. *J Appl Polym Sci.* 2005, vol. 96, no. 6, p. 2383–2391.

[51] BELTRAN, M., MIJANGOS, C. Silane Grafting and Moisture Crosslinking of Polypropylene. *Polym Eng Sci.* 2000, vol. 40, no. 7, p. 1534-1541.

[52] LOAN, L.D. Peroxide Crosslinking Reactions of Polymers. *Pure Appl Chem.* 1972, vol. 30, no. 1-2, p. 173-180.

[53] ANBARASAN, R., BABOT, O., MAILLARD, B. Crosslinking of High-Density Polyethylene in the Presence of Organic Peroxides. *J Appl Polym Sci.* 2004, vol. 93, no. 1, p. 75–81.

[54] MACHADO, A.V., COVAS, J.A., DUIN, M.V. Monitoring Polyolefin Modification Along the Axis of a Twin Screw Extruder. I. Effect of Peroxide Concentration. *J Appl Polym Sci.* 2001, vol. 81, no. 1, p. 58–68.

[55] GHOSH, P., DEV, D., CHAKRABARTI, A. Reactive Melt Processing of Polyethylene : Effect of Peroxide Action on Polymer Structure, Melt Rheology and Relaxation Behaviour. *Polymer.* 1997, vol. 38 no. 25, p. 6175-6180.

[56] PARENT, J.S., TRIPP, M., DUPONT, J. Selectivity of Peroxide-Initiated Graft Modification of Ethylene Copolymers. *Polym Eng Sci.* 2003, vol. 43, no. 1, p. 234 - 242.

[57] BABU, R.R., SINGHA, N.K., NASKAR, K. Dynamically Vulcanized Blends of Polypropylene and Ethylene Octene Copolymer: Influence of Various Coagents on Mechanical and Morphological Characteristics. *J Appl Polym Sci.* 2009, vol. 113, no. 5, p. 3207–3221.

[58] THITITHAMMAWONG, A., NAKASON, C., SAHAKARO, K., NOORDERMEER, J. Effect of Different Types of Peroxides on Rheological,

Mechanical, and Morphological Properties of Thermoplastic Vulcanizates Based on Natural Rubber/Polypropylene Blends. *Polym Test.* 2007, vol. 26, no. 4, p. 537–546.

[59] KANG, T.-K., HA, C.-S. Effect of Processing Variables on the Crosslinking of HDPE by Peroxide. *Polym Test.* 2000, vol. 19, no. 7, p. 773-783.

[60] CLASS, J.B. A Review of the Fundamentals of Crosslinking with Peroxides. *Rubber world.* 1999, vol. no., p. 35-39.

[61] WHITE, J., DE, S.K., NASKAR, K. *Rubber Technologist's Handbook Volume 2*, Shawbury: Smithers Rapra Technology Limited, 2009. 978-1-84735-099-2.

[62] FROUNCHI, M., DADBIN, S., PANAHINIA, F. Comparison between Electron-Beam and Chemical Crosslinking of Silicone Rubber. *Nucl Instrum Meth B.* 2006, vol. 243, no. 2, p. 354-358.

[63] DUBEY, K.A., BHARDWAJ, Y.K., CHAUDHARI, C.V., SARMA, K.S.S., GOEL, N.K., SABHARWAL, S. Electron Beam Processing of LDPE/EVA/PCR Ternary Blends: Radiation Sensitivity Evaluation and Physico-Mechanical Characterization. *J Polym Res.* 2011, vol. 18, no. 1, p. 95-103.

[64] NICOLA´S, J., RESSIA, J.A.B., VALLE´S, E.M., MERINO, J.C., PASTOR, J.M.A. Characterization of Metallocene EPDM Terpolymers with High Diene and Propylene Content Crosslinked by Dicumyl Peroxide and β-Radiation. *Macromol Chem Physic.* 2004, vol. 205, no. 15, p. 2080–2088.

[65] RDENAS, M.A.C., VILLARREAL, N., GOBERNADO-MITRE, I., MERINO, J.C., PASTOR, J.M.A. Characterization of Electron Beam Irradiation Blends Based on Metallocene Ethylene-1-Octene Copolymer. *J Polym Sci Pol Phys.* 2007, vol. 45, no. 17, p. 2432-2440.

[66] AL-MALAIKA, S., PENG, X., WATSON, H. Metallocene Ethylene-1-Octene Copolymers: Influence of Comonomer Content on Thermo-Mechanical, Rheological, and Thermo-Oxidative Behaviours before and after Melt Processing in an Internal Mixer. *Polym Degrad Stabil.* 2006, vol. 91, no. 12, p. 3131-3148.

[67] SIRISINHA, K., KAWKO, K. Crosslinkable Polypropylene Composites Made by the Introduction of Silane Moieties. *J Appl Polym Sci.* 2005, vol. 97, no. 4, p. 1476–1483.

[68] YANG, S., SONG, G., ZHAO, Y., YANG, C., SHE, X. Mechanism of a One-Step Method for Preparing Silane Grafting and Cross-Linking Polypropylene. *Polym Eng Sci.* 2007, vol. 47 no. 7, p. 1004 - 1008.

[69] FABRIS, F.W., STEDILE, F.C., MAULER, R.S., NACHTIGALL, S.M.B. Free Radical Modification of LDPE with Vinyltriethoxysilane. *Eur Polym J.* 2004, vol. 40, no. 6, p. 1119–1126.

[70] SHAH, G.B., FUZAIL, M., ANWAR, J. Aspects of the Crosslinking of Polyethylene with Vinyl Silane. *J Appl Polym Sci.* 2004, vol. 92, no. 6, p. 3796–3803.

[71] SIRISINHA, K., KAMPHUNTHONG, W. Rheological Analysis as a Means for Determining the Silane Crosslink Network Structure and Content in Crosslinked Polymer Composites. *Polym Test.* 2009, vol. 28, no. 6, p. 636-641.

[72] SIRISINHA, K., MEKSAWAT, D. Changes in Properties of Silane–Water Crosslinked Metallocene Ethylene-Octene Copolymer after Prolonged Crosslinking Time. *J Appl Polym Sci.* 2004, vol. 93, no. 2, p. 901–906.

[73] SIRISINHA, K., KAWKO, K. Crosslinkable Polypropylene Composites Made by the Introduction of Silane Moieties. *J Appl Polym Sci.* 2005, vol. 97, no. 4, p. 1476-1483.

[74] DIMONIE, D., DIMONIE, M., VASILIEVICI, G. Polyolefines Mechanical Recycling Considering the Carbonyl Variation During the First Life. *Mater Plast.* 2007, vol. 44, no. 4, p. 361-364.

[75] ODONNELL, J.H., RAHMAN, N.P., SMITH, C.A., WINZOR, D.J. Chain Scission and Cross-Linking in the Radiation Degradation of Polymers - Limitations on the Utilization of Theoretical Expressions and Experimental Results in the Pregel Region. *Macromolecules.* 1979, vol. 12, no. 1, p. 113-119.

[76] SJOQVIST, M., BOLDIZAR, A. Molecular Modification and Compatibilization of Collected Polyethylene. *J Polym Environ.* 2011, vol. 19, no. 2, p. 335-340.

[77] SLIMANI, K., MOINE, L., AYMES-CHODUR, C., LAURENT, A., LABARRE, D., YAGOUBI, N. Determination of Scission, Crosslinking and Branching Parameters of Electron Beam Irradiated Methacrylate-Acrylamide Copolymer. *Polym Degrad Stabil.* 2009, vol. 94, no. 4, p. 584-590.

[78] STEWART, F.F., SINGLER, R.E., HARRUP, M.K., PETERSON, E.S., LASH, R.P. Electron Beam Crosslinking of Fluoroalkoxy, Methoxyethoxyethoxy, and Substituted Phenoxy Polyphosphazenes: Physical and Chemical Characterization and Comparison to a Thermally Induced Free Radical Process and Ionic Complexation. *J Appl Polym Sci.* 2000, vol. 76, no. 1, p. 55-66.

[79] LAZAR, M., HRCKOVA, L., BORSIG, E., MARCINCIN, A., REICHELT, N., RATZSCH, M. Course of Degradation and Build-up Reactions in Isotactic Polypropylene During Peroxide Decomposition. *J Appl Polym Sci.* 2000, vol. 78, no. 4, p. 886–893.

[80] NASKAR, K., KOKOT, D., NOORDERMEER, J.W.M. Influence of Various Stabilizers on Ageing of Dicumyl Peroxide-Cured Polypropylene/Ethylene-

Propylene-Diene Thermoplastic Vulcanizates. *Polym Degrad Stabil.* 2004, vol. 85, no. 2, p. 831-839.

[81] MACHADO, A.V., MAIA, J.M., CANEVAROLO, S.V., COVAS, J.A. Evolution of Peroxide-Induced Thermomechanical Degradation of Polypropylene Along the Extruder. *J Appl Polym Sci.* 2004, vol. 91, no. 4, p. 2711-2720.

[82] MADANI, M., SHARIFI-SANJANI, N., REZAEI-ZARE, E., FARIDI-MAJIDI, R. Preparation of Granular Crosslinkable Medium-Density Polyethylene. *J Appl Polym Sci.* 2007, vol. 104, no. 3, p. 1873–1879.

[83] MORSHEDIAN, J., KHONAKDAR, H.A., MEHRABZADEH, M., ESLAMI, H. Preparation and Properties of Heat-Shrinkable Cross-Linked Low-Density Polyethylene. *Adv Polym Tech.* 2003, vol. 22, no. 2, p. 112–119.

[84] ROMANI, F., CORRIERI, R., BRAGA, V., CIARDELLI, F. Monitoring the Chemical Crosslinking of Propylene Polymers through Rheology. *Polymer.* 2002, vol. 43, no. 4, p. 1115-1131.

[85] BOUHELAL, S., CAGIAO, M.E., BARTOLOTTA, A., MARCO, G.D., GARRIDO, L., BENACHOUR, D., CALLEJA, F.J.B. On Polyethylene Chain Generation through Chemical Crosslinking of Isotactic Polypropylene. *J Appl Polym Sci.* 2010, vol. 116, no. 1, p. 394–403.

[86] SCORAH, M.J., ZHU, S., PSARREAS, A., MCMANUS, N.T., DHIB, R., TZOGANAKIS, C., PENLIDIS, A. Peroxide-Controlled Degradation of Polypropylene Using a Tetra-Functional Initiator. *Polym Eng Sci.* 2009, vol. 49, no. 9, p. 1760 - 1766.

[87] YU, Q., ZHU, S. Peroxide Crosslinking of Isotactic and Syndiotactic Polypropylene. *Polymer.* 1999, vol. 40 no. 11, p. 2961–2968.

[88] BRAUN, D., RICHTER, S., HELLMANN, G.P., RÄTZSCH, M. Peroxy-Initiated Chain Degradation, Crosslinking, and Grafting in PP–PE Blends. *J Appl Polym Sci.* 1998, vol. 68, no. 12, p. 2019–2028.

[89] SAJKIEWICZ, P., PHILLIPS, P.J. Peroxide Crosslinking of Linear Low-Density Polyethylenes with Homogeneous Distribution of Short Chain Branching. *J Polym Sci A.* 1995, vol. 33, no. 5, p. 853-862.

[90] Dicumyl Peroxide. *http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=329541|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC* /Data 2011.

[91] Irganox 1010. *http://www.polivinilplastik.com/urunler/I1010.pdf* /Data 2011.

[92] Brabender PL-2000 Plasti-Corder *http://www.artisan-scientific.com/73520.htm* /Data 2011.

[93] Rubber Process Analyzer. http://www.alpha-technologies.com/rubber-process-analyzer-rpa-2000-dynamic-mechanical-rheological-tester /Data 2011.

[94] BURHIN, H.G. The Monsanto MDR 2000E in Testing of Cure Kinetics - A Tool to Improve Cured Rubber Article Quality. *Kaut Gummi Kunstst.* 1992, vol. 45, no. 10, p. 866-870.

[95] BARROW, G.M., Physical Chemistry, 5 Ed., McGRAW-HILL, Singapore, 1988. ISBN 0-07-003905-4.

[96] EHRENSTEIN, G.W., RIEDEL, G., TRAWIEL, P. *Thermal Analysis of Plastics: Theory and Practice*, Munich: Hanser Gardner Publications, 2004. ISBN 156990362X.

[97] Differential Scanning Calorimeter. http://smart.tamu.edu/facilities/facilities/materialsandstructures.htm /Data 2011.

[98] DIAS, P., LIN, Y.J., POON, B., CHEN, H.Y., HILTNER, A., BAER, E. Adhesion of Statistical and Blocky Ethylene-Octene Copolymers to Polypropylene. *Polymer.* 2008, vol. 49, no. 12, p. 2937-2946.

[99] Dynamic Mechanical Analysis. http://www.perkinelmer.com/CMSResources/Images/44-74546GDE_IntroductionToDMA.pdf /Data 2011.

[100] BLANKSBY, S.J., ELLISON, G.B. Bond Dissociation Energies of Organic Molecules. *Accounts chem res.* 2003, vol. 36, no. 4, p. 255-263.

[101] PAUL, S., KALE, D.D. Impact Modification of Polypropylene Copolymer with a Polyolefinic Elastomer. *J Appl Polym Sci.* 2000, vol. 76, no. 9, p. 1480-1484.

[102] SIMANKE, A.G., GALLAND, G.B., FREITAS, L., JORNADA, J.O.A.H.D., QUIJADA, R., MAULER, R.S. Influence of the Comonomer Content on the Thermal and Dynamic Mechanical Properties of Metallocene Ethylene/1-Octene Copolymers. *Polymer.* 1999, vol. 40, no. 20, p. 5489-5495.

[103] KHANNA, Y.P., TURI, E.A., TAYLOR, T.J., VICKROY, V.V., ABBOTT, R.F. Dynamic Mechanical Relaxations in Polyethylene. *Macromolecules.* 1985, vol. 18, no. 6, p. 1302-1309.

[104] MIR, S., YASIN, T., HALLEY, P.J., SIDDIQI, H.M., NICHOLSON, T. Thermal, Rheological, Mechanical and Morphological Behavior of HDPE/Chitosan Blend. *Carbohyd Polym.* 2011, vol. 83, no. 2, p. 414-421.

[105] PERRAUD, S., VALLAT, M.F., KUCZYNSKI, J. Radiation Crosslinking of Poly (Ethylene-Co-Octene) with Electron Beam Radiation. *Macromol Mater Eng.* 2003, vol. 288, no. 2, p. 117-123.

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Publications:

Thesis

- **Sameepa. P.V.** Comparative study of Adhesives prepared from Phenol-Formaldehyde and Cashew Nut Shell Liquid (CNSL) (*M.Sc. thesis*). Adhesives Division, Western India Plywoods, Kannur, Kerala India (2007).

Journal (International)

- Petr Svoboda, **Sameepa Poongavalappil**, Rajesh Theravalappil, Dagmar Svobodova, Pavel Mokrejs, Karel Kolomaznik, Toshiaki Ougizawa, Takashi Inoue, Cross-linking of Ethylene-octene Copolymer (EOC) by Dicumyl Peroxide (DCP), *Journal of Applied Polymer Science,* 2011, Vol. 121(1), p. 521-530, (DOI: 10.1002/app.33655).

- **Sameepa Poongavalappil**, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Vladimir Vasek, Kittisak Jantanasakulwong, Toshiaki Ougizawa, Cross-linking kinetics study and high temperature mechanical properties of ethylene–octene copolymer (EOC)/dicumyl peroxide (DCP) system, *European Polymer Journal* 2011, vol. 47 (10), p. 1949-1955, (DOI: 10.1016/j.eurpolymj.2011.07.006).

- **Sameepa Poongavalappil**, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Tomas Sedlacek, Comparison of peroxide cross-linked ethylene-octene copolymers, *Polymer Bulletin* (Manuscript ID: PB-11-0746). Submitted in December 2011.

- **Sameepa Poongavalappil**, Petr Svoboda, Rajesh Theravalappil, Dagmar Svobodova, Michal Danek, Martin Zatloukal, Study on the influence of electron beam irradiation on the thermal, mechanical and rheological properties of ethylene-octene copolymer with high comonomer content, *European Polymer Journal* (Manuscript ID: EUROPOL-D-11-01336). Submitted in December 2011.

- Rajesh Theravalappil, Petr Svoboda, **Sameepa Poongavalappil,** Dagmar Svobodova, Creep and dynamic mechanical analysis studies of peroxide cross-linked ethylene-octene copolymer (accepted for publication in *Macromolecular Materials and Engineering*). DOI: 10.1002/mame.201100289.

- Petr Svoboda, Rajesh Theravalappil, **Sameepa Poongavalappil**, et al., A study on electrical and thermal conductivities of ethylene-octene copolymer/expandable graphite composites (accepted for publication in *Polymer Engineering & Science*).

Conference contributions (International)

- **Sameepa Poongavalappil**, Rajesh Theravalappil, Petr Svoboda, Cross-linking Kinetics Study in Ethylene-Octene Copolymer (EOC)/Dicumyl Peroxide (DCP) System, ANTEC 2011, May 1-5, 2011, Boston, USA. (Poster presentation).
- Rajesh Theravalappil, Petr Svoboda, **Sameepa Poongavalappil**, High Temperature Mechanical Properties of Peroxide Cross-linked Ethylene-octene Copolymer, ANTEC 2011, May 1-5, 2011, Boston, USA. (Oral presentation).
- Rajesh Theravalappil, Petr Svoboda, **Sameepa Poongavalappil**, Jarmila Vilcakova, Electrical, Thermal and Flame Properties of Ethylene-octene Copolymer/Expandable Graphite Composites, ANTEC 2011, May 1-5, 2011, Boston, USA. (Poster presentation).