



**UNIVERSITI PUTRA MALAYSIA**

**PREPARATION AND CHARACTERIZATION OF  
NATURAL RUBBER/BENTONITE  
NANOCOMPOSITES**

**MOHAMMAD HUSSEIN AL-KHAWALDEH  
FS 2004 13**



**PREPARATION AND CHARACTERIZATION OF  
NATURAL RUBBER/BENTONITE  
NANOCOMPOSITES**

**MOHAMMAD HUSSEIN AL-KHAWALDEH**

**MASTER OF SCIENCE  
UNIVERSITI PUTRA MALAYSIA**

**2004**



**PREPARATION AND CHARACTERIZATION OF  
NATURAL RUBBER/BENTONITE  
NANOCOMPOSITES**

**By**

**MOHAMMAD HUSSEIN AL-KHAWALDEH**

**Thesis Submitted to the School of Graduate Studies,  
Universiti Putra Malaysia, in Fulfilment of the Requirements  
for the Degree of Master of Science  
November 2004**



## DEDICATION

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ ﴿٣٢﴾

*Surat Al-Baqara.*

***Especially dedicated to my beloved parents....  
my wife and kids.....***

Abstract of thesis presented to the Senate of Universiti Putra  
Malaysia in fulfilment of the requirement for the degree of Master of  
Science

**PREPARATION AND CHARACTERIZATION OF  
NATURAL RUBBER/BENTONITE  
NANOCOMPOSITES**

By

**MOHAMMAD HUSSEIN AL-KHAWALDEH**

**November 2004**

**Chairman: Professor Wan Md Zin Wan Yunus, Ph.D.**

**Faculty : Science**

Natural rubber/bentonite nanocomposites were prepared from deproteinised natural rubber (dp-NR) and modified bentonite clay by both solvent casting and blending methods. To prepare the nanocomposites by the solvent method, the rubber was first dissolved in toluene and then mixed by stirring with the modified clay at room temperature. In the blending method, the rubber was first softened for 1 minute in an internal Haake mixer and then blended with the modified clay at 60°C.

Modification of the clay by replacing the clay's sodium ions with alkylammonium (cetyltrimethylammonium (CTA), dodecylammonium (DDA) and octadecylammonium (ODA)) groups was carried out through an ion-exchanger process. Elemental



analysis indicated that 0.59 mmol of CTA, 0.75 mmol of DDA and 0.98 mmol of ODA were sorbed by 1 g of the clay. FTIR spectra of the modified clays showed a peak at about  $3000\text{ cm}^{-1}$ , which indicated the presence of the amine group stretching. The increase in the degradation temperature of DDA, CTA and ODA in the organobentonite implied that there was a strong intermolecular interaction between the alkylammonium ions and the bentonite.

The nanocomposites produced were characterized by XRD and TEM. It was found the nanometer-scale silicate layers of organoclay were completely exfoliated in dp-NR if the organoclay concentration in the composites was less than 1%. However, increase the clay contents to 3% or higher, produced intercalated nanocomposites. The mechanical properties obtained were found to be affected strongly by the organoclay content and the type of alkylammonium groups. Tensile properties of the nanocomposites prepared using the ODA treated bentonite is better than that of the nanocomposites pretreated with the other alkylammonium groups. In addition, mechanical properties of the nanocomposites also effected by the method of their preparation. The solvent casting technique improved several mechanical properties of the nanocomposites compared with those of the nanocomposites produced by the blending method.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Master Sains

**SINTESIS DAN PENCIRIAN NANOKOMPOSIT  
GETAH ASLI-BENTONIT**

Oleh

**MOHAMMAD HUSSEIN AL-KHAWALDEH**

**November 2004**

**Pengerusi: Profesor Wan Md Zin Wan Yunus, Ph.D.**

**Fakulti: Sains**

Nanokomposit getah asli-bentonit telah disediakan daripada getah asli nyahprotein dan tanah liat bentonit terubahsuai menggunakan kaedah pengacuan pelarut dan kaedah adunan leburan. Bagi kaedah pelarut, getah asli dilarutkan didalam pelarut toluena dan kemudian ianya dikacau bersama dengan tanah liat terubahsuai pada suhu bilik. Untuk kaedah pengadunan leburan, getah asli terlebih dahulu dilembutkan selama satu minit didalam pencampur dalaman Haake sebelum dicampurkan dengan tanah liat terubahsuai pada suhu 60°C.

Pengubahsuaian tanah liat dilakukan melalui penukaran ion natrium dari tanah liat dengan kumpulan alkil ammonium



(setiltrimetilamonium (CTA), dodesilamonium (DDA) dan oktadesilamonium (ODA)). Analisis unsur menunjukkan 0.59 mmol CTA, 0.75 mmol DDA dan 0.98 mmol ODA telah diserap oleh satu gram tanah liat. Spektrum FTIR bagi tanah liat terubahsuai menunjukkan kewujudan puncak pada  $3000\text{ cm}^{-1}$ , menunjukkan kewujudan regangan kumpulan amonium. Peningkatan suhu digradasi bagi DDA, CTA dan ODA bagi bentonit-organo mencadangkan terdapatnya interaksi molekul yang kuat di antara ion alkil ammonium dengan bentonit.

nanokomposit yang terhasil dicirikan dengan menggunakan XRD. Lapisan silikat pada skala nanometer bagi tanah liat-organo terekpoliiasi sepenuhnya jika kandungan tanah liat organo didalam komposit kurang daripada satu peratus. Walau bagaimanapun, meningkatkan kandungan tanah liat kepada 3 peratus menghasilkan nanonomposit yang interkalasi. Sifat mekanikal komposit dipengaruhi oleh kandungan tanah liat organo dan jenis kumpulan alkil ammonium. Nanokomposit yang disediakan menggunakan tanah liat bentonit terubahsuai ODA menunjukkan kelebihan dari segi kekuatan regangan berbanding nanokomposit yang menggunakan kumpulan alkilamonium yang lain. Sifat mekanikal bagi nanokomposit juga bergantung kepada kaedah

penyediaan dimana teknik pelarut memberikan peningkatan beberapa ciri bagi nanokomposit berbanding dengan nanokomposit yang disediakan menggunakan kaedah pencampuran adunan leburan.

## **ACKNOWLEDGMENTS**

*In The Name of ALLAH, The Most Merciful and Most Beneficent*

I am very deeply grateful to ALLAH "S.W" for giving me the opportunity to study with strength and patience to complete this study.

I would like to express my gratitude to my advisor, Prof. Dr. Wan Md Zin Wan Yunus for his guidance and encouragement throughout this work. His generosity, patience and sense of humour have always been admired. Many thanks go to Associate Prof. Dr. Mansor Ahmad and Associate Prof. Dr. Mohamad Zaki Abd. Rhman for serving as my committee members. I would also like to thank my friends in the polymer research group for their help and advice not only in research problems but also in life especially Mr. Faraj Ahmad Abu-Ilaiwi. Words cannot express my profound gratitude and special thanks to my wife and kids in Jordan for their love and sacrifices through out the study period. I would like to express my most sincere and warmest gratitude to my father, mother, brothers, sisters and relatives for their prayers, loving, generous and moral support during my study. In addition, my study life here will never be warm, enjoyable and memorable



without my friends in Malaysia: Atef Al-khawaldeh, Mohammad Manna, Isam Qudsieh, Suliman Almsaeid, Ala Abd Arraouf, and the other Jordanian students here. Last but not least, I should not miss to mention several friends at my town in my country especially Mr. Abu Methqal, Dr. Tisser Al-khawaldeh, Mr. Saleh Al-khawaldeh and Mr. Ahmad Saud Al-khawaldeh.



I certify that an examination committee met on **8 November 2004** to conduct the final examination of **Mohammad Hussein Al-khawaldeh** on his **Master** thesis entitled “PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER/BENTONITE NANOCOMPOSITES” in accordance with Universiti Putra Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

**Mohd. Zobir Hussein, Ph.D.**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Anuar Kassim, Ph.D.**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Sidik Bin Silong, Ph.D.**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Ibrahim Abdullah, Ph.D.**

Professor  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
(Independent Examiner)

---

**GULAM RUSUL RAHMAT ALI, Ph.D.**

Professor/Deputy Dean  
School of Graduated Studies  
Universiti Putra Malaysia

Date:



This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Master**. The members of the Supervisory Committee are as follows:

**Wan Md Zin WanYunus, Ph.D.**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Mansor Hj. Ahmad, Ph.D.**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Mohamad Zaki Abdrhman, Ph.D.**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

---

**AINI IDERIS, Ph.D.**

Professor/Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:



## **DECLARATION**

I hereby declare that the thesis is based on my original work except for quotations and citation, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

---

**MOHAMMAD HUSSEIN AL-KHAWALDEH**

DATE:



## TABLE OF CONTENTS

	<b>Page</b>
<b>DEDICATION</b>	3
<b>ABSTRACT</b>	4
<b>ABSTRAK</b>	6
<b>ACKNOWLEDGEMENTS</b>	9
<b>APPROVAL</b>	11
<b>DECLARATION</b>	13
<b>LIST OF TABLES</b>	16
<b>LIST OF FIGURES</b>	17
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	21
Nanocomposites	21
Natural Rubber	23
Deproteinised Natural Rubber	25
Layered Silicates	27
Scope of Research	30
Objectives of the Study	31
<b>II LITERATURE REVIEW</b>	32
Nanocomposites	32
Polymer used in nanocomposites	33
Preparation of Nanocomposites	34
In situ intercalative polymerization method	34
Solvent casting method	45
Melt intercalation method	57
Natural Rubber	73
<b>III MATERIALS AND METHODOLOGYS</b>	75
Materials	75
Modification of bentonite	75
Conditioning of unmodified clay	76
Preparation of NR/Bentonite Nanocomposites	77
Solvent Method	77
Blending Method	78



Vulcanization of DPNR/organobentonite nanocomposites	78
Fourier Transform Infrared (FTIR) Spectroscopy	79
X-Ray Diffraction (XRD) Analysis	79
Nitrogen and Carbon content determination	80
Thermogravimetric Analysis (TGA)	80
Tensile properties determination	80
<b>IV RESULTS AND DISCUSSION</b>	<b>81</b>
Bentonite Modification	81
Alkyl Ammonium Exchange Capacity	82
FTIR Spectroscopy	84
CTA modified bentonite	84
DDA modified bentonite	86
ODA modified bentonite	87
XRD ANALYSIS	89
Thermogravimetric Analysis (TGA)	92
Preparation of natural rubber bentonite nanocomposites by blending method	97
Effects of the mixing period	97
Effects of the temperature	98
Nanocomposites Analysis	100
Effect of the amount of modified bentonite	100
Effect of the alkylammonium groups	104
Preparation of natural rubber bentonite nanocomposites by solvent casting method	108
Effect of the stirring period	108
Effects of the temperature	110
Effect of the amount of modified Bentonite	111
Effect of the alkylammonium groups	115
Mechanical properties of vulcanized natural rubber/organobentonite nanocomposites	119
Transmission Electron microscopy observations	125
<b>V CONCLUSION AND SUGGESTIONS FURTHER STUDIES</b>	<b>127</b>
Conclusion	127
Further Studies	129
<b>BIBLIOGRAPHY</b>	<b>130</b>
<b>APPENDIXES</b>	<b>145</b>
<b>BIODATA OF THE AUTHOR</b>	<b>152</b>



## LIST OF TABLES

<b>Table</b>		<b>Page</b>
1	Formulation used in the preparation of vulcanized DPNR/organobentonite nanocomposites	79
2	C, N and alkylammonium groups contents of the CTA, DDA and ODA modified bentonite	83
3	Band assignment of FTIR spectra of bentonite and CTA treated bentonite	85
4	Band assignment of FTIR spectra of bentonite and DDA treated bentonite	87
5	Band assignment of FTIR spectra of bentonite and ODA treated bentonite	88
6	Diffraction angle and basal spacing of bentonite and modified bentonite with different organic cations	91
7	Contents of the CTA, DDA and ODA/ 1g of modified bentonite based on TGA results	94
8	Tensile strength of nanocomposites containing 3% (w/w) of the CTA modified bentonite prepared under various mixing period (minutes) at 100 °C by blending method	146
9	Tensile strength of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared under several of stirring period at 70 °C by solvent method	146
10	Tensile strength of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared with several of temperatures, stirring 4 hours by solvent method	146



## LIST OF FIGURES

Figure		Page
1	Possible structures for clay polymer composite	22
2	Idealised structure for montmorillonite, proposed by Hoffmann, Endell and Wilm	28
3	Flowchart presenting the different steps of the “in-situ polymerisation” approach	35
4	The “in-situ polymerisation”- Polar monomer molecules diffuse between the layers and then polymerize to form the polymer	36
5	Flowchart presenting the different steps of the “solution” approach	45
6	The intercalation of the polymer by the “solution” approach. The black dots represent the solvent molecules	46
7	Flowchart presenting the different steps of the “melt intercalation” approach	59
8	The “melt intercalation” process	60
9	FTIR spectra of original bentonite (A) and CTA modified bentonite (B)	85
10	FTIR spectra of bentonite (A) and DDA modified bentonite (B)	86
11	FTIR spectra of bentonite (A) and ODA modified bentonite (B)	88
12	XRD patterns of CTA modified bentonite (A) and bentonite (B)	90
13	XRD patterns of DDA modified bentonite (A) and bentonite (B)	90
14	XRD patterns of ODA modified bentonite (A) and bentonite (B)	91
15	Thermogravimetric curves (relative weight loss as a function of temperature) for the original bentonite	94
16	Derivative thermograms of DDA and DDA modified bentonites	95
17	Derivative thermograms of CTAB and CTA modified bentonites	95



18	Derivative Thermograms of ODA and ODA modified bentonites	96
19	XRD patterns of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared under three mixing periods: (A) 10 min, (B) 20 min, and (C) 30 min. at 100°C by blending method	97
20	Tensile strength of nanocomposites containing 3% (w/w) of the CTA modified bentonite prepared by blending method under various mixing period (minutes) at 100°C	98
21	XRD patterns of nanocomposites containing 3% (w/w) of the CTA modified bentonite prepared under several of temperatures 60°C (21A), 80°C (21B) and 100°C (21C) by blending method	99
22	Tensile strength of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared by blending method at different mixing temperatures. Mixing period used is 10 minutes	100
23	XRD patterns of the nanocomposites containing various amount of (w/w) of CTA modified bentonite prepared by blending at 60°C	101
24	Tensile strength and tensile modulus (100%, 300%) of the nanocomposites containing various amount of CTA modified bentonite-rubber nanocomposites prepared by blending at 60°C	103
25	Elongation at break for the nanocomposites containing various amount of CTA modified bentonite-rubber nanocomposites prepared by blending at 60°C	103
26	XRD patterns of the nanocomposites containing 3% (w/w) of different alkylammonium groups modified bentonite which were prepared by blending method at 60°C	104
27	Tensile strength of NR and nanocomposites containing 3% (w/w) of different alkylammonium groups modified bentonite which were prepared by blending method at 60°C	106



28	Tensile modulus at various strain (100%, 300% of NR and nanocomposites containing 3% (w/w) of different alkylammonium groups modified bentonite which were prepared by blending method at 60°C	107
29	Elongation at break of NR and nanocomposites containing 3% (w/w) of different alkylammonium groups modified bentonite which were prepared by blending method at 60°C	107
30	XRD patterns of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared under four stirring period: (A) 2h, (B) 4h, (C) 8 and (D) 12h, and at 70°C by solvent method	109
31	Tensile strength of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared under several of stirring period at 70 °C by solvent method	109
32	XRD patterns of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared by solvent method under several of temperatures: (A) RT, (B) 50°C, (C) 70°C and (D) 90°C, stirring 4 hours	110
33	Tensile strength of nanocomposites containing 3% (w/w) of CTA modified bentonite prepared at four different temperatures. Stirring period was 4 hours	111
34	XRD patterns of the nanocomposites containing various amount of (w/w) of CTA modified bentonite prepared at RT by solvent method	112
35	Tensile strength and tensile modulus at various strain (100%, 300%) of the nanocomposites containing various amount of CTA modified bentonite-rubber nanocomposites prepared by solvent method at RT	114
36	Elongation at break for the nanocomposites containing various amount of CTA modified bentonite-rubber nanocomposites prepared by solvent method at RT	114
37	XRD pattern of the nanocomposites prepared using 3% (w/w) of three different alkylammonium groups (DDA, CTA and ODA) modified bentonite nanocomposites prepared by solvent casting at RT	115

38	Tensile modulus at various strains (100% and 300%) of NR and of the nanocomposites prepared using 3% (w/w) of three different alkylammonium groups (DDA, CTA and ODA) modified bentonite nanocomposites prepared by solvent casting at RT	117
39	Tensile strength of NR and the nanocomposites prepared using 3% (w/w) of three different alkylammonium groups (DDA, CTA and ODA) modified bentonite nanocomposites prepared by solvent casting at RT	117
40	Elongation at break of NR and the nanocomposites prepared using 3% (w/w) of three different alkylammonium groups (DDA, CTA and ODA) modified bentonite nanocomposites prepared by solvent casting at RT	118
41	Tensile strength and moduli at 100% and 300% strain of the nanocomposites containing various amounts of CTA modified bentonite prepared by blending method.	120
42	Tensile strength and moduli at 100% and 300% strain of the nanocomposites containing various amounts of CTA modified bentonite prepared by solvent method.	120
43	Tensile strength and tensile moduli at 100% and 300% strains of NR and the nanocomposites containing 3% (w/w) of three different alkylammonium group modified bentonites prepared by blending method.	123
44	Tensile strength and tensile moduli at 100% and 300% strains of NR and the nanocomposites containing 3% (w/w) of three different alkylammonium group modified bentonites prepared by solvent casting.	123
45	Elongation at break of the nanocomposites containing various amounts of CTA modified bentonites prepared by both solvent and blending methods.	124
46	TEM images of NR/organobentonite nanocomposites using different % (w/w) of the CTA, DDA and ODA modified bentonite.	146

# CHAPTER I

## INTRODUCTION

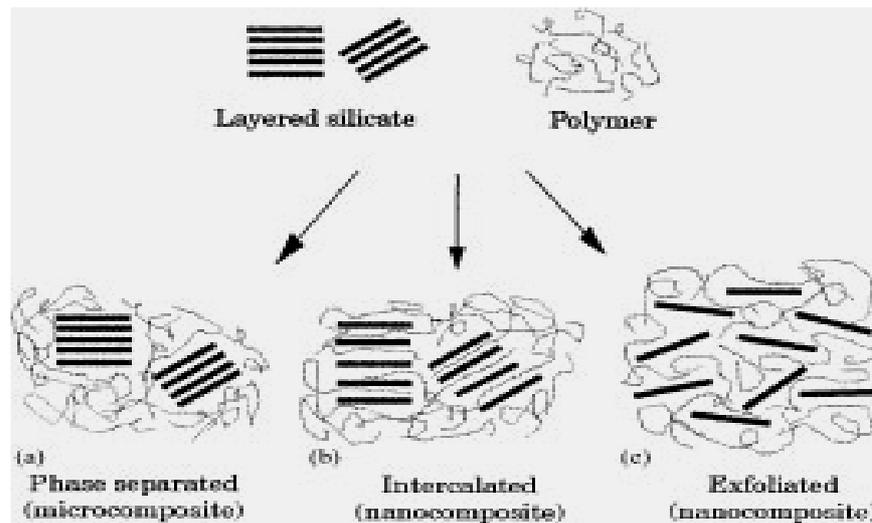
### **Nanocomposites**

Polymer layered nanocomposites have been the focus of attention of many researchers (Usuki et al., 1993a). They are a new class of composite materials, in which clay as a layered silicate is dispersed in nanoscale size in polymer matrix (Takeichi et al., 2001). Nanocomposites exhibit very different physical and chemical properties from their bulk counterparts because of the nanometer scale dispersion of reinforcement agents and the high surface-to-volume ratio (Arroyo et al., 2003).

The dispersion of clay particles in a monomer or polymer matrix can result in the formation of three types of composite materials (Lan et al., 1995). The first type is conventional composites that contain clay tactoids with layers aggregated in an unintercalated face to face form (Figure 1(a)). In this case the clay tactoids are dispersed simply as a segregated phase resulting in poor mechanical properties of the composite material. The second type is intercalated polymer clay nanocomposites, which are formed by the



insertion of one or more molecular layers of polymer into the clay host galleries (Figure 1(b)). The last type is exfoliated polymer clay nanocomposites, characterized by low clay content of the composites (Figure 1(c)). Exfoliated polymer clay nanocomposites are especially desirable for improved properties because of the homogeneous dispersion of clay and huge inter facial area between polymer and clay (Fu and Qutubuddin, 2001).



**Figure 1:** Possible structures for clay polymer composites.

Small amounts well-dispersed natural clay can lead to environmentally friendly and inexpensive plastic composites with improved specialized properties. Due to the nanoscale dispersion, when compared with the conventional fiber or filler-filled composites, nanocomposites exhibit outstanding improvement on

properties. These include the increasing of modulus, strength, thermal stability, solvent resistance, decreasing of gas permeability and flammability (Usuki et al., 1993b; Agag and Takeichi, 2000) and increased biodegradability of biodegradable polymers (Sinha et al., 2002a). Adding the clay into a polymer is not a simple process as they are not compatible. However, if the clay is treated with an organic surfactant, the hydrophobicity of the clay can be increased, their compatibility can be improved.

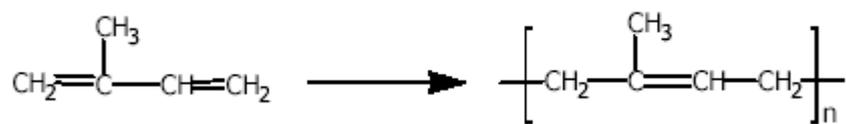
### **Natural rubber**

Rubber is collected in the form of latex that exudes from the bark of the tree when it is cut. The average rubber content of latex may range between 30-45%. This fresh 'field' latex is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate the latex, so that the end product is stable and contains 60 % or more of rubber. Latex concentrates are differentiated by the method of concentration, and type of preservative used. Concentration is achieved by centrifugation (most common), by creaming, or by evaporation. Currently, about 50% of all latex concentrate is consumed by the dipped goods industry (medical and household



gloves). Other uses of latex are in carpet backing, thread and adhesives (Tantatherdtam, 2003).

Natural rubber is a high molecular weight polymer of isoprene,  $C_5H_8$ . The repeating unit is  $-CH_2-C(CH_3)=CH-CH_2-$ . Hevea rubber which is extracted from the tree *Hevea Brasiliensis* is the major naturally occurring form of cis-1,4-polyisoprene. This rubber contains more than 98% of its double bonds in the cis configuration, which is essential for elasticity in polyisoprene. Over 90% of all cis -1,4-polyisoprene used industrially is natural Hevea rubber (O dian, 1991). 1,4 polymerization of the conjugated diene system of isoprene leads to a polymer structure with a repeating alkene double bond in the polymer chain (Scheme I).



**Scheme I.** 1,4-Isoprene and 1,4-Polyisoprene.

The double bond in each repeating unit in the polymer chain is a site of steric isomerism since it can have either a cis or a trans configuration. The polymer chain segments on each carbon atom of the double are located on the same side of the double bond in the