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UMREŽAVANJE PRIRODNOG KAUČUKA

CROSS-LINKING OF NATURAL RUBBER

SAŽETAK

Zahtjevi koji se postavljaju pred ploveće objekte nužno su doveli do primjene polimera kao konstrukcijskog materijala i kao suvremenog sustava zaštite u brodogradnji i pomorstvu. Prirodni kaučuk je poznat kao važan industrijski materijal koji se dobiva od drveta kaučukovca (Hevea brasiliensis). To je polimerni materijal, po kemijskom sastavu uglavnom cis 1,4-poliizopren, koji se ubraja u skupinu elastomera i zbog svojih specifičnih svojstava ima vrlo široku primjenu. Poznavanje njegove strukture (posebno nanostrukture gel faze) i molekulske dinamike vrlo je važno u određivanju mehaničkih i primjenskih svojstava. Prirodni se kaučuk, kao i sintetski elastomeri, mora podvrgnuti procesu umrežavanja pri čemu dolazi do poprečnog povezivanja lančastih molekula, a tim se postupkom dobivaju željena uporabna svojstva materijala. Tako pripravljen materijal odlikuje se odgovarajućom elastičnošću, prekidnom čvrstoćom, žilavošću i otpornošću na habanje.

Ključne riječi: *natural rubber, proces umrežavanja, svojstva primjene*

SUMMARY

Demands imposed on floating objects have necessarily resulted in applying polymer as construction material, as well as in protection systems in shipbuilding and maritime affairs. Natural rubber is known as a very important industrial material gained from (Hevea Brasiliensis). It is a polymeric material and by chemical structure it is mostly cis 1.4-polyisoprene, belonging to the group of elastomers and due to its special characteristics it has a wide usage. Familiarity with its structure (especially nanostructure of the gel phase) and with its molecular dynamics is very important in defining mechanical and application characteristics. Natural rubber, as well as synthetic elastomers, must be submitted to the process of cross-linking which causes transversal linking of chain molecules. This process results in desired usage characteristics of the material. The material prepared in this way shows appropriate elasticity, tensile strength, viscosity and resistance to wearing.

Key words: *Natural rubber; cross-linking process; application characteristics*

1. UVOD

Pod nazivom kaučuk podrazumijeva se *cis*-1,4-poliizopren, jedan od najvažnijih prirodnih polimera[1] kojeg su upotrebljavali Maje u Centralnoj i Južnoj Americi negdje oko 1600. godine prije Krista. U Europu ga je donio Kolumbo, ali sve do 19. stoljeća je služio samo za brisanje tragova olovke, pa mu od tuda i ime u engleskom jeziku *rubber*. Poliizopren u prirodi postoji u dvije konfiguracije: *cis*-1,4-poliizopren, prirodni kaučuk i *trans*-1,4-poliizopren, gutaperka ili balata.

Kemijska struktura poliizoprena prikazana je na slici 1.1.

Dobiva se od drveta vrste *Hevea brasiliensis (kaučukovac)* koje raste u tropskim krajevima Srednje i Južne Amerike te Azije. No, *trans*-1,4-poliizopren dobiva se od vrsta *Plaquium gutta* i *Mimusops balata* koji se uzgajaju na plantažama Jave i Malaje. Tankim zarezivanjem kore drveća počinje teći lateks koji se skuplja u posude.

Hevea daje lateks koji sadrži oko 35% poliizoprena i 5% ostalih otopljenih tvari kao što su proteini, lipidi i anorganske soli, a ostatak je voda.

Poliizopren sadržan u lateksu *Heveae* se sastoji od približno 98% *cis*-1,4 jedinica, 1% *trans*-1,4 jedinica te 1% *trans*-3,4 jedinica strukture *glava-rep*[2]. Molekulska masa prirodnog poliizoprena jako varira od vrlo niskih vrijednosti od svega nekoliko desetaka tisuća do vrlo visokih vrijednosti od čak 500 000.

Prije transporta lateks se stabilizira protiv djelovanja mikroorganizama dodatkom 5−7 g amonijaka na litru lateksa, a time se ujedno smanjuje vjerojatnost koagulacije poliizoprena. Koncentriranje lateksa provodi se zagrijavanjem u prisustvu lužine i dodatkom zaštitnih koloida. Na taj način se smanjuje udio vode i povećava sadržaj suhe tvari na oko 60%.

1. INTRODUCTION

The term rubber stands for *cis*-1.4- polyisoprene, one of the most important natural polymers[1], used by the Mayans in Central and South America, around 1600 year B.C. It was brought to Europe by Columbus, but it was used exclusively for erasing the pencil trail, until 19th century. That is where its name “rubber” in the English language originates from. In the nature polyisoprene exists in two configurations - *cis*-1.4- *trans*-1.4, natural rubber and *trans*-1.4-polyisoprene, gutta-percha or balata.

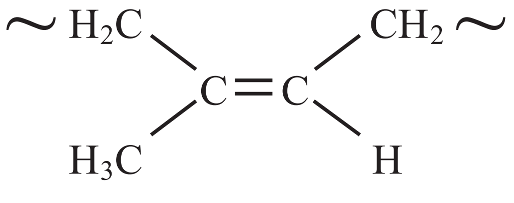
The chemical structure of polyisoprene is shown in figure 1.1.

It derives from the tree family *Hevea brasiliensis,* which grows in the warm parts of Middle and South America and in Asia. *Trans*-1.4-polyisoprene is derived from species *Plaquium gutta* and *Mimusops balata,* bred on the plantations on Java and Malaya. Cutting gashes in tree bark allows the flowing of latex which is collected in cups afterwards.

We tap the tree bark and allow latex to flow. Latex is collected in cups. *Hevea* produces latex which consists of 35% of polyisoprene and 5 % of proteins, lipids, inorganic salts, and the rest is water.

Polyisoprene derived from latex *Heveae* consisting of approximately 98% *cis*-1.4 units, 1% *trans*-1.4 units and 1% *trans*-3.4 units having the “head-tail” structure. The molecular mass of the natural polyisoprene ranges from very low readings, about tens of thousands to a very high reading of five hundred thousand.

Before transporting latex, it needs to be stabilized against microorganisms impact by adding 5-7 g of ammonium per 1 l of latex. In this way, we also minimize options for the coagulation of polyisoprene. Latex is concentrated through heating in the presence of alkali and by adding protective colloids. In this way we re-



Slika 1.1. *Skraćena strukturna formula ponavljajuće jedinice cis-14-poliizoprena* [9]
Figure 1.1 *Shortened structure formula for repeating unit cis-1.4-polyisopren* [9]

Slika 1.2. Skupljanje lateksa [12]
Figure 1.2 *Collecting latex* [12]

Osušeni kaučuk se preša u bale i transportira do prerađivača. Prirodni kaučuk sadrži masne kiseline, koje djeluju kao stabilizatori, i proteine koji ubrzavaju vulkanizaciju. Nasuprot tome, sintetskom kaučuku treba dodati stabilizatore i amine. Neke fizikalne konstante prirodnog kaučuka prikazane su u tablici 1.

Sirovi prirodni kaučuk, zbog određenog sadržaja gela [4] koji nije potpuno topljiv u organskim otapalima i ima molekulske mase nekoliko puta veće od sintetskog poliizoprena, nije prikladan za preradu te je neophodno prethodno cijepanje poliizoprenskih lanaca gel faze. Taj se proces naziva mastikacija, a uključuje postupak mehaničke i termooksidacijske razgradnje lanaca u kojima nastaju kraći lanci, manjih molekulskih masa.

duce the water content and increase the dry matter content to about 60 %.

Dried rubber is pressed in bundles and transported to the manufacturer. Natural rubber contains fat acid, which has a stabilizing effect, and proteins which accelerate vulcanization. Synthetic rubber, on the other hand, needs stabilizers and amines added. Some physical constants of natural rubber are shown below, in table 1.

Raw natural rubber is not suitable for manufacturing due to define content of gel [4] which is not completely dissoluble in organic solvents and its molecular mass is somewhat greater than the molecular mass of synthethic polyisoprene. Prior splitting of polyisoprenic chains in gel phase is therefore necessary. This process is called mastication. It refers to the process of a mechanical and thermal-oxidizing chain decompostition which results in shorter chains of lower molecular masses.

2. CROSS-LINKING PROCESS

Exposed to higher temperatures, natural rubber is soft and sticky, while at lower temperatures it turns hard and brittle and it is not directly applicable. Therefore it needs to be submitted to the process of cross-linking [2,3] which refers to the mutual cross-linking of polyisporene chains and creating three dimensional structure, figure 2.1. Rubber, the result of this process, is neither sticky nor soft, it is not brittle at low temperatures, and it shows great elasticity and solidity.

The American scientist Charles Goodyear was searching for a mode to improve rubberporta applicability properties, up to 1839 when he discovered that rubber and sulfur alloy, after heating, change their characteristics.

He named this process vulcanization, after Vulcan, the Roman God of Fire and Volcano, and he patented it in 1844 (US patent 3644).

Tablica 1. *Fizikalne karakteristike prirodnog kaučuka [10]*
Table 1 *Physical characterisics of natural rubber*[*10*]

Svojstvo ***Characteristic***	**Vrijednost** ***Value***
Gustoća / *Density*	0,913 gcm^{-3}
Volumni koeficijent ekspanzije / *Volumetric expansion coefficient*	670×10^{-6} K^{-1}
Staklište / *Glass transition*	− 72 °C
RavnoRavnotežna temperatura taljenja / *Balance melting point*	28 °C - 39 °C
Entalpija taljenja / *Melting enthalpy*	64 $kJkg^{-1}$

2. PROCES UMREŽAVANJA

Prirodni kaučuk je pri višim temperaturama mekan i ljepljiv, a pri nižim temperaturama tvrd i krt materijal i kao takav nije pogodan za izravnu uporabu. Stoga se mora podvrgnuti procesu umrežavanja [2,3], što podrazumijeva međusobno poprečno povezivanje lanaca poliizoprena i stvaranje trodimenzijske strukture, slika 2.1. Kao rezultat toga procesa dobiva se guma koja za razliku od kaučuka nije ljepljiva niti toliko mekana, nije krta na niskim temperaturama, a odlikuje se izvrsnom elestičnošću i određenom čvrstoćom.

Američki znanstvenik Charles Goodyear dugo je tražio način na koji bi poboljšao uporabna svojstva kaučuka, sve dok sasvim slučajno 1839. godine nije otkrio da smjesa kaučuka i sumpora nakon zagrijavanja mijenja svoja svojstva.

Taj je postupak nazvao vulkanizacija, prema Vulkanu, rimskom bogu vatre i vulkana, i patentirao ga 1844. godine (US patent 3644).

2.1. Kemijsko umrežavanje

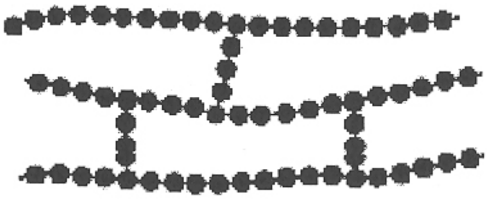
Vulkanizacija je kemijska reakcija kojom se linearne polimerne molekule poprečno povezuju u umreženu strukturu preko atoma sumpora. Fizikalna svojstva vulkaniziranog kaučuka ovise o gustoći umreženja, ali i o tipu premoštenja lančastih molekula koja mogu biti monosulfidna, disulfidna i polisulfidna.Vulkanizirani kaučuk poprima elastomerna svojstva, a vlačna čvrstoća je i do deset puta veća u odnosu na nevulkanizirani kaučuk.

Za malu gustoću umrežavanja dobiva se materijal velike elastičnosti (guma), a za veliku gustoću umreženja tvrd i neelastičan materijal (ebonit).

Za kemijsko se umrežavanje najčešće koristi sumpor, a sam se proces vulkanizacije obično odvija na temperaturi između 130 °C i 160 °C. Tijekom procesa vulkanizacije stvaraju se premoštenja između poliizoprenskih lanaca koja mogu biti tipa –C–S–C– (monosulfidna), –C–S –S–C– (disulfidna) ili –C–S$_n$–C– (polisulfidna), uz otvaranje nekih dvostrukih veza.

Na slici 2.1.1. prikazan je slučaj monosulfidnih premoštenja dvaju lanaca poliizoprena.

Procesom vulkanizacije smanjuje se gibljivost polimernih lanaca i onemogućava tečenje pri

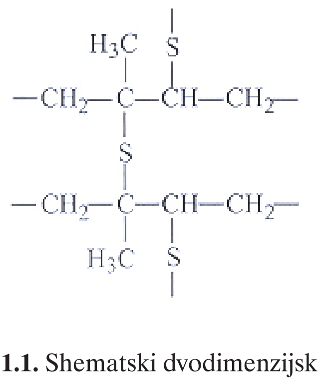


Slika 2.1. Shematski dvodimenzijski prikaz umreženih lančastih molekula poliizoprena [11]
Figure 2.1 *Two dimensional scheme of cross linked chained polyisoprene molecules* [11]

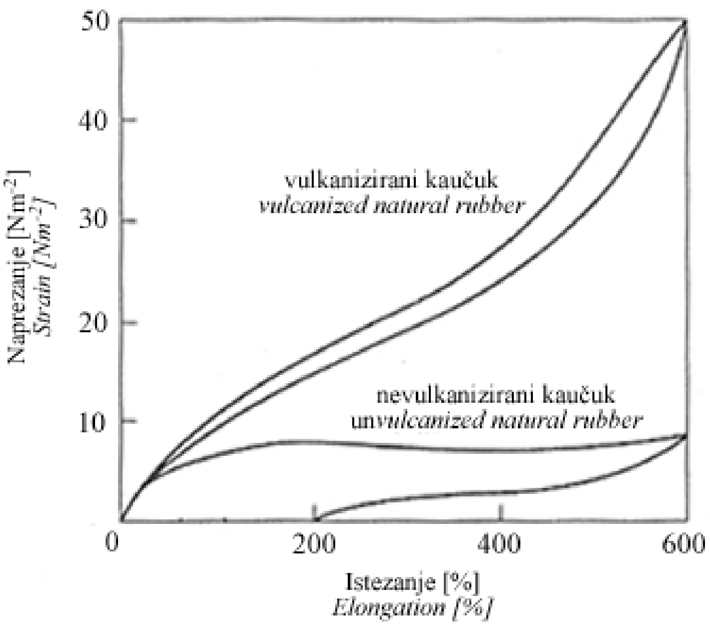
2.1 Chemical Cross-linking

Vulcanization is a chemical reaction where linear polymer molecules are transversally linked into a network structure by sulfur atoms. The physical properties of vucanized rubber depend on the network density, as well as on the type of the chain molecules which can be monosulfidic, disulfidic or polysufidic. Vulcanized rubber acquires elastomer properties and the ultimate tensile strength is ten times greater than in a non vulcanized rubber. For lesser cross linking density, we obtain material of greater elasticity, and for greater density we get a solid and non elastic material (vulcanite).

In the process of the chemical cross linking sulfur is mainly used. The process of vulcanization occurs under the temperatures between 130°C and 160°C. During vulcacnization the cross-linking between polyisoprenic chaines is created. This cross-linking can be of the –C–S–C– (monosulfide), –C–S –S–C– (disulfide) or –C–S$_n$–C– (polysulfide) type, along with the arising of some other double bonds. An example of the monosulfide cross-linking of two polyisoprene chains is shown in figure 2.1.1.



Slika 2.1.1. Shematski dvodimenzijski prikaz monosulfidno vulkaniziranog poliizoprena [11]
Figure 2.1.1 *Two dimensional presentation of the monosulfide vulcanized polyisoprene* [11]



Slika 2.1.2. Ovisnost naprezanja o istezanju (deformaciji) za nevulkanizirani i vulkanizirani kaučuk [11]
Figure 2.1.2 *Stress-strain curves to 600% elongation and back, typical of unvulcanized and vulcanized natural rubber* [11]

višim temperaturama. Materijal prestaje biti krt pri niskim temperaturama, jer su molekule čvrsto povezane jakim kovalentnim kemijskim vezama i stoga ih nije lako razdvojiti. Velike razlike u mehaničkim svojstvima neumreženog i umreženom prirodnog kaučuka mogu se lako potvrditi eksperimentalno, npr. mjerenjem ovisnosti deformacije o naprezanju [8], kao što je prikazano na slici 2.1.2.

Nevulkanizirani kaučuk istegne se i do šest puta u odnosu na početne dimenzije djelovanjem relativno malog opterećenja, a nakon prestanka djelovanja sile ne vraća se u prvobitno stanje, što znači da deformacija nije elastična. Kod vulkaniziranog kaučuka za isti iznos istezanja treba primijeniti i do pet puta veću silu, a prestankom djelovanja sile materijal poprima prvobitne dimenzije. Potrebno je napomenuti da osim sumpornog umrežavanja postoje i drugi načini kemijskog umrežavanja kaučuka, kao što je npr. umrežavanje primjenom organskih peroksida.

2.2. Fizikalno umrežavanje

Osim uz prisustvo kemijski reaktivnih tvari, poput ispred opisanog sumpora ili organskih peroksida, umrežavanje se može provesti i primjenom zračenja [5] visoke energije: γ-zračenjem, brzim elektronima te sporim elektronima. Kad je polimer izložen visokoenergijskom zračenju [7], prvenstveno dolazi do cijepanja

The process of vulcanization diminishes the mobility of polymeric chains and prevents flowing under higher temperatures. Material looses, its property of brittleness when exposed to lower temperatures, because molecules are very tightly tied by strong covalent links and therefore it s very difficult to separate them. Substantial differences in mechanical properties between untied and tied natural rubber can be easily proved experimentally[8], i.e.. by measuring the correlation of deformation and constraint, as shown in figure 2.1.2.

Unvulcanized rubber can stretch up to six times his initial dimensions under little exertion, and when the tension is discontinued it does not contract to its original length, which signalizes that deformation is not elastic. With the vulcanized rubber, on the other hand, five times greater tension needs to be applied in order to achieve the same stretching and after discontinuation of the tension impact the material recovers its original state. It should be noted that, besides sulfide cross-linking, there are other ways of chemical cross-linking of the rubber, for example: cross-linking by applying organic peroxides.

2.2 Physical Cross-linking

Apart from the presence of chemically reactive substances, as above described sulphur or osnovnih lanaca i stvaranja slobodnih radikala, zatim cijepanja dvostrukih veza i stvaranja poprečnih veza između lanaca te međusobnog povezivanja krajeva fragmenata lanaca nastalih cijepanjem. Ovi učinci zračenja nužno mijenjaju raspodjelu molekulskih masa.

Statističku teoriju poprečnog povezivanja prvi je predložio Flory još 1941. godine [6]. On je teorijski pokazao da kod polimernih sustava s približno jednakim duljinama lanaca nastajanje premoštenja (poprečnih veza) dovodi do promjene raspodjele molekulskih masa. Značajan doprinos u rješavanju problema vezanih uz promjene molekulskih masa i raspodjele molekulskih masa izazvanih cijepanjem i umrežavanjem lanaca pod utjecajem zračenja visoke energije dao je A. Charlesby 1953. godine. On je računski riješio problem poprečnog povezivanja lančastih molekula polimera, a svoju teoriju je temeljio na računu vjerojatnosti [6].

Većina današnjih teorijskih pristupa koji pokušavaju objasniti eksperimentalno ponašanje umreženih polimera temelje se na sljedećim pretpostavkama:

a) poprečno povezivanje događa se slučajno,

b) svakoj strukturnoj jedinici pripisuje se jednaka vjerojatnost povezivanja, bez obzira na njezin položaj unutar lančaste molekule,

c) broj poprečnih veza je dovoljno mali u usporedbi s ukupnim brojem strukturnih jedinica,

d) intramolekulske veze unutar molekula konačnih veličina su zanemarive.

Najbitniji učinak poprečnog povezivanja je promjena raspodjele molekulskih masa. Ako stupanj polimerizacije molekule označimo s $\overline{DP}$, ukupni broj veza s X, ukupni broj strukturnih jedinica s N, tada je gustoća umreženja γ jednaka: $\gamma = X/N$. Budući da je N ekstremno velik broj, pretpostavlja se da se g mijenja kontinuirano.

Molekulska masa $w(\gamma,p)$ u skladu s gustoćom umreženja γ zadovoljava sljedeću jednadžbu [7]:

$$\frac{1}{p}\frac{\partial w(p,\gamma)}{\partial \gamma} = -2w(p,\gamma)\int_0^\infty w(l,\gamma)\,dl +$$

$$+\int_0^p w(l,\gamma)\,w(p-l,\gamma)\,dl \;. \qquad (2.2.1)$$

organic peroxides, cross-linking can be carried out by applying radiation of high energy[5]: γ-radiation, fast electrons and slow electrons.

When a polymer is exposed to high energy radiation [7], splitting of the basic chains and creating free radicals is what occurs first. What follows is the splitting of double bonds and creating transversal bonds between chains and linking of the ends of chain fragments produced in the process of splitting. These impacts necessarily change the division of the molecular masses.

The statistic theory of cross-linking was proposed by Flory in 1941 [6]. He demonstrated the theory of polymeric systems with an approximately similar chain length where the generating of bypasses results in a diverse distribution of the molecular masses. A substantial contribution in solving problems related to the changes in molecular masses caused by splitting and chain cross-linking under the exposure of high energy was given by A. Charlesby in 1953. He calculated the solution to the problem of cross-linking of the chain polymer molecules, and he formulated his theory according to the law of averages.

Most of the contemporary theoretical approaches which aim at explaining the experimental behaviour of the linked polymer are based on the following assumptions:

a) cross-linking occurs accidentally,

b) each structural unit is attributed with equal probability of linking, regardless of its position – location within the chain molecule,

b) the number of transversal bonds is low enough, in comparison to the total number of structure units,

d) intramolecular bonds within molecules of final size are irrelevant.

The most important effect of cross-linking is the change in the distribution of molecular masses. If the degree of polymerisation is marked $\overline{DP}$, the total number of bonds is X, the total number of the structural unit s is N, the density of cross-linking γ equals: $\gamma = X/N$. Since N is an extremely high number, it is assumed that γ changes continuously.

The molecular mass $w\ (\gamma,p)$, in accordance with the density of the cross-linking γ, satisfies the following equation:

Lijeva strana jednadžbe izražava omjer porasta broja molekula koje imaju p konstitucijskih jedinica, prvi izraz na desnoj strani daje učestalost s kojom se molekule sastavljene od p konstitucijskih jedinica mijenjaju u veće poprečno povezane s drugim molekulama. Jednadžba se može riješiti sa zadanom početnom vrijednošću $w(p,0)$. Ako pretpostavimo da je:

$$f_n(\gamma)=\int_0^\infty p^{n-1}w(p,\gamma)dp\,,\ n = 0, 1, 2, \ldots \tag{2.2.2}$$

tada jednadžba (2.2.2) poprima oblik:

$$\frac{df_n}{d\gamma}=-2f_1f_{n+1}+\sum_{k=0}^{n}\binom{n}{k}f_{k+1}f_{n-k+1}\ . \tag{2.2.3}$$

Za $n = 1$, dobiva se $\frac{df_1}{d\gamma}=0$, što pokazuje da je f_1 konstanta, što je jednako 1 u skladu s definicijom.

Za $n = 0$ i $n = 2$, dobiva se:

$$\frac{df_0}{d\gamma}=-f_1^2=-1,\frac{df_2}{d\gamma}=2f_2^2\Rightarrow$$

$$f_0(\gamma)=f_0(0)-\gamma\ \text{ i }\ f_2(\gamma)=\frac{f_2(0)}{1-2\gamma f_2(0)}. \tag{2.2.3 a}$$

Sukcesivnim rješavanjem jednadžbe (2.2.1) dobiva se $f_n(x)$. Prosječni stupanj polimerizacije može se prikazati:

$$P_j(\gamma)=\frac{f_j(\gamma)}{f_{j-1}(\gamma)}\ . \tag{2.2.4}$$

Ostale metode rješavanja ovoga problema temelje se uglavnom na Laplaceovim transformacijama.

Zaključak: Primjena polimernih materijala u brodogradnji i pomorstvu predstavlja u razvijenom svijetu novije područje fundamentalnih i aplikativnih istraživanja. Veće brzine brodova, zahtjevi za što lakšom konstrukcijom zbog većeg prijenosa roba, korozivna otpornost i sl., uvjetovali su sve veću primjenu polimernih materijala. Proučavanje strukture materijala na mikro i nano skali i dovođenje u vezu s makroskopskim svojstvima materijala od posebnog je značaja za primjenu. Zbog toga se danas provo-

$$\frac{1}{p}\frac{\partial w(p,\gamma)}{\partial\gamma}=-2w(p,\gamma)\int_0^\infty w(l,\gamma)dl+$$

$$+\int_0^p w(l,\gamma)w(p-l,\gamma)dl\ . \tag{2.2.1}$$

The left side of the equation stands for the ratio of increase in number of molecules with p constitution units, the first character on the right side shows the frequency of the transformation of molecules consisted of p constitution units changing in bigger units, cross- linked with other molecules. The equation can be solved by determining the initial value $w\ (p,0)$. If we assume that:

$$f_n(\gamma)=\int_0^\infty p^{n-1}w(p,\gamma)dp\,,\ n = 0, 1, 2, \ldots \tag{2.2.2}$$

the equation (2.2.2) then takes the following form:

$$\frac{df_n}{d\gamma}=-2f_1f_{n+1}+\sum_{k=0}^{n}\binom{n}{k}f_{k+1}f_{n-k+1}\ . \tag{2.2.3}$$

For $n = 1$, we get $\frac{df_1}{d\gamma}=0$, which shows that f_1 is a constant which equals 1, in accordance with the definition.

For $n = 0$ and $n = 2$, we get:

$$\frac{df_0}{d\gamma}=-f_1^2=-1,\frac{df_2}{d\gamma}=2f_2^2\Rightarrow$$

$$f_0(\gamma)=f_0(0)-\gamma\ \text{ i }\ f_2(\gamma)=\frac{f_2(0)}{1-2\gamma f_2(0)}. \tag{2.2.3 a}$$

By solving the equation successively (2.2.1) we get $f_n(x)$. The average degree of polymerisation can be presented as:

$$P_j(\gamma)=\frac{f_j(\gamma)}{f_{j-1}(\gamma)}\ . \tag{2.2.4}$$

The other methods of solving this problem are mostly based upon Laplace transformations.

Conclusion: Applying polymeric materials in shipbuilding and maritime affairs represents a new field of fundamental and applicable researches in developed countries. A greater ship speed, demands for simple constructions aimdi velik broj istraživanja različitim eksperimentalnim tehnikama, kako bi se što bolje mogla razumjeti povezanost strukture i segmentne dinamike s mehaničkim svojstvima.

ing at a greater transport of goods, corrosive resistance, etc. have caused the growing use of polymeric materials. Studying the material structure on micro and nano scales and associating it with macroscopic properties is extremely important in usage.

That is why a great number of researches is carried out, applying various experimenting techniques in order to fully understand the connection between the structure and segment dynamics with the mechanical characteristics.

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