



## Chapter II

### Experimental

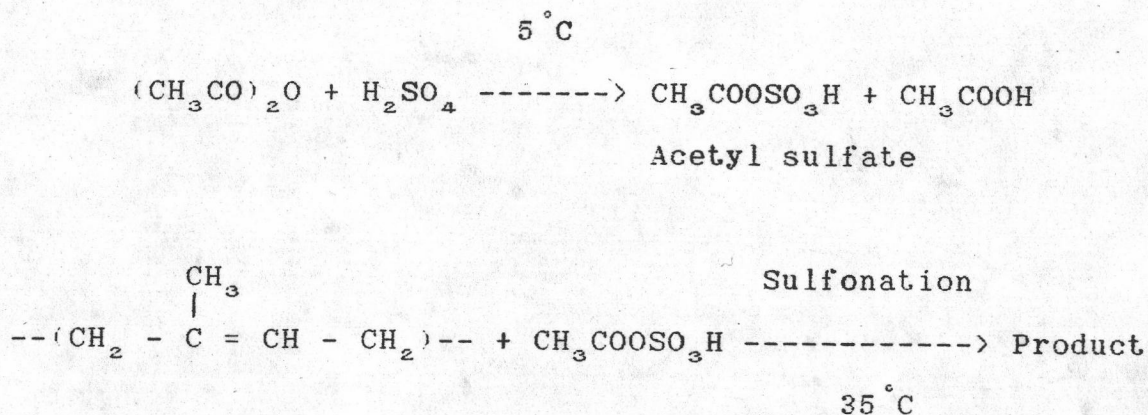
#### 2.1 Materials

2.1.1 Natural Rubber (NR): NR-latex (60% concentrated low ammonia grade) was bought from Patex company. The dry rubber was prepared by coagulating the latex using 1% v/v acetic acid, washed several times with distilled water and dried for two weeks at room temperature, yielding a light brown rubber. Due to the high molecular weight (MW) of NR which makes it difficult to dissolve in organic solvents, mastication was necessary in order to decrease the MW to make the rubber soluble. For this purpose a two-roll mill, Nishimura (NO. 4-38 Ryogoku, Sumidaku), was used for twenty minutes. The viscosity-average molecular weight,  $\bar{M}_v$ , was determined by dilute solution viscosity according to McCaffery [24].

2.1.2 Chemical Reagents: Chloroform was bought from Mallinckrodt Inc.; sulfuric acid (96%), methanol absolute, magnesium and lead acetate, and ethylene dichloride from E. Merck Co.; acetic anhydride from BDH Chemical Ltd.; ethanol absolute, zinc acetate and potassium hydroxide from Carlo Erba. All of the reagents were high purity grade, and were not further purified. The methanol and toluene were purified by fractional distillation.

## 2.2 Procedure

The synthesis of sulfonated NR was carried out according to the reaction scheme shown below:



2.2.1 Sulfonating Reagent [25]: Acetyl sulfate was prepared by reacting concentrated sulfuric acid and acetic anhydride in ethylene dichloride. In a 100 ml volumetric flask, 16 ml (172.1 mmole) of acetic anhydride was cooled to 5°C and 1.4 ml (25.2 mmole) of sulfuric acid were added dropwise. For each sulfonation, a new solution of acetyl sulfate was prepared. The mole % of sulfonic acid content in NR that were used for the sulfonation were: 0.18, 0.24, 0.30, 0.38, 0.62 and 0.82.

2.2.2 Sulfonation of NR: Prior to sulfonation, 20 g of NR was dissolved overnight in 400 ml  $\text{CHCl}_3$ . Then in a 500 ml four-necked round bottom flask equipped with a mechanical stirrer and a thermometer, and mounted with a condenser, a specific amount of acetyl sulfate was added dropwise to the NR solution. The reaction was carried out for one hour at

35 °C. This temperature was chosen since it was found that at elevated temperature, a desulfonation process occurred causing a low yield [22].

The sulfonated rubber was precipitated in methanol and washed several times with the same solvent. Partially dried, the modified polymer was redissolved in chloroform and reprecipitated as above for further purification. The final product was dried in the vacuum oven at 60 °C for 3 hours. The sulfonic acid content was determined by titration with a 0.01 N ethanolic KOH solution.

2.2.3 Yield %: The reaction yield of sulfonated NR was determined according to the following formula:

$$\text{Yield \%} = \frac{(\text{weight of sulfonated NR}) \times 100}{(\text{weight of NR})}$$

2.2.4 Neutralization of Sulfonated NR by Zn(OAc)<sub>2</sub>, Mg(OAc)<sub>2</sub> and Pb(OAc)<sub>2</sub>: Neutralization of the polymeric sulfonic acid was performed by using an amount of metal acetate solution necessary to achieve stoichiometric equivalence in order to form an ionic bridge (i.e. two equivalents of M<sup>2+</sup> per one equivalent of -SO<sub>3</sub>H). After stirring the solution for 30 minutes, the neutralized polymer was precipitated and washed with methanol and dried again in the vacuum oven at 60 °C for 3 hours.

### 2.3 Relative Viscosity Measurement, $\eta_{rel}$

$\eta_{rel}$  of the sulfonated and neutralized products was determined at 30°C in a 95/5 toluene/MeOH solvent mixture using a Cannon-Fenske viscometer NO 100 [24]. The solution concentration was 0.500 g/dL.

$\bar{M}_v$  was calculated by using the relative viscosity value, that is, the average flow-time of sample solution divided by the average flow-time of the solvent,  $\eta_{rel} = t/t_0$ . Knowing  $\bar{M}_v$  and  $\eta_{rel}$  of NR, we calculated  $\bar{M}_v$  of the sulfonated NR as follows:

$$\bar{M}_v \text{ of Sul.NR} = \frac{(\bar{M}_v \text{ of NR}) \times (\eta_{rel} \text{ of Sul.NR})}{(\eta_{rel} \text{ of NR})}$$

### 2.4 Water Absorption

Samples of sulfonated neutralized rubber with a 20 mm diameter disc and a 2-3 mm thickness were prepared by compression molding at 3500 psi for 5 minutes. Each sample was then placed in a beaker containing distilled water and put in the oven at 35°C. At defined intervals the samples were removed and weighed after the excess water was wiped up with tissue paper from the surfaces of the sample. The samples were then placed back into the beaker and the same procedure was repeated at intervals of 24, 48, 72, 144, 192 and 312 hours. The total water absorption was

determined by comparing the weight of the water absorbed by the sample during immersion with that of the dry sample. The percentage increase in weight during immersion was calculated according to the ASTM D 570-81 method:

$$\text{Increase in weight, \%} = \frac{\text{wet wt-conditioned wt} \times 100}{\text{conditioned wt}}$$

## 2.5 Plasticity Measurement

The plasticity was determined with a Wallace Rapid Plastimeter model MK II using the ISO 2007 method. The plasticity was measured by measuring the force required to compress the testing sample of a given thickness at a given time. The sample was cut with a puncher yielding a 3 mm thick and 13 mm in diameter disc. The sample was placed between a cigarette paper on each side to prevent it from sticking to the instrument, and was then precompressed to a thickness of  $1 \pm 0.01$  mm within 2 sec and heated for 15 sec at  $100^\circ\text{C}$ . Then a load of 100N (Newton) was applied for 15 sec and the restrained thickness was measured in mm. The measurement is called the rapid plasticity number or Wallace number. The Wallace plasticity number can be defined as the "ease of deformation" on a scale from 0-100. A low number means that the rubber sample is a soft material, with low hardness and stiffness, and easy to deform in contrast with a high plasticity number indicating a harder and stiffer material.

## 2.6 Infrared Spectra Analysis

IR spectra were obtained using a Shimadzu model IR-440 grating spectrometer. The samples were prepared in a KBr pellet form.

## 2.7 Nuclear Magnetic Resonance Spectra

NMR spectra were obtained using a Nuclear Magnetic Resonance Spectrometer Model JOEL FX-90. The samples were dissolved in deuterated chloroform using TMS as internal reference at 35 °C and analyzed for their proton and  $^{13}\text{C}$  resonance.

## 2.8 Trial and Error to Determine the Correct Experimental Conditions

### 2.8.1. Stirring Effect on $\bar{M}_v$ of NR

Table 2.1 shows the effect of the rate of stirring on  $\bar{M}_v$  and Wallace number.

Table 2.1. Effect of shearing on NR (temperature = 35°C  
Concentration = 50 g/l of CHCl<sub>3</sub>)

Sample	$\bar{M}_v$	Wallace number
NR	$4.1 \times 10^5$	21.5
NR I	$3.9 \times 10^5$	21.6
NR II	$3.9 \times 10^5$	19.6

NR I = NR dissolved in CHCl<sub>3</sub>, precipitated in MeOH and dried.

NR II = NR I dissolved in 95/5 toluene/MeOH, precipitated and dried.

$\bar{M}_v$  = Determined by using benzene as a solvent,  
 $K = 18.5 \times 10^{-3}$ ,  $a = 0.74$ , at 30°C.

The effect of the reaction system on NR is shown in Table 2.1. It indicates that  $\bar{M}_v$  decreased slightly during stirring when compared with NR and NR I. After neutralization, the Wallace plasticity number of NR II decreased slightly as well. The small decrease observed in both cases can either be a result of the shearing effect and/or experimental error. In our subsequent calculations, therefore, we will use as a reference a  $\bar{M}_v$  of  $3.9 \times 10^5$  and a Wallace number of 19.6.

### 2.8.2 Reaction Time Effect on Sulfonation

Table 2.2 shows the effect of the reaction time on sulfonation.

Table 2.2. Effect of reaction time on sulfonation.  
(Acetyl sulfate added = 20 ml)

Time (min)	mmole $-SO_3H/100$ g NR
30	2.84
60	2.83
120	2.87

The reaction time for sulfonation was 30, 60 and 120 minutes at 35°C, giving only slight difference in the sulfonic group content. Gilbert [23] in his study on sulfonation and related reactions mentioned that in order to prevent desulfonation and to be able to control the formation of a specific sulfonated product, the reaction should be carried out for a short period of time only. We selected the reaction time to be one hour.

### 2.8.3. Solvent Effect

Solvents are known to affect chemical reactions. In our case, in order to select the appropriate solvent for sulfonation, we carried out trial reactions with benzene,



chloroform, and hexane. Table 2.3 shows the solvent effect on the % acid conversion and the type of reaction it formed.

Table 2.3. Effect of solvent on sulfonation reaction.

Solvent	Acetyl sulfate(ml)	%Acid conversion	Solution
Benzene	20	37.8	Heterogeneous
Hexane	5	48.8	Heterogeneous
CHCl <sub>3</sub>	20	11.0	Homogeneous

The above data indicate that benzene and hexane produced heterogeneous solutions, that is, an insoluble black material precipitated out while the other sulfonated part remained in solution. The black product was insoluble in any organic solvents, which indicated a material of a high sulfonic content. Only CHCl<sub>3</sub> gave a homogeneous solution. On the basis of these results, we used CHCl<sub>3</sub> as the reaction medium since heterogeneous solution did not allow us to characterize the complete reaction product.