

FINAL REPORT

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Development Of Novel Products From Guayule Rubber

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Executive Summary

Guayule is a shrub found in the North Mexican deserts and which has been successfully cultivated in semi-arid lands. Its main distinction is in the ability to extract natural rubber (polyisoprene) from its stems, roots, and branches. Since most polyisoprene used today is manufactured from chemicals originating from the petrochemical industry, the advantages of developing a natural, renewable, source for polyisoprene (PIP) is obvious. Presently, the negative economics of rubber extraction from the Guayule plant are preventing its commercialization. The present project represents an attempt to increase the appeal of the Guayule rubber by chemical modification of its polyisoprene molecule. New materials based on polyisoprene-co-polydimethylsiloxane polymers and assorted silicone containing rubbery molecules have been synthesized. The incorporation of silicone and siloxane entities enhance several properties such as surface activity, oxygen permeability and temperature endurance of the PIP.

PIP is a high molecular weight polymer chain. The approach used in this project is based on selective chemical cleavage of these chains and incorporation of silicone based polymers and chemicals into the points of scission. Two different chemical routes have been successfully developed for the silicone incorporation process. Over a dozen of new silicone and siloxane containing PIP materials and PIP-polydimethylsiloxane copolymers have been obtained. Tests have shown these new materials possess properties of interest warranting further development.

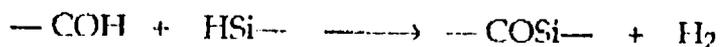
The present project is probably the first major externally funded research project undertaken by the School of Chemistry of the collaborating university. The funds made available enabled the collaborating scientists to furnish and equip a large sized laboratory which will serve them in future years. It also enabled several graduate and undergraduate students to be exposed to research activity. Finally, the project provided the collaborating scientists with experience concerning the planning and execution of a long term research program. This experience will prove invaluable in their future scientific development.

Research Objectives

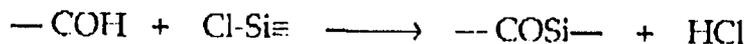
Guayule is a desert shrub which grows wild in the Mexican desert, has been successfully cultivated in several semi-arid regions around the world. The Guayule plant has been identified as a potential source of a polymer (polyisoprene) which is similar to a large extent to the natural rubber presently obtained from trees mostly in southeast Asia. Presently, the negative economics of rubber extraction from the Guayule plant are standing in the way of its commercialization. The present project represents an attempt to increase the appeal of the Guayule rubber by chemical modification of its polyisoprene to produce new materials based on polyisoprene co polydimethylsiloxane polymers and assorted silicone containing rubbery molecules. The incorporation of silicone and siloxane entities will enhance several properties such as surface activity, oxygen permeability and temperature endurance. The goal of this project was to identify chemical routes which may be used to produce these polyisoprene-silicone materials. These objectives have been successfully accomplished as is described in detail in the following sections.

Methods and Results

The procedure used to obtain the desired products consisted of cleaving the rubber molecule and converting the points of cleavage into reactive functional anchor points capable of reacting with the desired materials. Thus the first step in the project was the development of a reliable, controlled procedure for the synthesis of functional rubber molecules. Once the procedure has been defined it was adopted by both groups as the starting point for the production of subsequent materials. One group concentrated on the use of the reaction between silane and hydroxyl groups :



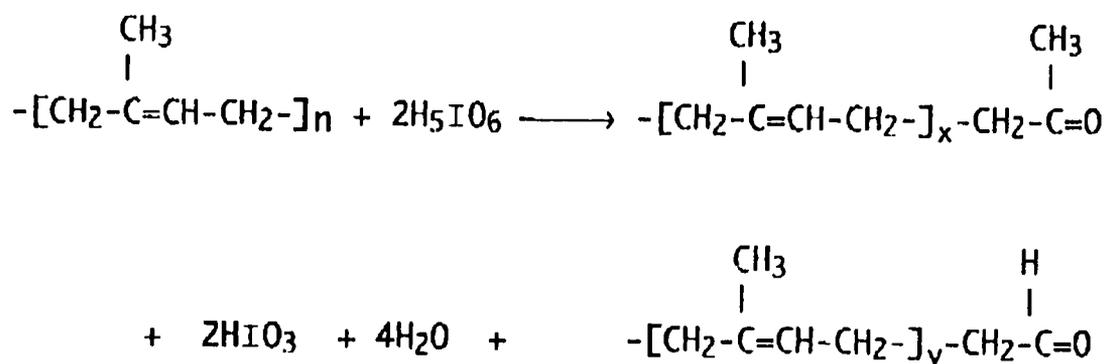
These route was used to produce Poly isoprene-block-dimethylsiloxane copolymers and crosslinked rubbers. The second group explored the reaction:



to obtain silicone containing products.

PIP Cleavage

Reactive PIP carbonyl telechelics are created by the selective cleavage reaction [1]:



The cleavage of the synthetic PIP was carried out using periodic acid leading to α,ω carbonyl PIP telechelics [1]. Typically, 10g of Guayule or regular PIP are dissolved in toluene under dry nitrogen. A solution of H_5IO_6 (5g) in ethanol/toluene (2:1) is added dropwise. Nitrogen atmosphere is necessary during the reaction. The reaction is quenched at the desired point by the addition of water to the reaction mixture. The mixture is filtered in order to remove the resulting HIO_3 . The filtrate is diluted with petrol ether, washed several times with treated water, and then with 0.25% wt. aqueous Na_2SO_3 until neutral pH is obtained, and washed again with treated water until the interphase has been eliminated. The organic phase is subsequently dried with MgSO_4 . The mixture is filtered, and the solvent evaporated. The yield of the cleavage reaction was 80-90%. The product is characterized by quantitative FTIR analysis (5ZDX Nicolet) for the end group concentration which yields the Mn of the telechelics. Calibration was performed with equimolar solutions of aldehyde and ketone standards (6-methyl-5-heptane-2-one, as the ketone standard and 2,2-dimethyl-4-pentenal as the aldehyde standard) in carbon tetrachloride.

The increase in the carbonyl group concentration during the reaction time is followed by means of FTIR spectroscopy (Fig 1). By altering the duration of the reaction we can prepare the desired polymer molecular weight. The M_n (number average molecular weight) of the carbonyl telechelics is determined using appropriate calibration curves (Fig 2). The decrease in the polymer molecular weight vs. reaction time is illustrated in Fig 3.

Kinetics of the cleavage reaction

The rate of the ketone and aldehyde group formation can be described using the following kinetic equation:

$$d[\text{Ket}] / dt = k[\text{C}=\text{C}]^a [\text{H}_5\text{IO}_6]^b$$

where [Ket] is the concentration of ketone groups [mol/lit], [C=C] is the concentration of isoprene monomers (same as concentration of double bonds) [mol/lit], [H₅IO₆] is the concentration of periodic acid [mol/lit], k is the reaction rate constant, a,b are the partial reaction orders, and t is the reaction time [min].

This kinetic model assumes that the reactivity of all the carbon-carbon double bonds is equal irrespective of the length of the polymer chain on which the bond resides. The concentration of the reactants is given by:

$$[\text{C}=\text{C}] = [\text{C}=\text{C}]_0 - [\text{Ket}]$$

$$[\text{H}_5\text{IO}_6] = [\text{H}_5\text{IO}_6]_0 - 2[\text{Ket}]$$

The subscript 0 indicated concentration at t=0 the onset of the reaction. Since both reactants are present in large excess in our experiments, equation (1) becomes:

$$d[\text{Ket}] / dt = k[\text{C}=\text{C}]_0^a [\text{H}_5\text{IO}_6]_0^b$$

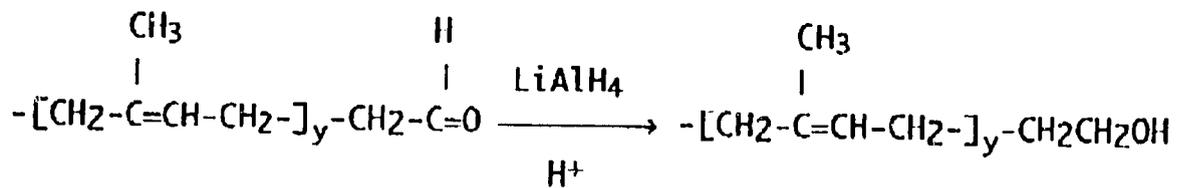
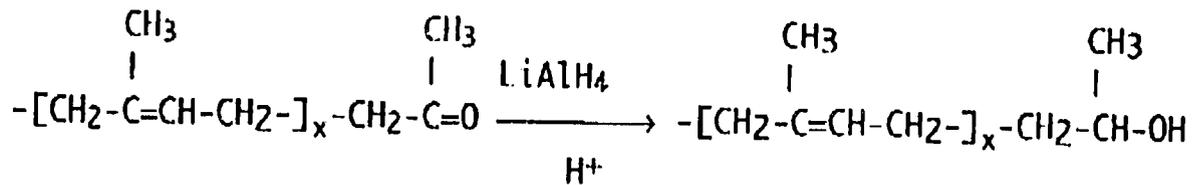
and the reaction rate is a pseudo zero order. In terms of number average molecular weight we can write:

$$1/ M_n = k''t$$

The k'' values for the reaction at different temperatures are shown in table 1. The activation energy for the cleavage reaction was calculated from this data (fig 5) and found to be $E_a=17$ Kcal/mol.

T (°C)	k'' (mol/g min)
30	6.2×10^{-8}
35	9.3×10^{-8}
40	1.1×10^{-7}
50	3.7×10^{-7}

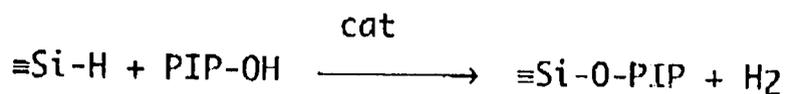
Reduction of carbonyl PIP telechelics to obtain reactive material



The reduction of the carbonyl end groups leading to α,ω diol PIP was carried out using LiAlH_4 as the reductant. The reaction takes place in an inert atmosphere and in a fume hood. 15ml of a LiAlH_4 solution in diethyl ether 1.0M (Aldrich sure-seal bottle), is added dropwise to the reaction flask containing the PIP carbonyl solution in diethyl ether (10g PIP in 150ml diethyl ether), initially placed in an ice bath. After one hour of ether reflux and constant stirring with a magnetic stirrer, the flask is returned to the ice bath, still under nitrogen blanket. Any excess LiAlH_4 is reacted initially with 6ml of ethylacetate, added dropwise at a very slow rate and then reacted with 15ml acetic acid. The mixture is subsequently refluxed for 30 minutes, followed by the addition of treated water. The etheric phase is washed several times with treated water. The acetic acid is removed by treatment with an aqueous 10% wt. solution of Na_2SO_3 until neutral pH is obtained. This is followed by additional washes with treated water. The etheric phase is dried over MgSO_4 , and the ether evaporated for a period of a few days. After most of the solvent is eliminated the polymer is further evaporated using an oil vacuum pump, in order to eliminate traces of the solvent. It is imperative to verify the absence of any traces of acetic acid, complexes of aluminum, aluminum hydroxide, lithium hydroxide, or ether in the organic phase or in the final product, since they interfere with hydrosilation by reacting with the silane group (cf next section). Characterization of the α,ω PIP diol and verification of the product's purity is achieved by FTIR spectroscopy and atomic absorption. The M_n values of the PIP telechelics are not modified during the reduction step. The PIP-diol is characterized qualitatively following the full conversion from carbonyl to hydroxyl groups by FTIR (Fig 4).

Endlinking of the diol PIP to form PIP/Silicone Elastomer

End linking between the α,ω diol PIP and the silane group of a multifunctional crosslinker has been attempted by means of the following reaction scheme [2,3,4,5]:



Possible catalysts to be used in this reaction are: chloroplatinic acid, tin octoate, zinc octoate, and other metal complexes [4,5]. Actual endlinking was achieved in this work

by means of the reaction with the silane group of tetra-kis-(dimethylsiloxy)-silane (obtained from Huls) using 2% wt. in toluene solution of cis-dichloro bis(diethylsulfide)-platinum II (Strem) as the catalyst [6]. Stoichiometric amounts of the diol-polymer and the crosslinker are dissolved in CCl₄ (30% wt.), 2μl/g mix of the catalyst solution are added. The mixture is stirred using a magnetic stirrer until it becomes homogeneous, then it is cast into a Teflon mold placed in a desiccator under a nitrogen blanket. The desiccator is kept in 65°C for 48 hours. The product is a rubber like membrane, and it was characterized using swelling measurements with toluene as a solvent at 25°C.

From swelling measurements on two different PIP networks prepared from PIP telechelics of different initial Mn, the molecular weight between linking points was determined using the following relation [7]:

$$\frac{\xi}{V_0} = \frac{\ln v_1 + v_2 + \chi v_2^2}{\tilde{v}_1 (v_2)^{1/3} \left[1 + \left(\frac{2}{\phi} - 2 \right) (1 - v_2^{2/3}) \right]} = \frac{v/2}{V_0}$$

where ξ is the network cycle rank ($\xi = v - \mu$), v/V_0 is the concentration of network strands, μ/V_0 the concentration of junctions, v_1 is the volume fraction of solvent v_2 is the volume fraction of polymer, \tilde{v}_1 is the molar volume of the solvent, χ is the Flory-Huggins interaction parameter, ϕ is the functionality of the junctions and M_C the molecular weight between crosslinks is given by:

$$M_C = \rho_2 / (v/V_0)$$

where ρ_2 is the density of the polymer. Values for the Mw of the polymer which equals M_C are shown in table 2. The polydispersity of the polymer for the two different experiments was calculated $PD \approx 2$.

exp.	M_n (FTIR)	v/V_0	M_C
1	1950	2.4×10^{-4}	3750
2	12000	3.6×10^{-5}	25000

Reactions with Chlorosilanes

This part of the project was the effort of the mexican group as described in the following:

A reduced PIP sample which was produced from an oxydized PIP for eight hours ($M_v = 9,800$) was reacted with stoichiometric amounts of a halosilane, at room temperature and N_2 atmosphere, using ethylic ether / pyridine as solvent, and heated under reflux for half hour.

The reaction was immediate and a white oily liquid was produced which was separate from the white powder product (pyridinium hydrochloride) by decantation, washed and dried under vacuum at $60^\circ C$.

An I.R. spectrum of this product shows the disappearance of the OH-band at $3,440\text{ cm}^{-1}$ and the appearance of the Si-O band at 1260 and 805 cm^{-1} .

THE TESTED HALOSILANES WERE:

- a) Diethyl dichloro silane
- b) Diphenyl dichloro silane
- c) Phenyl trichloro silane
- d) Methyl, phenyl dichlorosilane
- e) Methyl, vinyl dichlorosilane
- f) Octhyl , trichloro silane
- g) Vinyl , trichloro silane.

Several attempts were made under different conditions to obtain different copolymers. Table 4 gives a review of all the reactions and conditions we have done to copolymerize the α -o-Dihydroxyoligomers with several halosilanes. The used solvents were as follow:

- a) Oxidation: Toluene
- b) Reduction: diethyl ether and THF
- c) Copolymerization : diethyl ether, THF and Petroleum ether.

<u>OXIDATION OF PIP</u>	<u>REDUCTION OF PIP</u>	<u>HALOSILANE AGENT</u>	<u>COPO CONDITIONS</u>
2hr / 50°C	6 hr / 35°C	Diethyl	3 hr / 35°C
2hr / 50°C	10 hr / 35°C	Diethyl	6 hr / 35°C
2hr / 50°C	8 hr / 35°C	Diphenyl	3 hr / 35°C
2hr / 50°C	6 hr / 35°C	Phenyl	3 hr / 35°C
6hr / 40°C	4 hr / 35°C	Methyl-Phenyl	3 hr / 35°C
2hr / 50°C	5 hr / 35°C	Octyl	3 hr / 35°C
24hr / 25°C	2 hr / 35°C	Vinyl	2 hr / 35°C
24hr / 30°C	0.5 hr / 25°C	Vinyl	0.5 hr / 25°C
2hr / 50°C	5 hr / 35°C	Vinyl	3 hr / 35°C
2hr / 50°C	10 hr / 35°C	Vinyl	3 hr / 35°C
2hr / 50°C	10 hr / 35°C	Vinyl	2 hr / 35°C
2hr / 50°C	10 hr / 35°C	Vinyl	2 hr / 35°C
8hr / 25°C	2.5hr / 35°C	Methyl-Vinyl	2 hr / 35°C
6hr / 40°C	3.1hr / 38°C	Methyl-Vinyl	2 hr / 30°C
2hr / 50°C	5.0hr / 35°C	Methyl-Vinyl	3 hr / 35°C
2hr / 50°C	8 hr / 35°C	Methyl-Vinyl	3 hr / 35°C
2hr / 50°C	10 hr / 35°C	Methyl-Vinyl	2 hr / 35°C

D) Curing of QR by hydrosilation reaction.

We did not work with hydrosilanes, for this reason this part of the project was not carried out.

E) Conversion, reaction time, and limited kinetic study of reactions.

The copolymerization reaction was too fast, that it was not possible for us to follow it with the equipment we have in our lab, for this reason, this part of the project was not made.

F) Separation of products from reaction mixture.

The subproduct from the copolymerization reaction (pyridinium chloride), was separated from the solution by centrifugation, a Centrifuge Hermle Z-230 was used for this purpose.

The halosilane excess was eliminated by extraction with acetonitrile according with the patent written by Liville and McEntee (6).

OBSERVATIONS AND CONCLUSIONS

A) Purification:

A modification of the Solche method of purification was made, and it is related with washing solution, using hot water ($60 \pm 5^\circ\text{C}$) to avoid the formation of emulsion. The Solache procedure is too slow and it takes a lot of time during purification due to the formation of emulsions.

B) Oxidation:

The Molecular Weight of the oxidized PIP can be controlled by controlling temperature and reaction time. The molecular weight can be followed by easy techniques in a short time and we can select the desired molecular weight.

C) Reduction:

Changing the reaction conditions (reaction time and temperature) , it is possible to get a complete reduction of carbonyl groups. Washing the solution with cold water ($2-3^\circ\text{C}$) makes easy and faster the procedure of purification of the reduced products.

D) Copolymerization:

The copolymerization reaction for all the halosilanes, was too fast to be followed with the equipment we have in our lab. However, the reaction is so simple, that the reaction products can be analyzed easily by I.R. and H-NMR Spectroscopy.

Using the H- NMR, it was possible to correlate different signals, and by their integration, it was possible to have any idea about the structure of each copolymer, as we are going to see later; however, in the case of diphenyl - dichloro silane and vinyl trichloro silane, it was little difficult to define the structure because it was found a higher number of PIP units vs those of halosilanes.

3-) PRODUCTS CHARACTERIZATION

A) Structural Analysis

The characterization of the products has been made by I.R. Spectroscopy, H-NMR and C13 - NMR. Some difficulties have raised with the last technic, because low molecular weight units of silane comonomer, attached to higher molecular weight units of PIP oligomers made impossible the interpretation.

The equipment we used for characterization was:

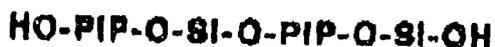
- a) Perkin Elmer I.R. Spectrophotometer Model 257.
- b) Brücker NMR Spectrometer 300 MHz with Fourier transformation and TMS as reference for chemical shifts.

With this information we found that for one PIP unit (17 u.e) there exist 3 protons from the methyl group (one Si atom) and 3 vinyl protons (one Si atom), the proposed structure is shown at the end of this section.

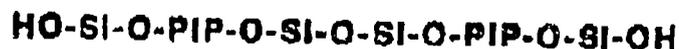
We were trying to correlate the signal integration for the proton of the terminal group OH⁻ with a theoretical value, and we found that it integrates for one proton, which does not correspond to the expected value (two protons), and this is due to the hydrolysis of the chlorosilanes which give terminal OH⁻ groups. This argument is supported by the IR spectra which show the hydroxile groups, and this allow us to conclude that the structure should be duplicated in order to fit with the experimental values.

The final structures for all the cases except for the Phenyl, Methyl silane are:

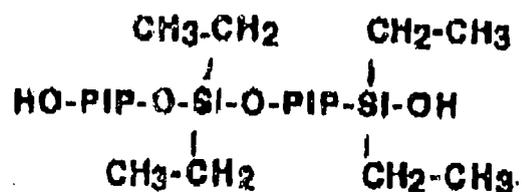
PIP:Si 1:1



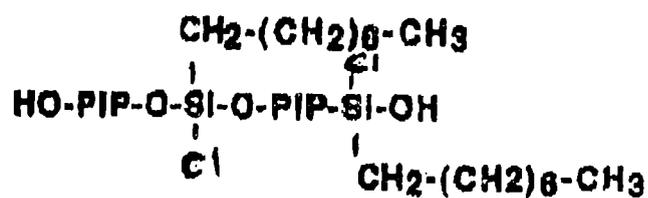
For the Phenyl, Methyl silane we propose a structure: PIP:Si 1:2



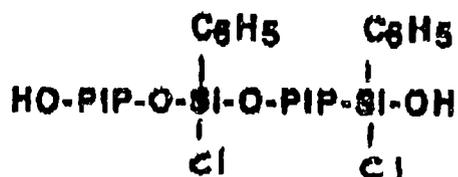
1-) Diethyl silane copolymer



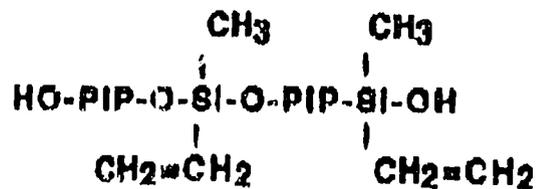
2-) Octyl silane copolymer



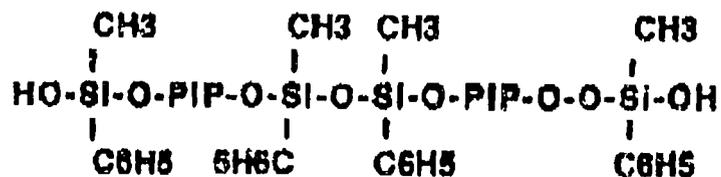
3-) Phenyl silane copolymer



4-) Methyl, vinyl silane copolymer.



5-) Methyl, phenyl silane copolymer.



B) Mechanical and Rheological study

We were trying to fix our rheometer to carry out our measurements but it was not possible because it requires very expensive mechanical parts that we were not able to get; also, we did look for an equipment in U.S.A. but sample was the main problem, because it was requested high amount of product for analyzing and we had only several grams to send and serious difficulties to make more product.

D) Chemical and environmental resistance

Several tests were made with our products, we tested the chemical resistance with acids and some other solvents at room temperature and at 120 °C, also, we tested the effect of curing to see the behavior of the products. We can see on the next pages the results of these tests.

4- Final Product Optimization.

A) Detailed kinetic study for the selected product (s).

In all the cases, the reaction was too fast that we were not able to follow up because the lack of appropriate equipment, for this reason, we did not work on this area, hence, we decided instead to study some kinetic aspects of the PIP oxidation and the results are shown later on this report.

Behavior with different solvents.

All copolymers are dissolved by: THF

· Toluene

Ethyl ether

Petroleum ether

All copolymers are coagulated by:

Acetone

Methanol

Ethanol

CURING FOR 1 HOUR AT 120°C

COPOLYMER	HCl	HNO ₃	H ₂ SO ₄	HClO ₄	HOAc	H ₂ O ₂	NH ₄ OH
DIETHYL	2	2	2	2	3	1	1
DIPHENYL	2	2	2	2	3	1	1
OCTYL	2	2	2	2	3		1
PHENYL	2	2	2	2	3	1	1
METHYL,PHENYL	2	2	2	2	3	1	1
METHYL,VINYL	2	2	2	2	3	1	1
VINYL	2	2	2	2	3	1	1

1-) It does not change of color, It does not show hardness

2-) It shows color change and change in hardness

3-) It shows color change and hardness

Notes: Octyl and Phenyl were attacked easily

The reactivity of all the acids was immediate.

CHEMICAL AND ENVIRONMENTAL RESISTANCE

COPOLYMER	CURING 100 °C	HNO3	HCl	H2SO4	HClO4	HOAc	H2O2	NH4OH
DIETHYL	1	3	2	2	3	1	1	1
DIPHENYL	1	3	2	2	3	1	1	1
OCTIL	1	3	2	2	3	1	1	1
PHENYL	1	3	2	2	3	1	1	1
METHYL,PHENYL	1	2	2	2	3	1	1	1
METHYL,VINYL	1	2	2	2	3	1	1	1
VINYL	1	2	2	2	3	1	1	1

1-) It does not change of color and hardness

2-) It shows color change and hardness

3-) It does not show color change, but it shows change in hardness

Notes: Reactivity $HCl < HNO_3 < H_2SO_4$

Changes were less affected in those cases with HNO_3

Impact, Relevance and Technology Transfer

The usefulness of this project should be evaluated at two different levels: the scientific success and contribution of the project and the benefit to the developing country. Although the project was successful by all standard criteria and accomplished the goals set forth at the beginning as far as research results are concerned the greatest benefit from this project is in the later facet. An extraordinary improvement in research infrastructure and experience has been achieved in the collaborating institution. The Universidad Autonoma de Nueve Leon is a public institution with a very large body of undergraduate students but very poorly equipped for research. The University staff has little or no experience in conducting research a fact that will impact on level and relevance of faculty. The present project is probably the first major externally funded research project undertaken by the School of Chemistry in this university. The fund made available enabled the collaborating scientists to furnish and equip a large sized laboratory which will undoubtedly serve them in future years. It also enabled several graduate and undergraduate students to be exposed to research activity. Finally, the project provided the collaborating scientists with experience concerning the planning and execution of a long term research program. This experience will prove invaluable in their future scientific endeavors.

Project Activities and Output

During the duration of the project three visits were undertaken two by the Israeli PI and one by the two collaborating investigators in the partner institutions. These visits proved extremely important in forging communications, understanding, and work practices. These type of visits important in any type of collaborative work is essential in this case due to the enormous technical difficulties in communication and the big difference in scientific culture. The results of the work have been presented in several scientific meetings including the Freiburg Polymer Networks meeting, the 10th IUPAC meeting on Polymer Networks in Jerusalem, the Gordon Research Meeting on elastomers, the Annual Meeting of the Israel Society of Chemistry, and a Russia-Israel Binational meeting.

Project Productivity

The project goals as outlined in the original proposal have been met to a large extent. All the major items contemplated were successfully executed. The only portions of the work that were not carried out were because as result of the data gathered were deemed unnecessary (e.g. we were initially concerned about possible interference of impurities present in the Guayule rubber with the kinetics of the reactions studied. Tests found no evidence of such a problem and hence the study initially planed was not required). Another reason for abandoning some tests of minor significance was due to hardware problems encountered by our LDC partners and their inability to remedy the problems due to lack of spare part and access to technical service.

Future Work

As result of the research results obtained in relation with the present project we are contemplating the continuation of the work in our laboratory on two related topics: 1.The synthesis of ampiphilic networks based on PIP/PEO copolymer and PIP/PDMS/PEO tert polymer. 2. Synthesis of degradable rubbers. Funding for the two projects has been requested from several agencies.

Literature Cited

1. Solache-Orozco J., Cantow H.J., *Polym. Bull.*, 1984, 312, 203.
2. Noll W., *Chemistry and Technology of Polymers*, Academic Press INC., London, 1968
3. Eaborn C., *Organosilicone Compounds*, Butterworths, London, 1960.
4. Petrov A.D. *Synthesis of Organosilicon Monomers and Polymers*, Consultant Bureau, New York, 1964
5. Voorhoeve R.J.H., *Organohalosilanes*, Elsevier, Amsterdam, 1967
6. Fischer A., Gottlieb M., *Proc. Network 86*, 1986, Elsinore, P-14
7. Gottlieb M., *Biological and Synthetic Polymer Networks*, Sec.4, Chap. 27, Elsevier Applied Science Publishers, 1986, pp. 403
8. Brandrup J., Immergut E.H., *Polymer Handbook*, Third Ed., John Wiley & Sons, New York, 1989.
9. Cunningham R.E., *J. Polym. Sci.*, 1960, 3XLII, 571.
10. Guizard, C., and Cheradame, H., *Europ. Polym. J.* 1979, 15, 689.
11. Haiduc, I., and Zuckerman, J.J., *Basic Organometallic Chemistry*, Walter de Gruyter, Berlin, 1985.
12. Linville, R.G., and McEntee, R. (General Electric), *Separation of Chlorosilanes from their Mixture*, US Pat. 3,007,956, 1960.