Hydrogen Peroxide Oxidative Degradation of Liquid Cyclic Natural Rubber : Molecular Weight and Functional Group Analysis

Leni Widiarti[a*], Sajaratuddur[a], Basuki Wirjosentono[b], Eddyanto[c]

Abstract. The research about molecular weight and functional group analysis of low molecular weight liquid cyclic natural rubber has been done. The aim of this research is to achievement the quality of low molecular weight of liquid cyclic natural rubber. This research has been made in several steps such as preparation of the sample of rubber, the process of molecular degradation of cyclic rubber, and characterization of LCNR by using FTIR, GPC and viscosity test. Degradation is done with the help of the phenylhydrazine reagent with oxygen gas atmosphere with a flow rate of 2 $LMin^{-1}$ for 24 hours. Molecular weight analysis by GPC had result the LCNR sample had a Mw is 60,556, a Mn is 6,661, and a PDI is 11,08613. The intrinsic viscosity can be used by relating it to the molecular weight by the Mark Houwink – Sakurada (MHS) equation and get the result 63.533 for LCNR molecular weight. The C-H stretching and bending region are two of the most difficult regions to interpret in infrared spectra. The ranges between 3300 to 2750 cm^{-1} is the C-H stretching region, is the more practical of the two regions. The frequency with which C-H bonds are obstructed is largely determined by the type of hybridization attributed to the bond. The stronger the vibrational force constant, the higher the vibration frequency.

Keywords : LCNR, Low Molecular Weight, GPC, FTIR, Viscosity

[a]*Universitas Islam Negeri Sumatera Utara, William Iskandar Street, Medan 20371*
[b]*University of North Sumatera, Dr. T. Mansur Street, Medan 20222*
[c]*Medan State University, Dr. T. Mansur Street, Medan 20222, Indonesia*
Correspondence and requests for materials should be addressed to Widiarti, L. (email: leniwidiarti@uinsu.ac.id)

Introduction

Rubber plantations in Indonesia are differentiated according to their operations into a large plantation and people's plantation. Large Plantations consist of Large State Plantations and Large Private Plantations. In 2020, the total area of Indonesian rubber plantations was recorded at 3.7 million hectares [1].

NR is a type of elastomer manufactured from the latex of the Hevea brasiliensis tree. It accounts for 42 percent of global elastomer use. Despite the fact that this substance is frequently utilized in the tyre and anti-vibration industries due to its exceptional qualities. Cis-1,4-polyisoprene, which makes up roughly 94 percent of the material weight, is the most important constituent of NR. Lipids (1.5-3 percent w/w), proteins and polypeptides (2 percent w/w), carbohydrates (0.4 percent w/w), and minerals make up the remaining 6%, sometimes known as non-rubber or non-isoprene substances. (0.2 percent by weight) [2]. Rubber materials are appealing for engineering applications because of their ability to endure massive deformations [3]. Rubber-like materials are used in various industrial applications. Elastomeric parts are particularly suitable for engineering applications designed to be submitted to cyclic loading conditions, like tires or vibration isolators [4], the comparison of material behavior to its original qualities is of great interest. [5].

The properties and appearance of the cyclised rubber will depend on the degree of cyclisation. Elastomeric behaviour is retained with cyclisation up to 30%, while a leather-like characteristic is observed when the level of cyclisation reaches around 60%. The cyclised material becomes powdery if the degree of modification is higher than 90%. Cyclised NR becomes a resinous thermoplastic, hard and non-rubbery and could be used in new applications such as adhesives, printing inks and paints. Breakage of the NR chain by chemical

methods has been widely investigated. The reaction is carried out in the presence of chemical reagents and can be done in the organic or latex phase, using a heat or light source. The process transforms high molecular weight NR into products with a low molecular weight which are known as low molecular weight NR or liquid NR (LNR) (Mn of < 20,000). Several methods may be used to break the molecular chain of NR. These are based on oxidative degradation which may employ hydrogen peroxide or an organic hydroperoxide, oxygen from the atmosphere or ferric chloride-oxygen, plus a reducing agent such aromatic hydrazine or sulphanilic acid. One of the most economic processes uses phenylhydrazine and atmospheric oxygen and was developed by a French researcher [6].

Expanding awareness of the environment encourages both analysts and producers to make environmentally-friendly items. For example, Cyclic Natural Rubber (CNR) could be a characteristic elastic subordinate within the shape of a granular strong and is known as resiprene-35 [7]. Due to its chemical resilience, water resistance, and excellent cement characteristics on metal, glass, wood, and paper, CNR is often used as a paint folio, printed ink, and cement specialist. CNR, on the other hand, lacks physicochemical properties, such as its compatibility with polar surfaces and the fact that its paint folio is ineffective against polymers with polar qualities, such as polyimide. [8]. Fatigue-induced stress softening and hysteresis, as well as dissipative heating, characterize a complicated history-dependent response in cyclically loaded rubbers. The relationship between these several inelastic effects that frequently emerge together is far from clear. [9]. The method of oxidative degradation can be used to generate Liquid Cyclic Natural Rubber (LCNR) (Brosse's method) [10].

FTIR spectroscopy is an analytical method used for the characterization of polymeric materials and functional group analysis by
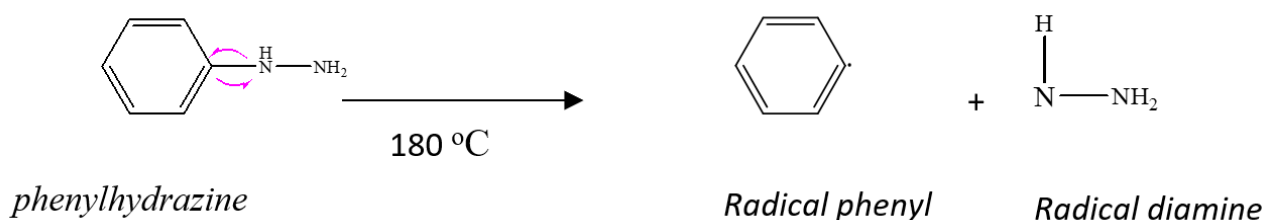

Figure 1. Chain Breaking Process Initiated by Ph Radical

determine and record the results of residual spectra with energy absorption by organic molecules in infrared light by infrared defined as an area that has a wavelength from 1-500 cm^{-1}. Every groups in a molecule generally have their own characteristics so that FTIR spectroscopy can be used to detect specific groups on the polymer. The intensity of the absorption band is a measure of the concentration of the group characteristic of polymers. This method is based on the interaction between infrared radiation and matter (atomic or molecular interactions with electromagnetic radiation). This interaction is in the form of absorbance at certain frequencies or wavelengths associated with energy transitions between various vibrational, rotational and molecular energy states. Infrared radiation is important in structural determination or analysis the functional groups are located at 650 cm^{-1} – 4000 cm^{-1} [11].

The natural rubber has a strong propensity to crystallize properties due to the large strain effect. Its mechanical behavior will impact filled natural rubber. At high strain, material stiffness can be increased due to the crystallization process [12]. The stereoregularity properties, when natural rubber stretched more than 300% of its original length, it allows its rapid crystallization, named strain-induced crystallization, which acts as the main factor responsible for the heaviest mechanical properties [13]. Therefore, if the rubber has a strain-induced crystallization problem, the solution is to add filler to the rubber matrix to induce this effect [14]. The possible compound can be detected from degradation products from any functional group can be shown by the Infra-Red spectra which has supported by principal component analysis, was used in the band area to obtain a material degradation profile. IR spectroscopy in a Tensor 27 spectrometer (Bruker

Optic, Madrid, Spain) monitored the chemical changes in the cyclic liquid natural rubber samples and the attenuated total multiple reflection (ATR-IR) method was employed. The depth of penetration (DP) of the IR radiation in ATR mode

$$DP = \frac{\lambda}{2\pi n c \left(sen^2\,\theta - \left(\frac{ns}{nc}\right)^2\right)^{\frac{1}{2}}}$$

where θ is the incident angle of the IR beam, λ is the wave length of the IR radiation, and n_p and n_c are the indices of refraction of the polymer and prism, respectively.

NR is attracting attention as a polyol because it has excellent physical properties such as elasticity, the chain length of molecules can be easily changed, and Mn can be easily modified [16]. Because all synthetic polymers comprise polymer chains of varying length, the atomic weight isn't a single value - the polymer exists as a collection of chain lengths and atomic weights. Following that, a polymer's atomic weight must be represented as a few normal molecular weights determined from the atomic weights of all the chains in the test. This diagram depicts the most often used atomic weight midpoints that may be determined using gel permeation chromatography (GPC) and size exclusion chromatography (SEC), as well as how they are described and the traditional methods used to determine them. [17]. Molecular weight measurement with GPC) uses a conductivity measuring detector. Measurements are made by calibration using standard polymer solutions and internal calibration of the GPC equipment [11].

The viscosity of a polymer solution is a type of transport property that is critical in polymer synthesis and research, as well as equipment design and optimization. Because of the complexity of the polymer structure, large molecular
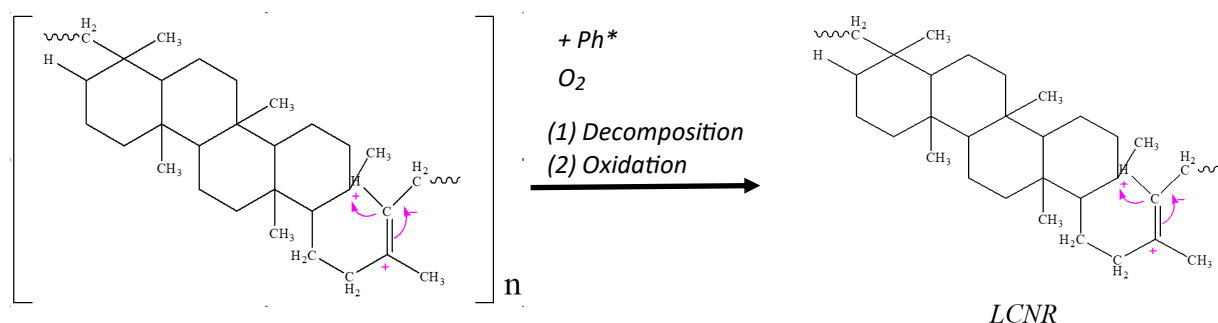

Figure 2. Mechanism of Reaction Formation of LCNR

weight, and polydispersity, in conformity of the degree of polymerization and branching of the molecules, and the difference in the aggregation state of the polymer of amorphous and crystalline states, polymer dissolution is much more complex than small molecules, and viscosity is more difficult to predict. Long-chain polymer molecules swell and expand to form spherical coils when dissolved in a solvent, and the hydrodynamic volume of a polymer coil is proportional to the molecular weight of the polymer, the characteristics of solvents and the concentration of solutions Polymer intrinsic viscosities and expansion factors are hydrodynamic characteristics related to polymer-solvent interactions, while polymer-solvent interactions are intimately related to thermodynamic parameters. As a result, the intrinsic viscosity data can be used to calculate thermodynamic parameters [18].

NR is so high molecular weight that it is too viscous to be treated or blended as a solid rubber using current techniques. Viscosity can be reduced by destroying rubber molecules and lowering their molecular weight. The degree of degradation depends on the application required. Degradation can be caused by mechanical or chemical processes. The use of mechanically generated shear forces in an open mill or internal mixer to break molecular chains is called mastication. The goal is usually to reduce the intrinsic viscosity to obtain a mastic rubber that is easy to process. [6].

As rubber applications need low molecular weight, so in this study has the goals how to do the process transforms high molecular weight NR into products with a low molecular weight which are known as low molecular weight NR or liquid NR (LNR) (Mn of < 20,000) using oxidative degradation method.

Experimental

Cyclic Natural Rubber Molecular Weight Reduction

Place 50 grams of CNR into a glass beaker, dissolved with xylene until completely dissolved. Place the dissolved solution into a three neck flask which is then assembled with a three neck flask connected to the O_2 gas regulator through a gas hose, and hang a 100 °C thermometer that has been connected to the inside. boiling flask, covered with aluminum foil thoroughly the three neck flask and heated using a hot plate until the temperature reached 60 °C temperature and then added phenylhydrazine drop by drop as much as 25.31 g and flowed O_2 gas into the mixture at a flow rate of 2 L/minute and stirred at

Liquid Cyclic Natural Rubber (LCNR) obtained by precipitation with methanol as much as 1.25 L and dried in an oven at a temperature of 40 °C until the weight is constant. The resulting LCNR was characterized using functional group analysis with Fourier Transform InfraRed (FTIR), molecular weight analysis with Ostwald viscometer and gel permeation chromatography analysis.

Fourier Transform InfraRed (FTIR) Analysis

Mixed about 10 mg of CNR sample was mixed with 90 mg of KOH and stirred until homogeneous. The sample is taken and then placed into the sample holder provided in the form of a cuvette on the PerkinElmer brand FTIR device with Spectrum Version 10.03.07. The tool is turned on and then directed to infrared rays and detected wavelengths and the results are recorded.
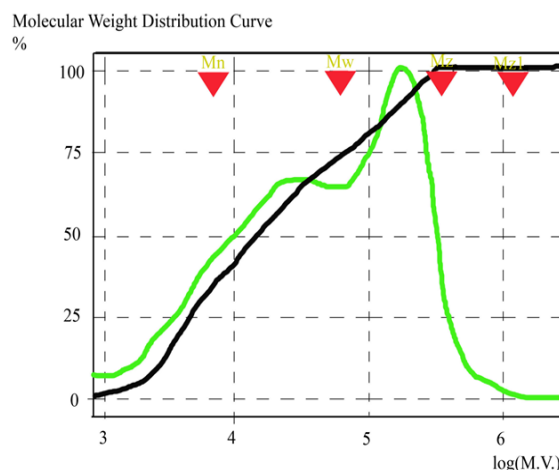

Figure 3. The thick, brown and sticky solution of LCNR

Figure 4. The molecular weight distribution curve of LCNR

Gel Permeation Chromatography (GPC) Analysis

GPC, also known as size exclusion chromatography (SEC), is a type of liquid chromatography that separates polymer samples depending on their size, or more precisely, their molecular hydrodynamic volume. The separation takes place in continuous columns loaded with stationary phase materials like polystyrene and silica gel. Weighing 0.02 gram of LCNR sample and put it in

tetrahydrofuran solvent at 60 °C At 30 °C, the molecular weight was determined at a rate of 1 ml/min.

The Molecular Weight Analysis by Ostwald viscometer

The Ostwald viscometer is assembled in such a way, then 10 ml of toluene is put into the Ostwald Viscometer and pull the toluene solution with a rubber ball up to the line, then after stopping the
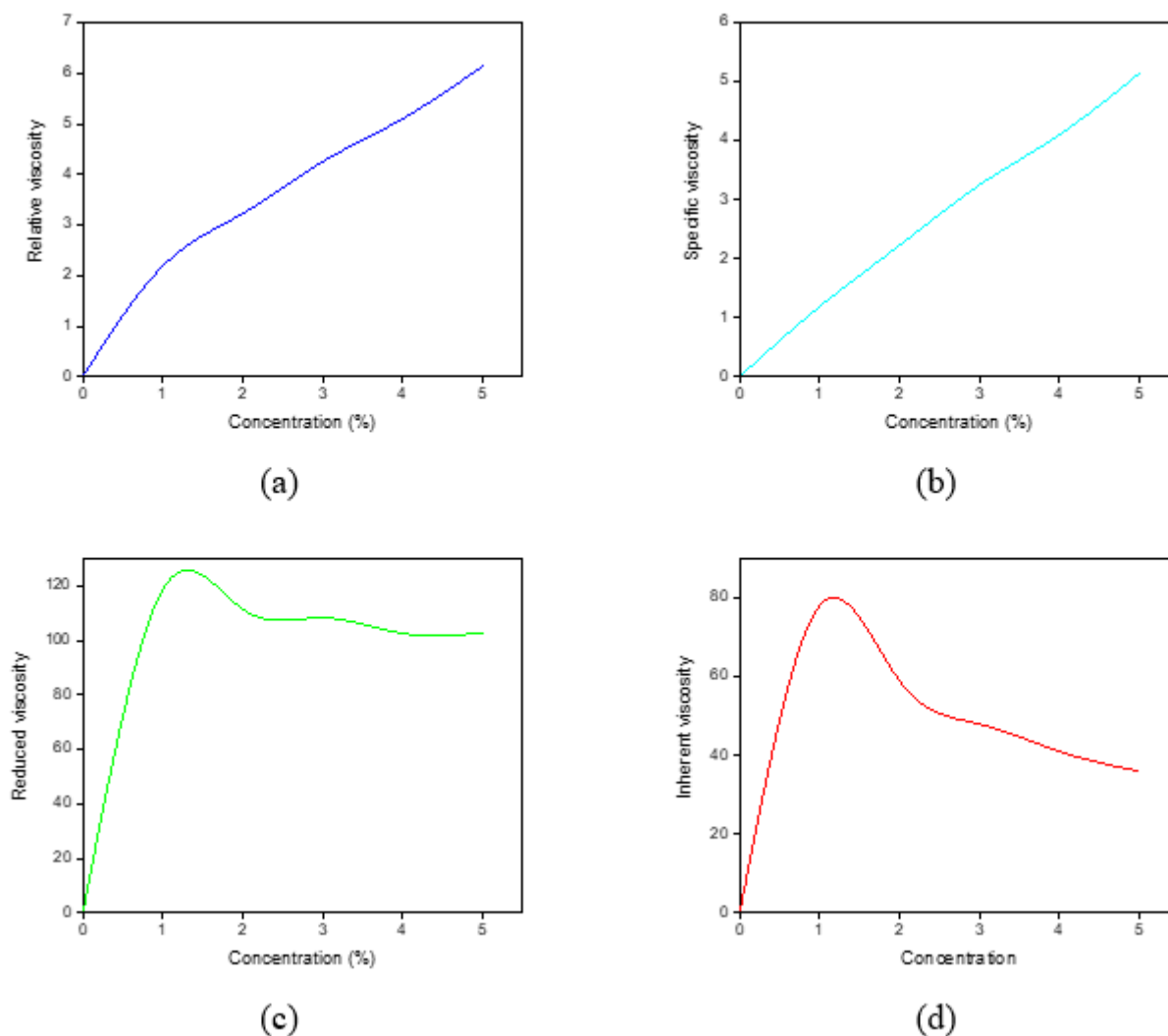

Figure 5. (a) The relative viscosity vs Concentration, (b) The specific viscosity vs Concentration (c) The reduced viscosity vs Concentration, (d) The inherent viscosity vs Concentration.

Table 1. The result of measuring the molecular weight of the sample with GPC

Sample	Result		
	Mw	Mn	PDI
	60,193	6,590	9.13643
Liquid Cyclical Natural Rubber	61,685	6,812	9.05579
	59,792	6,582	9.08451
Average	60,556	6,661	9.09164

suction, measure the time required for the toluene. to go down from the upper limit to the lower limit. Then add 0.1 g of LCNR to 10 ml of toluene to make a polymer solution of 0.01 g/ml and further make up to 0.02 g/ml; 0.03 g/ml ; 0.04 g/ml ; 0.05 g/ml which then put the polymer solution into the Ostwald Viscometer with the same steps as above which was repeated 3 times and the intrinsic viscosity value was searched and the molecular weight was calculated.

Results and Discussion

CNR degradation step to LCNR

Dilution of CNR is the initial stage in this study which is used as material for LCNR procedure. Where in this study CNR is first diluted with xylene solvent at a ratio of 1:5. The 50 grams of CNR was used and 250 mL of xylene solvent was used and dissolved and stirred with a magnetic stirrer at 60 $^{\circ}$C to facilitate dissolution, then dissolved completely.

The CNR solution is then heated at a temperature of 60 $^{\circ}$C with the aim of optimizing the performance of phenylhydrazine which is carried by O_2 gas in breaking the rubber molecular chain into rubber which has a short molecular chain. Phenylhydrazine's reaction mechanism by forming phenyl radicals and diamine

radicals due to the heating process which reacts with the addition of oxygen (Figure 1) . The presence of oxygen will form radicals that attack the double bond of the natural rubber carbon chain so that it becomes bonded.

The synthesis reaction of Cyclic Liquid Natural Rubber (Figure 3) through a chain-breaking reaction with phenylhydrazine can be seen in Figure 2. The addition reaction of phenyl radicals that attacks the double bonds of the carbon chain in the rubber molecule will decompose and bind to each other so that the double bond is broken.

Gel Permeation Chromatography (GPC) Result

The order of molecular weight is Mn < Mv < Mw < Mz < Mz + 1. The greater the polydispersity index, the wider the molecular weight. Polymer monodispers in which all chain lengths are the same (such as proteins) have Mw/Mn = 1. The polymerization step reactions typically yield Mw/Mn values of about 2.0, whereas chain reactions produce Mw/Mn values between 1.5 and 20. The molecular weight distribution curve of LCNR can be seen in Figure 4.

Number average molecular weight (Mn) is the number average molecular weight is the statistical average molecular weight of all the polymer chains in the sample. Weight average molecular weight (Mw) is determined by methods that

Table 2. Intrinsic viscosity and molecular weight of LCNR.

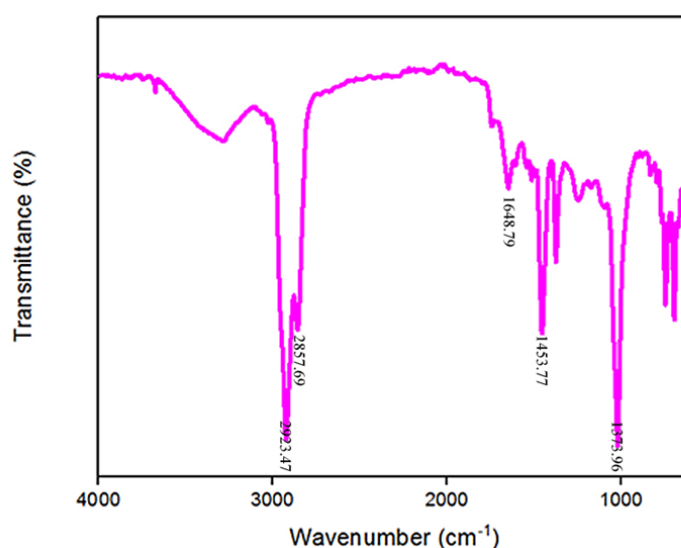| Sample	Intrinsic viscosity (ɳ$_{int}$)	Molecular Weight (Mw)
LCNR	82,952	63.533

Figure 6. The FTIR spectrum of LCNR

Table 3. The group and the stretching vibration of LCNR

Group	Stretching vibration, cm^{-1}
-CH$_2$- methylene asymmetric	2923.47
-CH$_2$- methylene symmetric	2857.69
C=C stretch	1648.79
CH$_2$ methylene	1453.77
CH$_3$ methyl groups	1373.96

are sensitive to the molecular size rather than just their number, such as light scattering techniques. Higher average molecular weights (Mz, Mz+1), higher mean values become more and more sensitive to high molecular weight polymers and therefore more difficult to measure accurately. It is usually associated with a method of measuring the movement of polymer molecules. Diffusion or sedimentation techniques, etc. Although z-means has not been universally reported on polymers, there are some important ways to measure dimensions. z Of the chain that gives the average molecular weight.

The LCNR sample has 60,556 of Mw, 6661 of Mn, and 9.09164 of PDI (Table 1). Mn is related to the properties of tensile strength, impact strength, and hardness. The greater the Mn, the greater the tensile strength, impact strength, and hardness. Mw is related to brittleness. The larger the Mw, the smaller the brittleness. Mz is related to the deflection and stiffness properties. Polymers with high Mw have higher viscosity, lower melting point, and are more difficult to dissolve, due to higher chemical resistance; very high Mw polymers are more difficult to process and require higher temperatures to process. Molecules in the high molecular weight range are involved in mechanical strength and molecules in the low molecular weight range are involved in rheological properties [3]. For example, studies have shown that the Polymer Dispersity Index (PDI) is associated with zero shear viscosity and shear thinning effects [19].

Determination of Molecular Weight with Ostwald Viscometer Method

Polymer blend viscosity is one of the most important and common methods for comparing polymer-solvent interactions, polymer-polymer interactions, atomic weights, atomic shapes, and conformations in dilute solutions [20].

When the concentration increases, the viscosity also increases (see Figure 5). Therefore to eliminate the concentration effect, the specific viscosity is divided by the concentration and extrapolated to zero concentration to give the intrinsic viscosity (Ηint) or a finite number of viscosity. Intrinsic viscosity (Ηint) can be obtained through the following equation

$$[\text{Η}] = K . M_v{}^a$$

Where:

Intrinsic viscosity (Ηint) = (Ηinh)$_{c=0}$

Among the various types of viscosity, the intrinsic viscosity can be used by relating it to the molecular weight by the Mark Houwink – Sakurada (MHS) equation. Where the MHS equation is as follows.

Obtained intrinsic viscosity and molecular weight of LCNR can be seen in Table 2.

The Functional Group Analysis Result by using FTIR Instrument

The C-H stretch and bend portions of the infrared spectrum are two of the hardest to interpret (Figure 6). The stretch areas in C-H that range from 3300 to 2750 cm^{-1} are the more beneficial of the two. The sort of hybridization that occurs as a result of C-H binding determines the frequency with which it inhibits (Table 3).

The frequency is high and the vibrational force constant is significant. The type of carbon to which hydrogen is linked is determined by the frequency with which C-H absorption occurs. The symmetric and asymmetric stretch modes of the group are represented by two C-H stretch bands produced by methylene hydrogen (CH$_2$). At roughly 1375 cm^{-1}, the CH$_3$ methyl group exhibits typical absorption.

Conclusion

The oxidative degradation method with the help of phenylhydrazine reagent and oxygen gas atmosphere succeeded in reducing the molecular weight of rubber < 20,000 to 6,661. From the molecular weight analysis with the Ostwalt viscometer, Mw was obtained at 63,553. The C-H stretch and bend portions of the infrared spectrum are two of the hardest to interpret. The stretch areas in C-H that range from 3300 to 2750 cm^{-1} are the more beneficial of the two. The sort of hybridization that occurs as a result of C-H binding determines the frequency with which it inhibits.

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