

## **Production of Sponge Rubber for Monolayer Rubber Stamp Using Salt Leaching Method**

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### **Abstract**

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Sponge rubber used for monolayer rubber stamp was produced from nitrile butadiene rubber (NBR). Open cells in sponge rubber were created using salt leaching method. Effect of size and amount of sodium chloride which was used as a water soluble salt on the creation of open cells in the rubber was investigated. Carbon black was used as a filler. A different type of surfactant was added to increase the leaching out of salt from the rubber. Cure characteristics of the compound rubbers: maximum torque, minimum torque, scorch time and cure time as well as hardness of the prepared sponge rubber were determined. Morphology of the produced sponge rubber by scanning electron micrographs displayed interconnecting open cells. The monolayer sponge rubber assembled in rubber stamp had high oil ink absorption and gave clear imprint.

**Key words:** Open cell, sponge rubber, NBR, soluble salt

### **Introduction**

A printing material composed of a sponge rubber having open cells, wherein voids consist of small cells and large cells. These cells are interconnected with one another and are distributed uniformly in the rubber substrate. Open cell sponge rubber is capable of retaining a colored ink, which does not necessitate a stamp pad for the stamping operation. If a lowly viscous ink containing a dye is used, clear prints can be obtained. The rubber stamp is constructed of two layers. The upper layer is an ink-retaining portion and the lower layer is a printing portion. These two layers are different from each other with respect to properties of the formed open cells. For the lower layer (print layer), a salt having a smaller particle size and for the upper layer (ink-occluding layer), a salt should have a larger size. The print layer should have higher hardness than the ink-occluding layer. An integral laminate was made by superposing an unvulcanized rubber sheet containing a water-soluble powder NaCl on a rubber sheet containing an acid-soluble powder CaCO<sub>3</sub> and pressing them. Then this integral laminate was treated with water to make the upper layer porous. The open cell in the rubber was formed from the decomposition or gasification of CaCO<sub>3</sub> added. The surface of the layers is engraved using a laser beam to

manufacture the rubber stamp.<sup>(1)</sup> Alternatively, water soluble salt is added in the mixture of a starting rubber, following addition of a curing agent and a filler. The rubber commonly used for the printing application is synthetic rubber, for example butadiene-styrene copolymers (nitrile content of 31-42%) as they have good elasticity, toughness, oil and ageing resistance.

The preparation of open-cell sponge rubber printing materials from NBR was reported to consist of soluble starch and water soluble salt, the suitable weight ratio of the soluble starch to the water-soluble salt was found in the range of 1:9-1:3.<sup>(2)</sup> The amount and size of salt is important as they affect the property of the sponge rubber. For the double layer rubber stamp, the print layer has a spring hardness of 30-40 when 600 phr NaCl was added to NBR rubber while the ink-occluding layer has a spring hardness of 10-20 when 700 phr NaCl was used.<sup>(3)</sup> In some papers, organic synthetic fiber (fiber length of 0.2-2.0 mm) was also added together with sodium chloride.<sup>(4)</sup> Use of dilute HCl helps the dissolution of CaCO<sub>3</sub> salt.<sup>(5)</sup>

In this work, the production of open-cell sponge rubbers for monolayer rubber stamp from NBR (nitrile content 40%) is presented. The process comprised incorporating fine powders of

water-soluble sodium chloride in the NBR rubber filled with carbon black as a reinforcement filler. Surfactant was added to increase leaching out of salt. Parameters influencing the properties of the sponge rubbers were studied. Cure characteristics and hardness of the compound rubbers were investigated. The printing quality of the rubber stamp assembled from the resulting compound rubbers was examined.

## Materials and Experimental Procedures

### Materials

Nitrile butadiene rubber (NBR, 40% acrylonitrile), accelerators: MBTS (mercaptobenzothiazole disulfide) and DPG (diphenyl guanidine); activator: zinc oxide and stearic acid; plasticizer: DOP (di(2-ethylhexyl) phthalate); antioxidant: Ralox<sup>®</sup>LC; intermediate superabrasion furnace carbon black (ISAF) (particle size 24-34 nm, relative abrasion 1.25) supplied by Cosan (Thailand) Co. Ltd.; surfactants supplied by Kao Industrial Co., Ltd. and NaCl from Union Chemical.

**Table 1.** Types of Surfactant

Surfactant	Active ingredients(%)
S1 (nonionic, polyethylene glycol distearate)	95
S2 (anionic, sodium lauryl ether sulfate)	70
S3 (anionic, sodium alkyl benzene sulfonate)	50

### Characterization

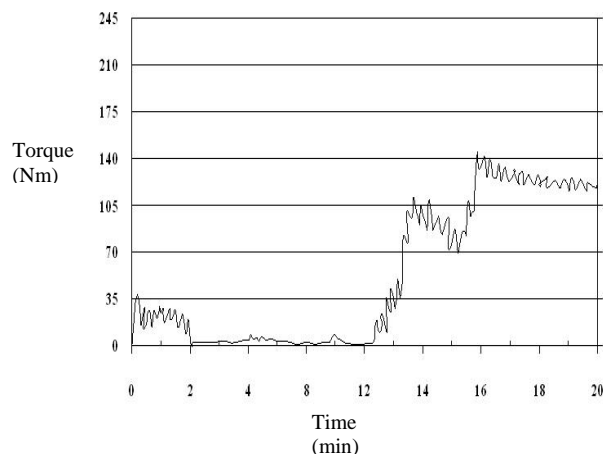
The acrylonitrile content in the NBR was measured by determining the nitrogen content and then back calculating the acrylonitrile content. The nitrogen content was measured by the Kjeldhal method (ISO1656). The hardness of the rubber sample was measured by type C Shore durometer (ASTM D2240, used for the soft sample). The thickness of sample was 6 mm. The fracture surface of sample was characterized with Scanning Electron Microscope (SEM), JEOL model: JSM-6301F and 5410. Moving Die Rheometer MDR 2000 was used to determine minimum torque, maximum torque, scorch time and cure time. The temperature was set at 155°C.

### Mixing of Rubber Compound

The NBR rubber was compounded in an internal mixer (Banbury mixer) with ingredients of vulcanization system at 95°C. The weight (phr) of each is shown in Table 2. Carbon black (ISAF) was used as a reinforcement filler. Sulfur was a vulcanizing agent, less sulfur was used when accelerators (zinc oxide and stearic acid) were added. The vulcanizing process was accelerated with MBTS and DPG. The addition step of each ingredient is shown by the profile of torque on mixer with the mixing time in Figure 1.

**Table 2.** Weight of ingredient in rubber compound

Ingredient	Weight (phr)
NBR	100
DOP (plasticizer)	30
ZnO (activator)	5
Stearic acid (activator)	2
Ralox <sup>®</sup> LC (antioxidant)	2
MBTS (accelerator)	1
DPG (accelerator)	0.3
Sulfur(vulcanizing agent)	1.5
Surfactant	120
Carbon black	amount: 20, 30 and 50 phr
NaCl	size: 100, 200, 300 and 400 mesh amount: 600, 700 and 800 phr



**Figure 1.** Profile of torque on mixer with mixing time.

To the NBR rubber, the following ingredients were added: activators and antioxidants (at 2<sup>nd</sup> min), filler (at 4<sup>th</sup> min), subsequent portions of mixture of plasticizer, surfactant and salt (during 8<sup>th</sup> min-16<sup>th</sup> min), vulcanizing agent and accelerator (at 18<sup>th</sup> min). The total mixing time is 20 min. Then the rubber compound was transferred to a two-roll mill.

### Hot Compression

In the first step the rubber compound was preheated for 15 min to a temperature of 155°C. Then, the compound rubber was placed in a mold. There are two types of molds prepared in this work: character mold and smooth surface mold. The mold is closed with a top force or plug member, pressure was applied to force the material into contact with all mold areas, heating was supplied and pressure was maintained until the molding material has cured. Time used in the compression process depends on cure time of each compound rubber. A rubber sheet of 5 mm thickness was obtained.

### Salt Leaching

Salt in the vulcanized rubber was removed by immersing the sample in water for 15 h in the ultrasonic cleaner at 60°C, then the sample was dried at 40°C in an oven and weight difference before and after washing was taken as % salt leaching.

### Absorption of Oil Ink and Impression Test

After salt leaching, the monolayer of sponge rubber was investigated in terms of its ink absorption capacity and quality of printing. Oil ink (viscosity 50-100 centipoises (25°C) was dropped over all its surface. Then weight of ink adsorbed was determined after a dropping time period of 1 h (1 drop/min). After the sponge rubber was fully filled with ink, it was assembled in the pre-ink stamp case and the quality of impression was then tested. This was performed by continuously pressing the stamp 300 times in 2 min. The quality of print was compared to the commercial double-layer rubber stamp.

## Results and Discussion

### Preparation of Rubber Compounds

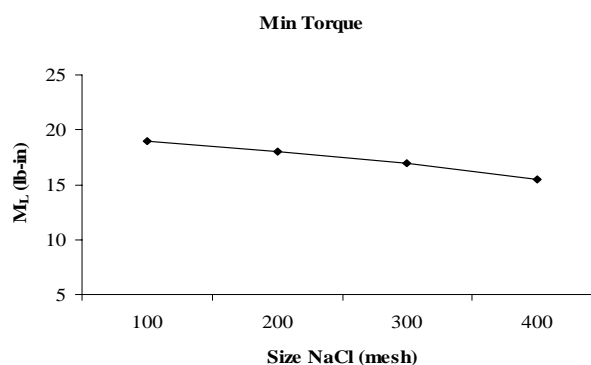
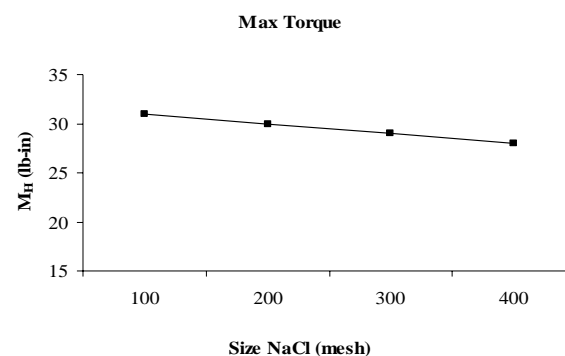
Rubber compound was prepared by mixing several ingredients. Carbon black is used as a filler. It is tightly bonded to the rubber to exert a reinforcing effect. The amount and size of carbon black are varied. Sulfur is used as a curing agent. The cured product is taken out from the mold and washed with warm water to remove the salt. At this washing step, the salt in the surface portion is first removed and water intrudes toward the interior of

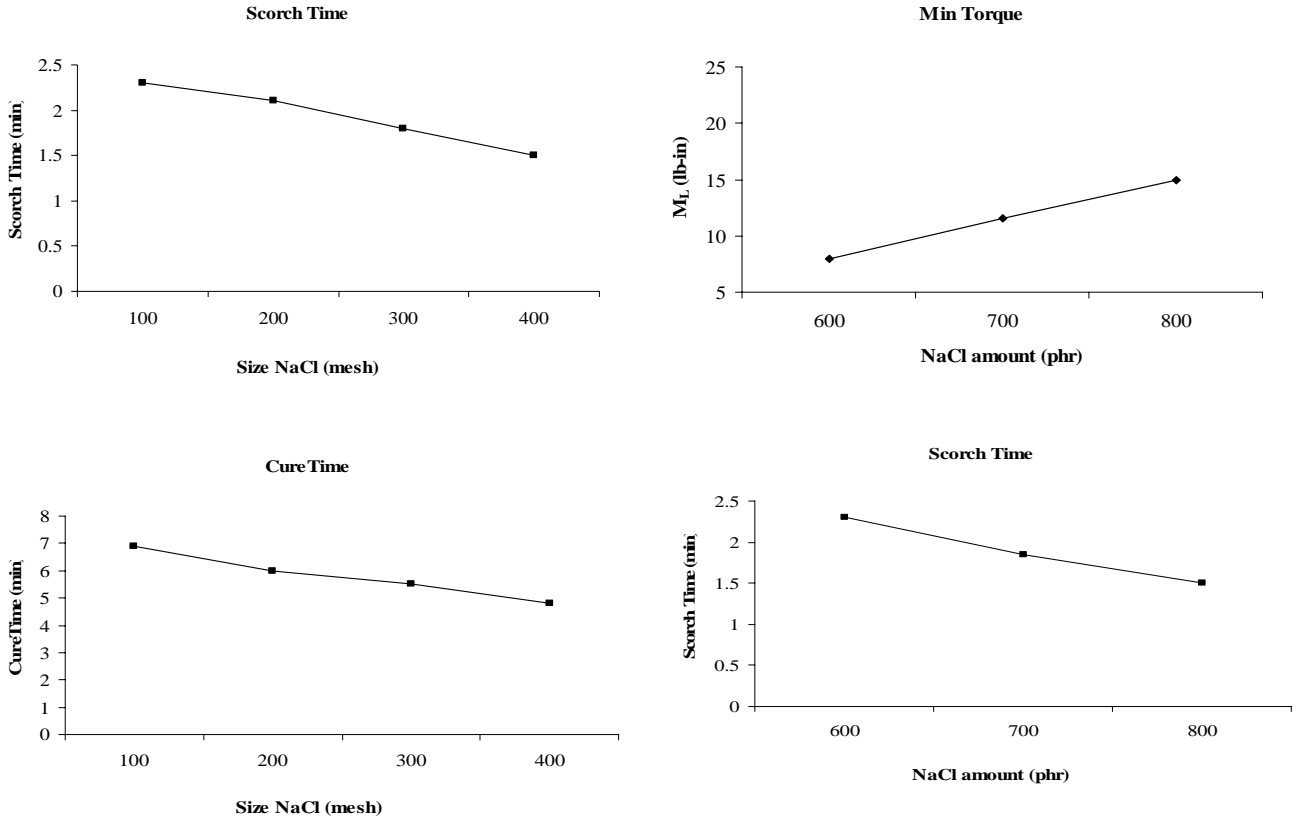
the cured product through numerous open cells in the surface portion formed by the removal of the salt.

### Curing Characteristics of Rubber Compounds

Cure characteristics determine the elasticity modulus of rubber compound. By using Moving Die Rheometer, the minimum ( $M_L$ ) and maximum torque ( $M_H$ ) values of the rubber compound were obtained. The onset of crosslinking-so-called scorch time-was measured when the torque curve increased from minimum torque in two units. The cure time was measured when the torque curve increased from the minimum torque in 90% of the difference between maximum torque and minimum torque. The scorch time generally defines the time to onset of vulcanization at a particular temperature and thus represents the time available for processing. Cure time is the time required during the vulcanization step for the required amount of crosslinking to occur, yielding the desired level of properties.<sup>(6)</sup>

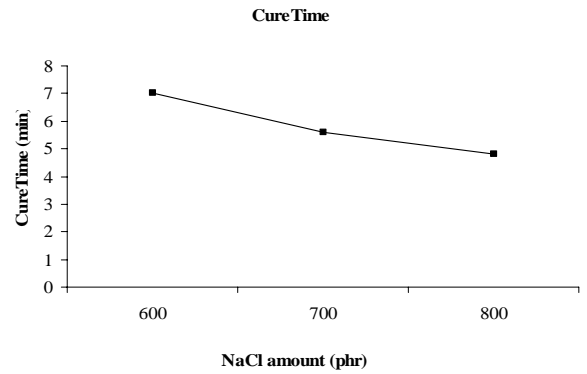
Rubber compounds prepared using the 20 phr carbon black which is used as a reinforcement filler due to its low cost and good physical and mechanical properties. Effect of size of NaCl (amount 800 phr) on the curing characteristics of rubber: maximum torque, minimum torque, scorch time and cure time were determined. Results are shown in Figure 2.



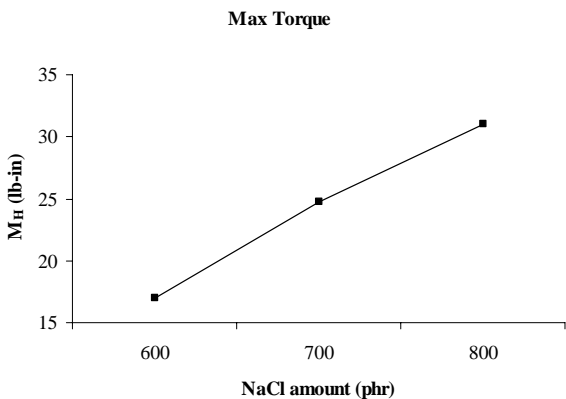


**Figure 2.**  $M_H$ ,  $M_L$ , scorch time and cure time of the rubber samples with different sizes of NaCl (fixed amount of NaCl = 800 phr).

The results show that the  $M_H$ ,  $M_L$ , scorch time and cure time of the rubber samples are affected by the size of NaCl. The  $M_H$  and  $M_L$  values were decreased with decreasing size of salt. The smaller size or the higher surface area of salt reduces the scorch time and cure time. Therefore the NaCl size of 400 mesh (0.034 mm) was chosen for next batches to investigate the effect of amount of NaCl. Results are shown in Figure 3.



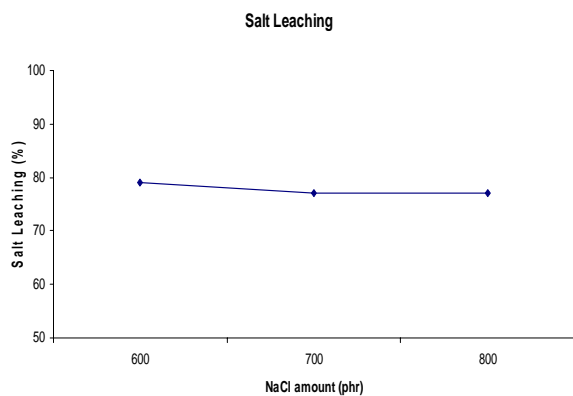
**Figure 3.**  $M_H$ ,  $M_L$ , scorch time and cure time of the rubber samples with different amount of NaCl (NaCl size 400 mesh).



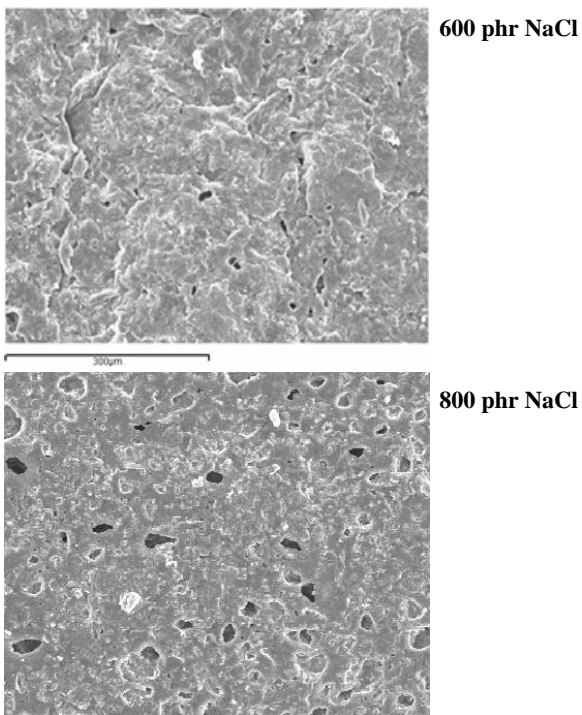
The results reveal that the maximum torque and minimum torque were increased when higher amount of NaCl was added in the rubber compounds due to increasing viscosity of the sample. As for the scorch time and cure time, the results show that higher amount of NaCl shortens the scorch time and cure time. Attempts to increase amount of NaCl to 1000 phr failed due to problems in mixing, high shear stress in the side the chamber of the banbury mixer.

*Production of Sponge Rubber for Monolayer Rubber Stamp Using Salt Leaching Method*

To see whether a high amount (800 phr) of NaCl in the rubber compound affects the ability of salt leaching out from the rubber compound, a test of salt leaching was performed by immersing the sample in water for 15 h in the ultrasonic cleaner at 60°C the weight difference before and after washing was taken as % salt leaching. The results are shown in Figure 4. It can be seen that the amount of NaCl did not affect % salt leaching. All samples show similar % salt leaching (~79%). Morphology of the rubber was examined using scanning electron micrograph, as shown in Figure 5.



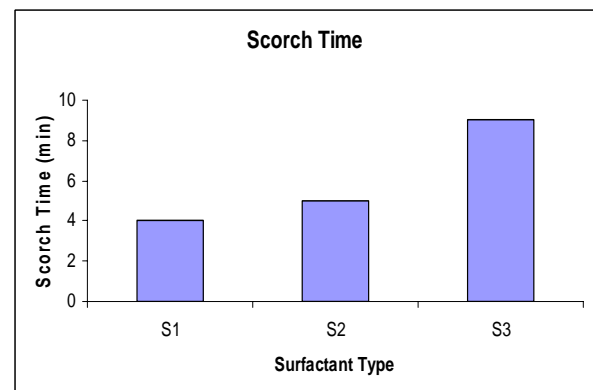
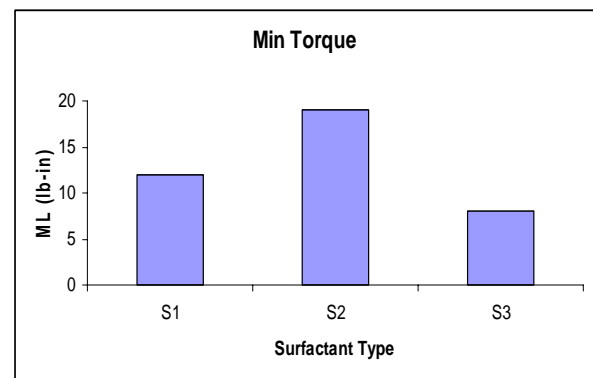
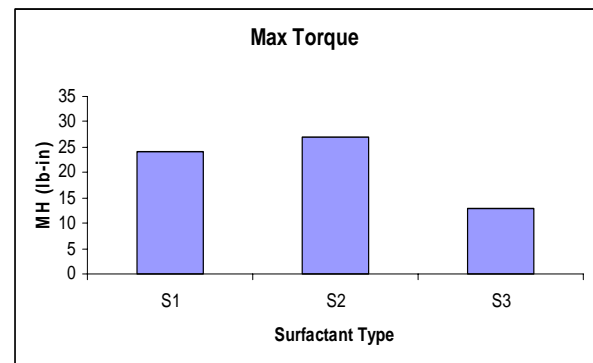
**Figure 4.** Salt leaching of the rubber samples with Different amount of NaCl (NaCl size 400 mesh)

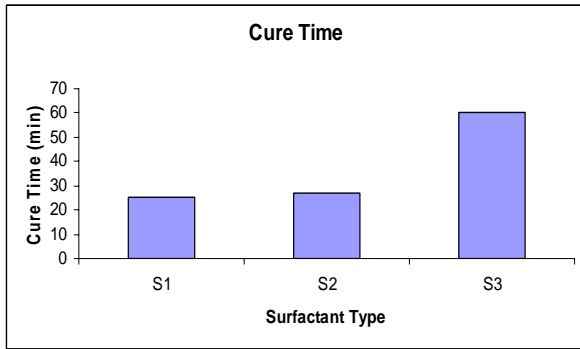


**Figure 5.** SEM micrographs of the rubber samples filled with 600 and 800 phr NaCl (NaCl size 400 mesh) after salt leaching.

The SEMs in Figure 5 demonstrate that after salt leaching out of the rubber samples, the sample with higher amount of NaCl shows higher numbers of open cells. Therefore the amount of 800 phr NaCl was chosen for further experiments.

In order to improve salt leaching from the sample and also to create higher numbers of open cells in the rubber sample, addition of surfactant was studied. The three types of surfactant used consist of one nonionic surfactant (S1, polyethylene glycol distearate) and two anionic surfactants (S2, sodium lauryl ether sulfate and S3, sodium alkyl benzene sulfonate). The amount of the surfactant added was fixed at 120 phr. Cure characteristics and hardness of the rubber samples were determined. The results are shown in Figure 6.

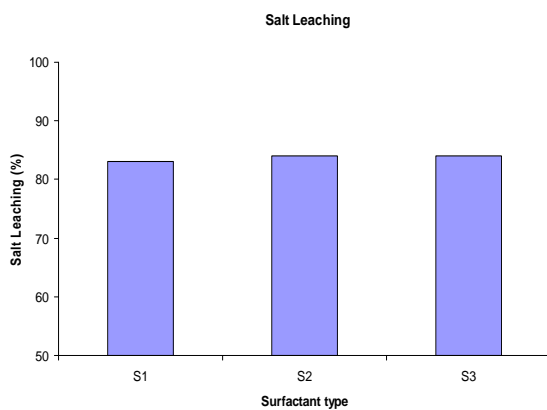




**Figure 6.**  $M_H$ ,  $M_L$ , scorch time and cure time of the rubber samples with different surfactants (NaCl size 400 mesh, NaCl amount 800 phr).

The above results clarify that among three types of surfactants tested in this work, the rubber sample mixed with S2 gave the highest values of  $M_H$  and  $M_L$ . This is due to its higher active ingredients (80%) compared to the other two surfactants. This is also revealed by the scorch time and cure time which are shorter than those from S3 (active ingredients 50%).

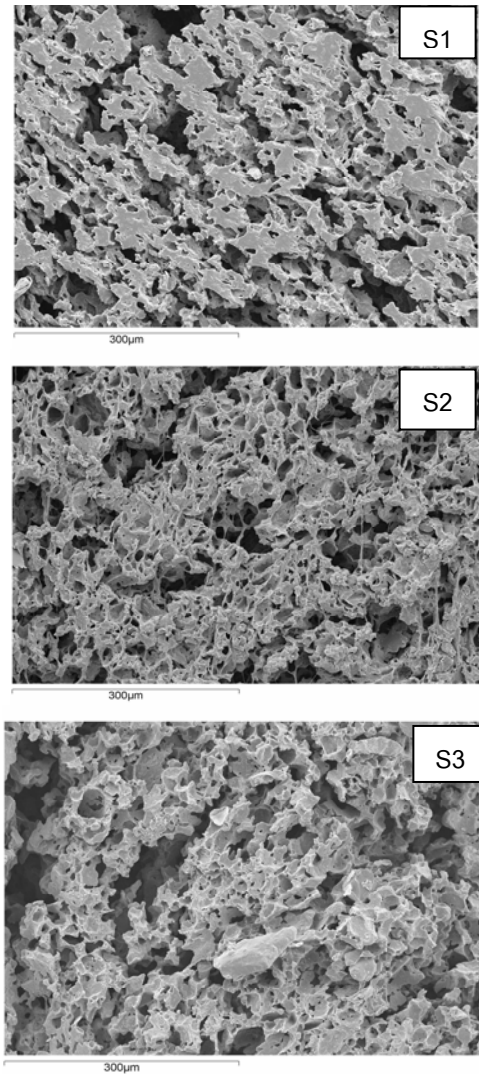
The three rubber samples were tested salt leaching and the results are shown in Figure 7. Addition of surfactant to the rubber compound can increase the leaching of NaCl from 79% to 84%. It should be noted that washing time required is much shortened (from 15 to 3 h), for all three types of surfactant.



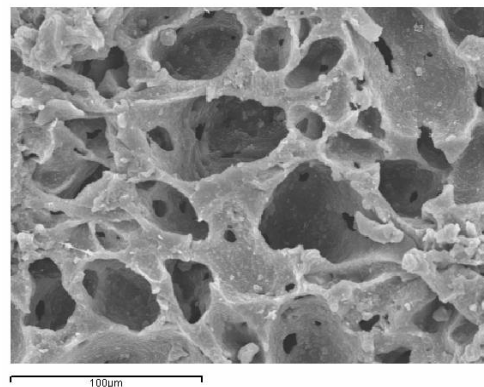
**Figure 7.** Salt leaching from the rubber samples added with different types of surfactant.

Micrographs of all samples were taken as shown in Figure 8. It can be seen that after salt leaching the rubber sample filled with S1 has thicker cell walls compared to the two anionic surfactants. In the case of the anionic surfactants, the S2 surfactant shows smaller and higher numbers of open cells than the S3 surfactant. An

enlarged SEM micrograph of the rubber sample prepared with the S2 surfactant is also shown in Figure 9.

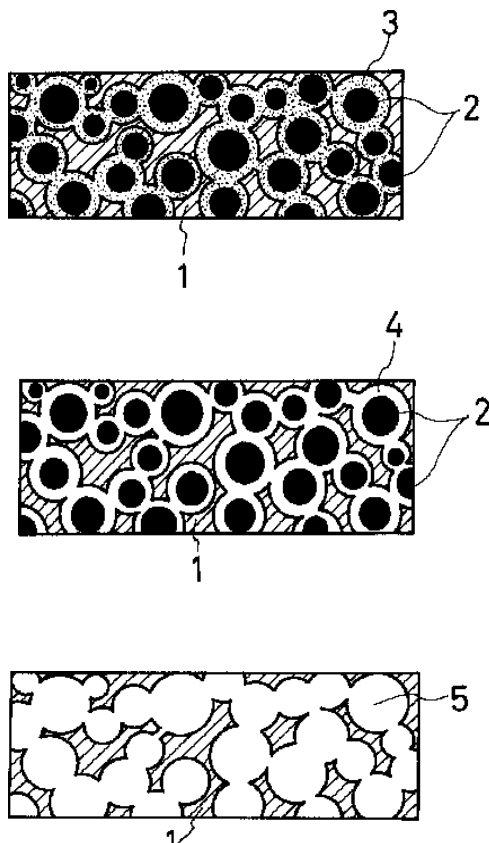


**Figure 8.** SEM micrographs of the rubber samples filled with different types of surfactant.



**Figure 9.** Enlarged SEM micrograph of the rubber sample filled with S2 surfactant.

The formation of open cells in the rubber sample can be described as shown in Figure 10. First, surfactant thin film (No.3) surrounds salt powders (No. 2) in rubber matrix (1). After washing with water, a continuous path (No. 4) was formed, allowing easy approach of water to dissolve or leach out the salt. Finally the open cells (No. 5) were formed.



**Figure 10.** Sectional views showing formation of open cells in the rubber sample.

The hardness of the rubber samples was determined and the results show that all samples have hardness in the range of 8-11. In order to increase hardness to above 15, which is suitable for use in rubber stamp, the amount of carbon black was increased. The reinforcement of rubber by carbon black is caused by Van der Waal's type interaction between rubber and carbon black. In this work, intermediate superabrasion furnace carbon black (ISAF) was used. Chemical reactivity of this type of carbon black is attributed to the presence of oxygen-containing functional groups such as phenol, quinone and lactone.<sup>(7)</sup> It was found that 50 phr carbon black can increase the hardness to 15.

## Absorption of Ink

The rubber samples with different types of surfactant are tested in terms of their ability in absorption of oil ink. Ink (viscosity 50-100 centipoises) was dropped onto the rubber sample in a period of 1 h, then weight of ink absorbed was determined. The results show that the sample prepared with anionic surfactant can absorb a higher amount of ink (2.6 and 2.3 g for S2 and S3, respectively) than that with nonionic surfactant (S1) (1.8 g). Higher absorption of ink represents longer use in the rubber stamp.

## Impression Test

Impression test was performed on the three rubber samples with different types of surfactant to compare the printing quality. When the rubber stamp is used continuously, the sharpness of the imprint is important. The results indicate that the rubber sample prepared with anionic surfactant S2 gave better quality of imprints than the other two samples.

## Conclusions

Open cell sponge rubber can be produced from synthetic rubber, NBR using salt leaching method. The optimum size and amount of water soluble salt, NaCl, was found at 400 mesh and 800 phr, respectively. By adding surfactant, more open cells were formed in the rubber as revealed by SEM. The anionic surfactant is more suitable than nonionic surfactant. This method is economical and can produce monolayer sponge rubber with good printing ability.

## Acknowledgments

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