İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ORGANOGELS BASED ON BUTYL RUBBER, POLYBUTADIENE AND STYRENE-BUTADIENE RUBBER FOR OIL SPILL REMOVAL

M.Sc. Thesis by
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Programme : Chemistry

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PETROL DÖKÜNTÜLERİNİ TEMİZLEMEK İÇİN BUTİL, POLİBUTADİEN VE STİREN-BUTADİEN KAUÇUK ESASLI ORGANOJELLER

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FOREWORD

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Above all, I would like to dedicate this thesis to my family Şevket,Nezaket and İlker KARAKÜTÜK. In addition, thanks to my beloved fiance Ercan TORLAK and my aunt and uncle Zübeyda and ismail KARAKÜTÜK for their understanding in every stage of my life. I owe much to my family for all their self-sacrifice, patience and support during all my education.

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Chemist

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ABBREVIATIONS

PIB	: Butyl rubber
CBR	: Cis-polybutadiene rubber
SBR	: Styrene butadiene rubber
PP	: Polypropylene
AAm	: Acrylamide
BAAm	: N,N-methylene(bis)acrylamide
PNIPA	: Poly(N-isopropylacrylamide)
PAAm	: Poly(acrylamide)
DMSO	: Dimethyl sulfoxide
AMPS	: Sodium salt of 2-acrylamido-2-methylpropane sulfonic acid
SEM	: Scanning Electron Microscope
S2CI2	: Sulfur monochloride

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ORGANOGELS BASED ON BUTYL RUBBER, POLYBUTADIENE AND STYRENE-BUTADIENE RUBBER FOR OIL SPILL REMOVAL

SUMMARY

Industrial countries consuming large amounts of crude oil locate oversea distance from oil producing countries. As a consequence, 2.4 milliard tones of crude oil are transported annually over the sea. Accidents of oil tankers cause serious pollution of the marine environment and large amounts of oil are spilled into the sea water within a short time. Therefore, removal of crude oil and petroleum products that are spilled at sea is a serious problem of the last decades. Among existing techniques for the removal of oil, the use of sorbents is generally considered to be one of the most efficient techniques. The aim of this thesis is the preparation of sorbents based on various rubbers for the removal of crude oil and petroleum products from waters. To achieve this aim, macroporous organogels were prepared by crosslinking of various rubbers in frozen benzene solutions using sulfur monochloride (S_2Cl_2) as a crosslinking agent. Our strategy to synthesize such organogel sorbents is the application of the cryogelation technique which is based on conducting the crosslinking reactions below the freezing point of the reaction system.

Macroporous organogels were prepared from frozen solutions of butyl rubber (PIB), polybutadiene (CBR), and styrene-butadiene rubber (SBR) in benzene at -18^{o}C using sulfur monochloride as the crosslinker. It was found that the pores in CBR and SBR networks are regular and oriented along a common direction, whereas those in PIB networks are irregular with broad size distributions from μm to mm sizes. The regular morphology of CBR and SBR networks is due to the fact that benzene is a good solvent for CBR and SBR chains such that pores are only generated by the cryogelation mechanism. Sorption tests conducted using the organogels demonstrate that they are efficient materials for the removal of crude oil, petroleum products and olive oil from surface waters.

The most important feature of the rubber gels is their reusability after simply being squeezed; the continuous sorption capacities of CBR and SBR gels for crude oil and olive oil are 33–38 and 24–27 g/g, which are two to three times the capacity of the gels derived from PIB. The measured sorption capacities of all organogels are also much higher than those of commercial oil sorbents, suggesting that the rubber gels are a better alternative to the widely used polypropylene sorbents because of their improved efficiency for oil sorption and their reusability.

PETROL DÖKÜNTÜLERİNİ TEMİZLEMEK İÇİN BUTİL,POLİBUTADİEN VE STİREN-BUTADİEN KAUÇUK ESASLI ORGANOJELLER

ÖZET

Endüstriyel ülkeler fazla miktarlarda ham petrol tüketirler. Bu ülkeler üreten ülkelere deniz aşırı mesafede bulunurlar. Sonuç olarak yılda 2,4 milyar ton ham petrol deniz yoluyla taşınmaktadır. Tanker kazalarında kısa zaman içinde denizin içine yayılan petrol deniz çevresinde ciddi kirliliğe neden olur. Bu nedenle son yıllarda petrol ve petrol ürünlerinin denizden çıkarılması ciddi bir sorun oluşturmuştur.

Petrolün çıkarılması için mevcut teknikler arasında, sorbentlerin kullanmak genellikle en etkili tekniklerden biri olarak kabul edilir. Bu tezin amacı, sulardan ham petrol ve petrol ürünlerinin uzaklaştırılması için çeşitli kauçuk esaslı sorbentlerin hazırlanmasıdır. Bu amaca ulaşmak için, makrogözenekli organojeller çapraz bağlayıcı olarak kükürt monoklorür (S_2Cl_2) kullanılarak donmuş benzen çözeltileri içinde çeşitli kauçukların çapraz bağlanması ile hazırlanmıştır. Böyle organogel sorbentler sentezlemek için stratejimiz kriyojellesme tekniğinin uygulamasıdır. Bu teknik reaksiyon sisteminin donma noktasının altında çapraz bağlanma reaksiyonlarına dayanmaktadır.

Makrogözenekli organojeller bütil (PIB), polybutadiene (CBR) ve stiren-butadien (SBR) kauçuklarının benzen içinde donmuş çözeltilerinin çapraz bağlayıcı olarak kükürt monoklorür kullanılmasıyla -18^{o}C 'de hazırlanmıştır. CBR ve SBR ağları içindeki gözeneklerin düzenli ve yönlenmiş olduğu , PIB ağlarının ise düzensiz olduğu ve boyutlarının μm ile mm arasında değiştiği bulumuştur. Kriyojelleşme mekanizması sonucunda CBR ve SBR jellerinde elde edilen düzenli morfoloji benzenin CBR ve SBR için iyi solvent olmasından kaynaklanmaktadır. Organojellerin su yüzeyinden ham petrol, petrol ürünleri ve sıvı yağ gibi kirleticilerinin giderilmesinde etkili olduğu emme testleriyle gösterilmiştir.

Kauçuk jellerinin en önemli özelliği tekrar tekrar kullanılabilir oluşlarıdır. CBR ve SBR jelleri ham petrol ve sıvı yağ sürekli emme kapasiteleri sırasıyla 33–38 ve 24 - 27 g/g'dır. Jellerin bu kapasitesi PIB jelinin yaklaşık iki üç katıdır. Tüm organojeller ölçülen emiş kapasiteleri ticari olarak kullanılan sorbentlerdenkinde çok daha yüksektir. Kauçuk jellerinin yüksek emiş kapasitesi ve tekrar kullanılabilmesi gibi özellikleri nedeniyle geniş kullanım alanı bulunan polipropilen easalı sorbentlerden daha iyi bir aletnatif olduğu düşünülüyor.

1. INTRODUCTION

Accidents involving oil tankers can result in the release of large volumes of crude oil, and this risk significantly increases along narrow seaways with heavy maritime traffic. Therefore, removal of crude oil and petroleum products that are spilled at sea is a serious problem of the last decades [1]. Among existing techniques for the removal of oil, the use of sorbents is generally considered to be one of the most efficient techniques [2-4]. Properties of an ideal sorbent material for oil spill cleanup include hydrophobicity, high uptake capacity and high rate of up take, buoyancy, reusability or biodegradability, and recoverability of oil.

Recently, we have reported the preparation of macroporous organogels based on butyl rubber (PIB), which is a linear polyisobutylene containing small amounts of internal unsaturated groups (isoprene units) [5-7]. It was shown that macroporous PIB gels are able to absorb large volume of organic solvents in a short period of time. The organogels were prepared by solution crosslinking of PIB using sulfur monochloride (S_2Cl_2) as a crosslinker by the cryogelation technique. This technique is based on the natural principle that sea ice is less salty than seawater, i.e., rejection of solutes from the growing ice crystals [8-13]. As in nature, during the freezing of a PIB solution in benzene or in cyclohexane with normal freezing temperatures of 5.5 and 6^{o}C, respectively, the solutes expelled from the solvent crystals concentrate within the channels between the crystals, so that the reactions only take place in these unfrozen liquid channels. After polymerization and, after thawing of solvent crystals, a macroporous material is produced whose microstructure is a negative replica of the crystal formed. It was shown that the frozen solutions of PIB in benzene or in cyclohexane can easily be crosslinked using S_2Cl_2 to produce responsive and durable materials with a macroporous structure [5,6]. Due to the hydrophobicity, fast-responsivity, and reusability, macroporous PIB gels are suitable sorbent materials in various applications including in the oil spill cleanup from surface waters [14].

Since the degree of unsaturation in PIB is low (1-3 %), one may expect that other rubbers with a higher degree of unsaturation will undergo the crosslinking reactions

at a lower rubber concentration, which would lead to the formation of organogels with higher sorption capacities. Here, we describe the preparation of macroporous organogels starting from various types of rubbers and compare their properties as a reusable sorbent for the removal of oil. In addition to PIB with two different degrees of unsaturation, cis-polybutadiene (CBR) and styrene-butadiene rubber (SBR) were used as the rubber component in the gel preparation. The crosslinking reactions were conducted in benzene using S_2Cl_2 as a crosslinker at -18^oC. As will be seen below, organogels derived from CBR and SBR exhibit different microstructures and much higher sorption capacities, as compared to those based on PIB.

2. BACKGROUND

2.1 Macroporous Gels

Polymeric gels are useful materials for drug delivery systems, artificial organs, actuators, on–off switches, separation operations in biotechnology, and processing of agricultural products. In these applications, the response rate of the conventional gel is not as fast as required due to the rate- limited diffusion process. In order to increase the response rate of these gels, several approaches were reported, such as reducing the size of the gel particles [15], creating dangling chains on the gel samples [16-18], or, constructing an interconnected pore structure within the polymeric matrices which is called macroporous gels [11,19,20].

Macroporous polymers emerged in the late 1950s as a result of the search for polymeric matrices suitable for the manufacture of ion-exchange resins with better osmotic shock resistance and faster kinetics [21]. In contrast to the polymers that require solvent swelling to become porous, macroporous polymers are characterized by a permanent porous structure formed during their preparation that persists even in the dry state. Their internal structure consists of numerous interconnected cavities (pores) of different sizes, and their structural rigidity is secured through extensive crosslinking.

In order to obtain macroporous gels, there are mainly two techniques, namely,

1. Phase separation technique that uses an inert diluent during the crosslinking reaction, and,
2. Cryogelation technique, which proceeds in the medium of a frozen reaction solution.

1.1.1 Macroporous gels formed by phase separation technique

Macroporous gels by this technique are mainly prepared by free-radical crosslinking copolymerization of vinyl and divinyl monomers in the presence of an inert diluent

(pore-forming agent) [22, 19, 23, 24]. A reaction-induced phase separation during the gel formation process and agglomeration of the phase-separated domains are responsible for the formation of macroporosity in the final material. By this technique, an inert diluent which is soluble in the monomer phase is used as a pore forming agent. After polymerization-crosslinking reactions, removing the diluent from the network results in a porous structure inside the gel matrix. The network synthesized without an inert diluent consists of a continuous polymer phase while the network synthesized in the presence of an inert diluent consists of voids (pores) of various sizes. Several inert diluents were used in the polymerization reactions to create pores, such as solvents or nonsolvents for polymer chains or inert linear polymers. In order to form a macroporous structure in dried state, a phase separation must occur during the crosslinking process [22, 25].

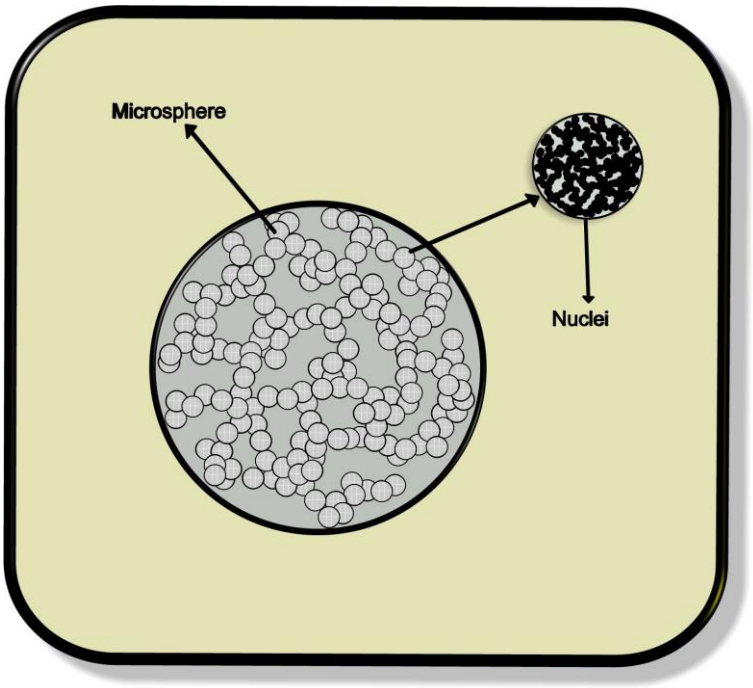

Figure 2.1: Schematic representation of various agglomerates in macroporous copolymer networks formed by phase separation technique.

The porous structure of such materials consists of agglomerates of domains of three different sizes (Figure 2.1). The definition of micro or macropores comes from the IUPAC classification of pores based on the pore width as follows [22].

1. The smaller particles called nuclei are about 10 nm in diameter. The nuclei are nonporous and constitute the highly crosslinked regions of the network. Microporous defined with widths of up to 2 nm appear between the nuclei.
2. The agglomerations of nuclei are called microspheres and they are about 10^2 nm in diameter. Mesopores defined with widths in the range 2 – 50 nm constitute the interstices between the microspheres.
3. Microspheres are agglomerated again into larger irregular moieties of 250 –1000 nm inside the polymer material. Meso and macropores appear between the agglomerates of the microspheres.

The divinyl monomer (crosslinker) content used in the gel preparation mainly determines the structure of the macroporous networks. At low crosslinker contents, the microspheres are more or less fused together to form large aggregates. As the crosslinker content is increased, the microspheres become less swollen and thus, more rigid, so that the voids between the microspheres (mesopores) become visible. The structures obtained at high crosslinker contents have nanometer to micrometer-sized pores and they look like cauliflowers, typical for a macroporous network [24]. As a result of this macroporous structure, these materials respond to the external stimuli very rapid.

From the above considerations, it is seen that, to obtain macroporous structures, that is to implement three hierarchies of pore structure at the same time, a high crosslinker content is needed, which necessarily results in low swelling ratios. This is the main disadvantage of such materials. Furthermore, due to the existence of polymer domains of various sizes, these materials have a broad and uncontrollable size distribution of pores.

2.1.2 Macroporous gels formed by low temperature gelation (cryogelation) technique

This technique consists of freezing the initial polymerization mixtures to an apparently solid monomer matrix before the gelation reactions [9]. Thus, the polymerization and crosslinking reactions are carried out below the bulk freezing

temperature of the reaction solution containing the monomers and the initiator [25]. During freezing of the reaction system, the unreacted monomers, initiator, as well as the polymer formed are expelled from the forming solid phase and entrapped within channels between the solvent crystals. As a result, the polymerization reactions can only take place in spatially restricted reaction fields, which are the unfrozen microchannels of the apparently frozen system [9-22,26-37, 24] (Figure 2.2). Since the actual concentrations of the monomer and the initiator in the microchannels are much larger than their nominal concentrations, the decrease of the rate constant of polymerization and crosslinking reactions at low temperatures is compensated by the increased monomer concentration in the reaction zones. Indeed, the critical monomer concentration for the onset of gelation is much lower in cryogelation systems compared with the conventional reaction systems, indicating the higher efficiency of crosslinking below the freezing temperature.

In these polymerization systems, although there is no phase separation during the course of the network formation process, the frozen zones of the reaction system act as templates during gelation, which can easily be removed from the gel by thawing, leading to macroporous structure. The reason why solvent in these solutions does not freeze at below the bulk freezing temperature is attributed, in the main, to the freezing point depression due to the solutes. Although the usual solute concentrations can lower the freezing point by only a few degrees, once solvent crystals are present, the effect is enhanced. This is because solutes are excluded from the solvent crystals and become more concentrated in the remaining unfrozen regions. Thus, as solvent freezes (crystallizes), the solute concentration in the liquid phase rises continuously, so that successively greater osmotic pressure is required to keep the liquid phase in the equilibrium with the pure solid phase.

Lozinsky and co-workers investigated in detail the polymerization – crosslinking reactions conducted below the freezing point of water [9] and called the resulting materials “cryogels”. Cryogels formed from dilute aqueous solutions of gelatin, poly(vinyl alcohol), chitosan, as well as from crosslinking copolymerization of acrylamide (AAm) and *N*,*N*-methylene(bis)acrylamide (BAAm) exhibit interconnected systems of macropores and, they have sponge-like morphologies [12, 13]. Xue et al. prepared fast responsive poly(N-isopropylacrylamide) (PNIPA) gels by using a two-step polymerization method, the initial polymerization being carried

out at 20°C, followed by cryopolymerization at -28°C for 24 hour [38]. Zhang and Chu demonstrated that the polymerization reactions in DMSO at temperatures below the melting point of DMSO produce macroporous PNIPA hydrogels with very regular pores of sizes 1 μm [25]. It was shown that the hydrogels exhibit superfast and stable oscillatory swelling-deswelling behavior in solvents. Other temperature sensitive hydrogels such as poly(N,N'-diethylacrylamide) hydrogels prepared by cryogelation technique also exhibit superfast response rates against temperature changes [37]. Plieva et al. showed that the pore size and the thickness of pore walls in poly(acrylamide) (PAAm) cryogels can be control by varying the initial monomer concentration of the reaction system [15]. Increasing monomer concentration increases the thickness of the pore walls but decreases the total porosity of the cryogels. Moreover, increasing the freezing rate of the reaction system during gelation also affects the size and the size distribution of pores in the cryogels [16].

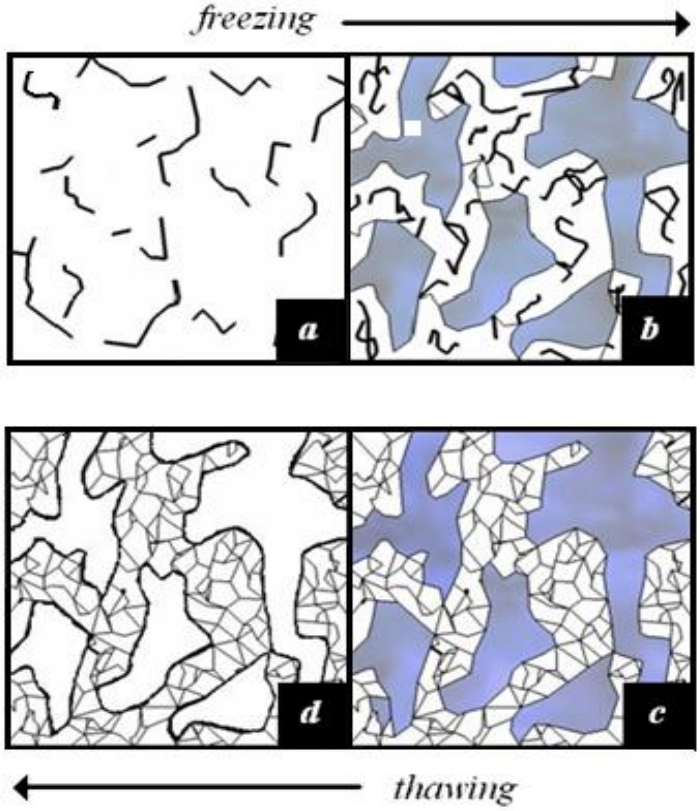

Figure 2.2: Schematic presentation of polymerization of apparently-frozen monomer solutions and formation of macroporous structure in a continuous polymer matrix. a) monomer solution; b) ice crystals in blue colour and monomer solution in the unfrozen liquid channels; c) crosslinked polymer and ice crystals; d) crosslinked polymer with macropores (cryogel). [39]

The main characteristic features of the cryogelation reaction can be summarized as below (Figure 2.2) [40]:

1. The reaction mixture containing gel-forming agents (e.g., monomer or polymer solution containing a crosslinker) is frozen at temperatures at least a few degrees centigrade below the solvent freezing point. The frozen system, despite looking as a single solid block, remains essentially heterogeneous and contains so-called unfrozen liquid microphase (UFLMP) along with the crystals of the frozen solvent.

2. Gel-forming reagents are concentrated in UFLMP, that is, cryoconcentration takes place. As UFLMP presents only a small portion of total initial volume, the concentration of gel precursors increases dramatically promoting the gel-formation.

3. The crystals of frozen solvent act as a pore-forming agent. When melted, they leave voids, macropores, filled with the solvent. The surface tension between solvent and gel phase rounds the shape of the pores, making pore surface smoother.

4. When freezing, the solvent crystals grow till they meet the facets of other crystals, so after thawing a system of interconnected pores arises inside the gel. The dimensions and shape of the pores depend on many factors; the most important are the concentration of precursors and the regimes of cryogenic treatment.

5. The polymer phase of the cryogel has micropores formed in between the polymer chains. Thus, cryogels have both heterophase and heteroporous structure (Figure 2.2).

Ozmen showed that the formation of a porous structure by the cryogelation technique leads to drastic changes in both the swelling and mechanical properties of the resulting hydrogels [28]. The hydrogels were prepared by free-radical crosslinking copolymerization of the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomer with BAAm crosslinker at an initial monomer concentration of 5 w/v % in water. The crosslinker (BAAm) content in the monomer mixture was 17 mol %. Depending on the gel preparation temperature T_{prep}, two different regimes were observed from the experiments. At T_{prep}= -8^{o}C or above, poly(AMPS)

(PAMPS) hydrogels exhibit relatively high swelling ratios V_{eq} of the order of 10^1 , and low moduli of elasticity G in the range of 10^2–10^3 Pa. However, decreasing T_{prep} below -8°C results in a tenfold decrease in the swelling ratio and about tenfold increase in the elastic modulus of gels. Thus, the swelling and elastic properties of PAMPS drastically change as T_{prep} is decreased below -8°C. The hydrogels formed at or above -8°C were transparent, while those formed at lower temperatures were opaque, indicating that these gels have separate domains in a spatial scale of submicrometers to micrometers [25]. Figure 2.3 showing SEM images of PAMPS networks formed at various T_{prep}, indicates that all of the polymer samples formed below -8°C have a porous structure with pore sizes of 30 – 50 μm while those formed at or above -8°C exhibit a continuous morphology. At -10°C, the pore walls seem to be too weak, so that they are more or less fused together to form large aggregates (Figure 2.3).

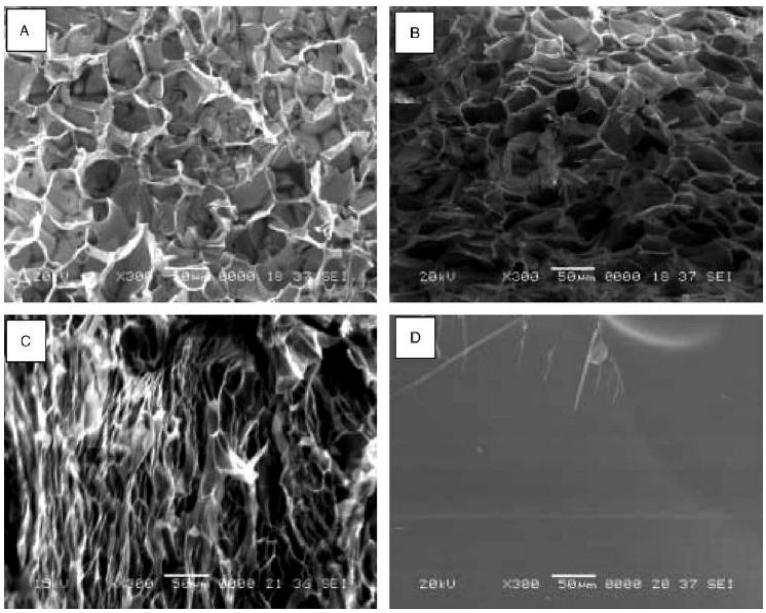

Figure 2.3: SEM of PAMPS networks formed at T_{prep} = -22(A), -18 (B), -10(C), and -8°C (D). The scaling bar is 50 μm. (Taken from [12])

It was shown that completely reversible swelling-deswelling cycles can be obtained using PAMPS hydrogels prepared below -8^{o}C [28, 23]. Gels formed below -8^{o}C attain their equilibrium swollen volumes in less than 30 sec, while those formed at higher temperatures require about 1 h to reach their equilibrium state in water. Moreover, if swollen PAMPS hydrogels are immersed in acetone, those prepared below -8^{o}C attain their equilibrium collapsed state in 5 to 10 min, while those formed at higher temperatures were too weak to withstand the volume changes. Thus, decreasing T_{prep} below -8^{o}C results the formation of superfast-responsive PAMPS hydrogels, which are also stable against volume changes.

Ceylan and Okay applied the cryogelation technique to organic reaction systems [29]. They showed that, using sulfur monochloride (S_2Cl_2) as a crosslinker, the solution crosslinking of butyl rubber in benzene at temperatures below the freezing point of the reaction system, followed removal of solvent crystals produce macroporous organogels containing pores with the approximate shape and dimensions of the solvent crystals. The organogels contained about 97 % organic liquid and they were very tough; they can be compressed up to about 100 % strain without any crack development. Further, the compressed gel immediately swells in contact with good solvents to recover its original shape. The critical polymer concentration for the onset of gelation was found to be much lower in the cryogels compared to the conventional organogels. It was shown that, decreasing the reaction temperature from 20^{o}C to -18^{o}C leads to a 50-fold decrease in the critical polymer concentration for the onset of gelation. As seen in Figure 2.4, where the gel fraction W_g is plotted against the BR concentration; a polymer concentration of about 0.05 w/v % was sufficient for the onset of gelation at -8^{o}C. The result demonstrated that S_2Cl_2 acts as an effective crosslinker at low temperatures due to the high local concentration of polymer and the crosslinker in the apparently frozen reaction system.

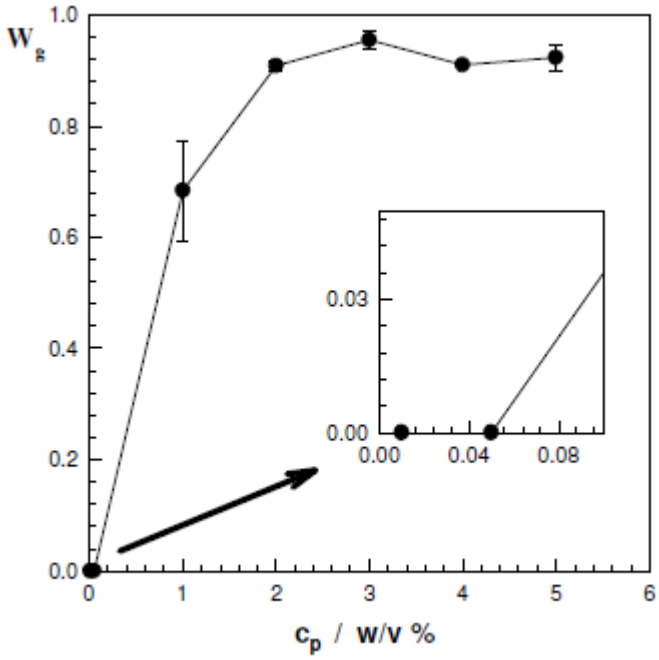

Figure 2.4: Gel fraction W_g plotted against the initial BR concentration c_P. S_2Cl_2 = 6 %, T_{prep} = -18°C [5].

2.2 Theory of Cryogelation

The occurrence of polymerization and crosslinking reactions below the freezing point of the reaction system is due to the presence of unfrozen regions in which the reactions proceed. Thus, even when cooled below bulk freezing temperature, some water in aqueous solutions remains unfrozen. The amount of the unfrozen water depends on the temperature and on the amount and type of the solute in the solution. Assuming a thermodynamic equilibrium condition between the ice and the gel phases at the gel preparation temperature T_{prep}, the relationship between the polymer concentration in the unfrozen gel phase and the temperature was given by [12].

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$$\frac{1}{T_f} = \frac{1}{T_f^o} - \frac{R}{\Delta H_m}\left[\ln(1-\nu_2) + \nu_2 + \chi\nu_2^2 + 0.5\nu_e V\nu_2 - f\nu_2\right] \quad \textbf{(2.1)}$$

where ΔH_m is the molar enthalpy of fusion of pure ice, T_f^0 is the normal freezing point of pure water, ν_2 is the volume fraction of polymer in the unfrozen zones of the reaction system, c is the polymer-solvent interaction parameter, ν_e is the effective crosslink density of the network, ν_1 is the molar volume of solvent, f is the effective charge density, i.e., the fraction of charged units in the network chains that are effective in gel swelling. Note that the polymer volume fraction ν_2 relates to the polymer concentration c in the unfrozen reaction zone (in w/v %) by.

$$c = \nu_2 \rho 10^2 \quad \textbf{(2.2)}$$

where ρ is the polymer density. Further, assuming complete monomer conversion, the volume fraction of ice in the reaction system f_{ice} can be calculated as

$$f_{ice} = 1 - \frac{c_o}{c} \quad \textbf{(2.3)}$$

where c_o is the initial monomer concentration. Calculations using above equations for various cross-link densities ν_e show that the effect of the gel elasticity on the freezing-point depression is negligible [12]. However, the gel preparation temperature T_{prep} and the degree of ionization of the reaction system have important effects on the freezing characteristics of the reaction system. For example, during the polymerization at an initial monomer concentration of c_0 = 5% and at T_{prep} = -22, -10, and -5°C, the respective polymer concentrations in the reaction zones are 30.6, 13.5, and 6.7%, while the ice fractions, i.e., the porosities of the resulting networks after thawing, are 0.84, 0.63, and 0.25, respectively. Thus, the lower the T_{prep}, the higher is the polymer concentration in the reaction zones and the larger ice fraction. Further, calculation results also predict that a decrease in the charge density f of the network chains would increase the volume fraction of ice in the reaction system, so that the pores in the final hydrogels would be larger.

2.3 Vulcanization of Butyl Rubber

Since the present work applies the cryogelation technique to the crosslinking reactions of various rubbers including butyl rubber (BR), some characteristics of BR are summarized in this section.

As is well known, vulcanization refers to a specific crosslinking (curing) process of rubber invented by Charles Goodyear in 1844, involving high heat and the addition of sulfur [36]. A method of cold vulcanization (treating rubber with a sulfur compound) was developed by Alexander Parkes in 1846. It is a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulfur atoms, the properties of the latter are decisively influenced by the course of vulcanization, as shown in Figure 2.5. In particular the modulus, hardness, elastic properties, resistance to swelling, etc. are considerably modified during the progress of vulcanization [12]. The invention of vulcanization made possible the wide use of rubber and aided the development of such industries as the automobile industry [15].

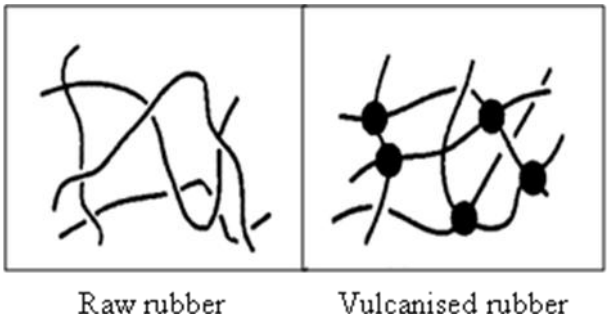
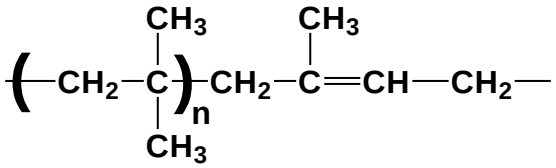


Figure 2.5: Schematic representation of a raw rubber (left) and vulcanised rubber.

Types of rubber in common use today are natural and synthetic. Even though only one chemical type of natural rubber exists, there are approximately twenty different chemical types of synthetic rubber, and within each type there are many distinguishable grades. The different types of rubber, each with its own properties and advantages, allow industry to choose the rubber that most clearly meets the demands of an intended use.

Butyl rubber (PIB) also known as polyisobutylene is a type of synthetic rubber consisting of poly(isobutylene) chains containing small amounts of (about 0.5 to 3 mol %) isoprene units. The structure of PIB may be represented as follows, where n is a number between 30 and 200:



butyl rubber

Figure 2.6: Formulation of butly rubber.

To obtain rubber products with the best possible properties which greatly differ according to the application concerned, it is necessary to use the most suitable combination of vulcanization conditions and auxiliaries [37]. Due to the low degree of unsaturation in butyl rubber, its vulcanization (crosslinking) requires much powerful accelerators than the natural rubber. Butyl rubber cannot be vulcanised with peroxides due to the chain scission reactions. For the preparation of heat resistant compounds, e.g., in cable insulation stocks, its vulcanization is carried out using dioximes. For exceptional heat resistant applications such as in tires, phenolic resins are used as the vulcanization agent.

2.3.1 Vulcanization in bulk

In general vulcanization of butyl rubber in bulk can be performed by three methods:

2.3.1.1 Using elemental sulfur and an organic accelerator

As mentioned above, butyl rubber is considerably more reluctant to vulcanize than natural rubber. The grades with the lowest degree of unsaturation are so inert they can only be vulcanized with difficulty when sulfur and accelerators are employed. The more unsaturated types can be vulcanized more easily with elemental sulfur.

2.3.1.2 Using polyfunctional nitroso compounds

Nitroso compounds such as p-benzoquinone dioxime has a crosslinking effect on many types of rubber because of their radical action. It is best known and most useful as a crosslinking agent for butyl rubber. As already mentioned, the vulcanization of buyl rubber with sulfur and organic accelerators does not give particularly good heat

resistance. In this respect, however, p-benzoquinone dioxime and dibenzoyl-p benzoquinone dioxime have proved particularly useful.

2.3.1.3 Using reactive methylol phenol resins

In a dissertation published in 1947, van der Meer examined the vulcanizing reaction of numerous phenol formaldehyde condensates including the halogen methyl phenols. Since then, many crosslinking mechanisms associated with the resin crosslinking. The results of the work described above have been applied methodically to the vulcanization of butyl rubber [18].

2.2.2 Vulcanization in solution

Although a large number of publications and patents have been reported on the vulcanization of butyl rubber in bulk, the first successful study concerned with the vulcanization of rubber in solution was published in 2000. According to this study, butyl rubber can easily be crosslinked in an organic solution using sulfur mono chloride as a crosslinking agent [19]. Sulfur monochloride, S_2Cl_2, is a liquid at room temperature and soluble in organic solvents. It was shown that sulfur monochloride is an effective crosslinking agent for butyl rubber in organic solutions. The crosslinking reaction between the PIB chains via sulfur monochloride is believed to proceed in steps as in the reaction between ethylene and sulfur monochloride [37, 19]. Attack of sulfur dichloride to the internal vinyl group of the polymer leads to the formation of pendant sulfur chloride groups on the PIB chains acting as potential crosslink points. Reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective crosslinks. In the work mentioned above, dried PIB gels were also subjected to sulfur analysis. The results show that, increasing crosslinker concentration in the feed also increases the sulfur content of the networks.

2.2.3 Vulcanization in frozen solutions

As mentioned in previous sections, Ceylan and Okay applied the cryogelation technique to the vulcanization of butyl rubber (PIB) in frozen solutions [19]. It was shown that PIB can be crosslinked using S_2Cl_2 as a crosslinker in benzene solutions at temperatures below the freezing point of the reaction system. After removing of benzene crystals, they produced PIB gels containing pores with the approximate

shape and dimensions of the solvent crystals. The organogels contained about 97 % organic liquid and they were very tough; they can be compressed up to about 100 % strain without any crack development. Further, the compressed gel immediately swells in contact with good solvents to recover its original shape. It was also shown that PIB gels are able to absorb large volume of organic solvents in a short period of time. The critical polymer concentration for the onset of gelation was found to be much lower in the cryogels compared to the conventional organogels. It was shown that, decreasing the reaction temperature from 20^{o}C to -18^{o}C leads to a 50-fold decrease in the critical polymer concentration for the onset of gelation. The result demonstrated that S_2Cl_2 acts as an effective crosslinker at low temperatures due to the high local concentration of polymer and the crosslinker in the apparently frozen reaction system.

Since the degree of unsaturation in PIB is low (1-3 %), one may expect that other rubbers with a higher degree of unsaturation such as polybutadiene will undergo the crosslinking reactions at a lower rubber concentration which would lead to the formation of organogels with higher sorption capacities. This is the main topic of the present thesis. Here, we describe the preparation of macroporous organogels starting from various types of rubbers and compare their properties as a reusable sorbent for the removal of oil. In addition to PIB with two different degrees of unsaturation, cis-polybutadiene (CBR) and styrene-butadiene rubber (SBR) were used as the rubber component in the gel preparation. The crosslinking reactions were conducted in benzene using S_2Cl_2 as a crosslinker at -18^{o}C. As will be seen below, organogels derived from CBR and SBR exhibit different microstructures and much higher sorption capacities, as compared to those based on PIB.

3. EXPERİMENTAL

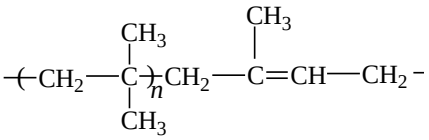
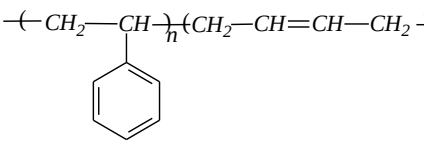
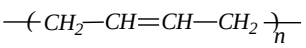
3.1 Materials

The materials used in the preparation of the organogels are described below.

Linear Polymer : Butyl rubber (PIB), cis-polybutadiene (CBR) and styrene butadiene rubber (SBR) were used as the starting materials for the organogel preparation (Table 3.1). PIB is a linear polyisobutylene containing small amounts of isoprene units. PIB-065 and PIB-365 used in this work contain 1.1 and 2.3 % unsaturations, which were denoted by PIB1 and PIB2, respectively. SBR is a copolymer with about 76 % unsaturated groups while each repeat unit of CBR has one unsaturated group.

The rubbers were purified by dissolving in toluene followed by precipitation into methanol and drying at room temperature under vacuum to constant mass. The molecular weights of the rubbers were determined in cyclohexane using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically polarized 30mW Gallium-arsenide laser operating at λ=690 nm and 18 scattering angles simultaneously detected scattering angles. Weight-averaged molecular weights, Mw of the rubbers PIB1, PIB2, SBR and CBR were found to be 310, 360, 210 and 371 kg/mol, respectively.

Table 3.1: Properties of the rubbers used in the preparation of the organogels.

RUBBER	CODE	PROPERTIES	FORMULA
Butyl rubber (Butyl 065)	PIB1	1.1 % unsaturation, density: 0.92 g/mL $\overline{M}_w$ = 3.1x10^5 g/mol	
Butyl rubber (Butyl 365)	PIB2	2.3 % unsaturation, density: 0.92 g/mL $\overline{M}_w$ = 3.6x10^5. g/mol	
Styrene-butadiene rubber (SBR-1502)	SBR	23.6 % bound styrene, density: 0.94 g/mL $\overline{M}_w$ = 2.1x10^5. g/mol	
Cis polybutadiene (CBR-1203)	CBR	9% cis-, 76% trans-1,4-butadiene, 15 % vinyl-1,2-butadiene, density: 0.93 g/mL $\overline{M}_w$ = 3.7x10^5. g/mol	

Crosslinker : Sulfur monochloride (S_2Cl_2)

The crosslinking agent sulfur monochloride was purchased from Aldrich Co.

Solvent : Benzene, toluene and methanol

Benzene (Merck) was used as the solvent for the solution crosslinking process. In the swelling- deswelling experiments, reagent grade toluene and methanol (Merck) were used without further purification.

3.2 Experimental Set-up and Equipment

3.2.1 Electronic digital compass

The diameters of the cylindrical gel samples were measured using a calibrated digital compass (Mitutoyo). The device has a measuring range between 0-150 mm with an accuracy ± 0.02 mm.

3.2.2 Digital thermometer

The digital thermometer (Hanna, Checktemp. Pocket Thermometer) was used in the experiments.

3.2.3 Uniaxial compression apparatus

In order to measure mechanical properties of the gel samples, a home-made uniaxial compression apparatus was used. This apparatus is consisted of three parts as shown in Figure 5.1. A digital comperator is sensitive to displacements of 10^{-3} mm and the balance is from Sartorius (IDC type Digimatic Indicator 543-262, Mitutoyo).

3.2.4 Desiccator

A Desiccator is used for removal of solvents from the gel.

3.2.5 Magnetic stirrer

AREX magnetic stirrer with a heating plate was used in the experiments. The instrument is equipped by a connection for a contact Vertex thermoregulator for the direct control of temperature from ambient to 150°C with an accuracy of 0.5°C.

3.2.6 Optical microscopy

An Olympus Biological Microscope Model CX31 was used to monitor the interior morphology of the organogels in their swollen state.

3.2.7 Syringes

Gelation experiments were carried out in plastic syringes with 16.4 mm internal diameters.

3.3 Synthesis of the Organogels

The organogels were prepared by solution crosslinking technique at various rubber concentrations (C_P) between 1 and 5 w/v % according to the following scheme: Rubber (1 to 5 g) was first dissolved in 100 mL of benzene at 20±1^{o}C overnight. Then, portions of this solution, each about 25 mL, were transferred to volumetric flasks and different amounts of sulfur monochloride were added under rigorous stirring. The homogeneous reaction solutions were transferred into plastic syringes of 16.4 mm internal diameter. The crosslinking reactions were carried out in a cryostat at -18^{o}C for 1 day. The crosslinker concentration in the reaction solution, S2Cl2 %, was expressed as the volume of S_2Cl_2 added per 100 g of butyl rubber. The organogels in the form of cylindrical tissues of about 14 cm in diameter were also prepared as described above, except that the gelation reactions were carried out in several glass petri dishes of 140 mm in diameter and 20 mm in height. The dishes were sealed with glass plates and the reaction was conducted in a cryostat at -18^{o}C for 1 day. After the reaction, the reaction system was thawed at room temperature for 1h and the gel formed was squeezed to remove benzene. It was then washed several times first with toluene then with methanol and finally dried under vacuum at room temperature.

4. CHARACTERIZATION METHODS

4.1 Equilibrium Swelling Measurements

The swelling behavior of gels was investigated in toluene. PIB gels were taken out of the syringes, and they were cut into specimens of approximately 10 mm in length. Each gel sample was immersed in an excess of toluene at 20^{o}C, and the toluene was replaced every other day over a period of at least for one month to wash out the soluble polymer and the unreacted crosslinker.

The swelling equilibrium was tested by measuring the diameter of the gel samples by using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. In order to dry the equilibrium swollen gel samples, they were first immersed in methanol over night and then dried under vacuum.

The gel fraction W_g defined as the amount of crosslinked (insoluble) polymer obtained from one gram of butyl rubber was calculated as:

$$W_g = \frac{m_{dry}}{10^{-2} m_o \, c_P / d_B} \qquad \textbf{(4.1)}$$

where m_{dry} and m_o are the weights of the gel samples after drying and just after preparation, respectively, C_P is the rubber concentration at the gel preparation in w/v %, and dB is the density of benzene at 20^{o}C (0.877 g/mL).

For volumetric measurements, the diameters of the gel rods after swelling D and after drying D_{dry} were measured by a calibrated digital compass as well as by the image analyzing system (Fig. 4.1). The equilibrium volume-swelling ratio of the gel samples with respect to the after drying state was calculated as:

$$q_v = \frac{V}{V_{dry}} = \left(\frac{D}{D_{dry}} \right)^3 \qquad \textbf{(4.2)}$$

where V_{dry} is the volume of the dry gel. D and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively.

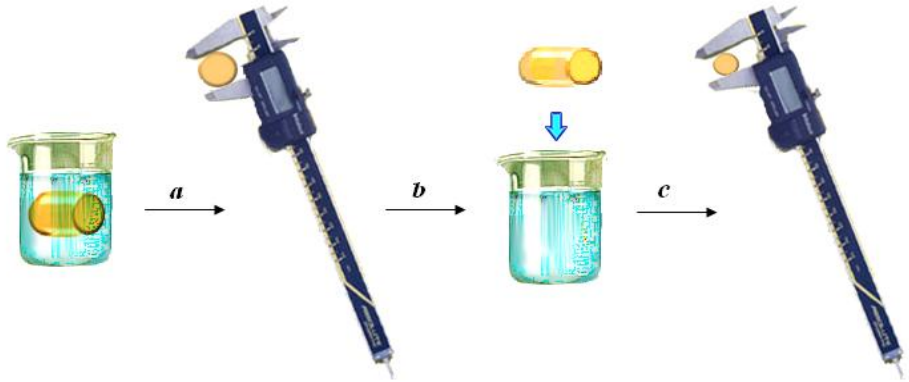


Figure 4.1: Schematic representation of the swelling measurements. a) measuring the diameter of the equilibrium swollen gel; b) immersing the gel to the bad solvent (methanol); c) measuring the diameter of the collapsed gel by a digital compass

For gravimetric measurements, the weights of the gel rods after drying m_{dry} and after swelling m_{sw} were measured on an electronic balance. The equilibrium weight swelling ratio of the gel samples with respect to the after their dry state was calculated as:

$$q_w = \frac{m_{sw}}{m_{dry}} \qquad \textbf{(4.3)}$$

where m_{dry} is the weight gel after drying.

4.2 Swelling-Deswelling Kinetics Measurements

For the deswelling kinetics measurements, the equilibrium swollen organogel samples in toluene were immersed in methanol at 20°C. The weight changes of gels were measured gravimetrically after blotting the excess surface solvent at regular time intervals (Figure 4.2). For the measurement of the swelling kinetic of gels, the collapsed gel samples in methanol were transferred into toluene at 20°C. The weight changes of gels were also determined gravimetrically as described above. The result were interpreted in terms of the normalized gel mass with respect to its swollen state

$$m_{rel} = m_t / m, \qquad \textbf{(4.4)}$$

where m_t is the mass of the gel sample at time t. The temperature dependent swelling measurements of gels were conducted in-situ by following the diameter of gel

samples immersed in benzene under microscope using the image analyzing system mentioned above. The results were given as the relative volume swelling ratio

$$V_{rel} = (D_t / D_o)^3 \quad \textbf{(4.5)}$$

where D_t and D_o are gel diameters at a given temperature ad after preparation, respectively.

4.3 Mechanical Measurements

For the mechanical measurements, the organogels were prepared in several plastic syringes of 16.4 mm internal diameters and about 100 mm length. After the reaction, the gels were cut into specimens of approximately 15 mm in length.

Uniaxial compression measurements were performed on equilibrium swollen gels in toluene and in a thermostated room of 20 ± 0.5°C by using an apparatus which is schematically shown in Figure 4.2.

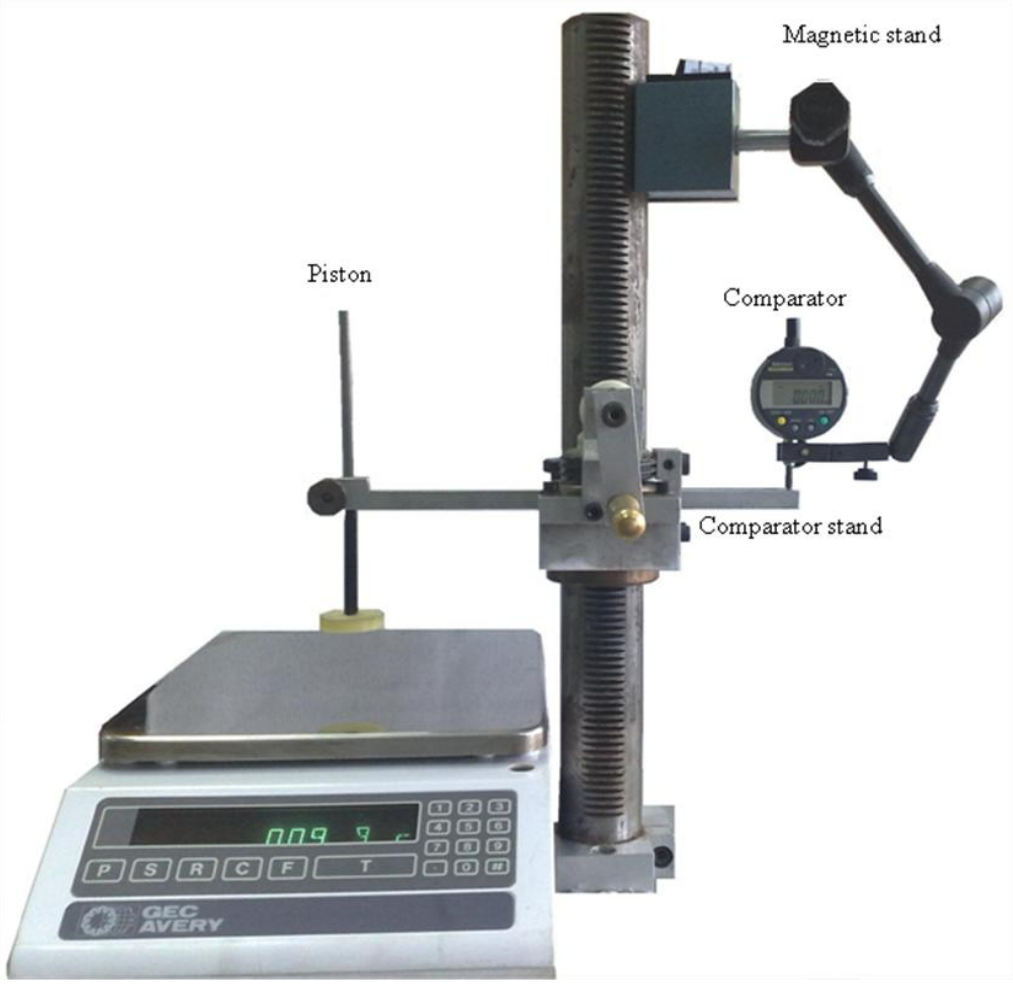


Figure 4.2: Uniaxial compression apparatus for measuring stress-strain data.

A cylindrical gel sample of about 16-20 mm in diameter and 15 mm in length was placed on a digital electronic balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE (Teflon) end-plate. The force acting on the gel *F* was calculated from the reading of the balance m as F = mg, where g is gravitational acceleration (g = 9.80 $m.s^{-2}$). The elastic modulus *G* was determined from the slope of linear dependence [40].

$$f = G(\alpha - \alpha^{-2}) \quad \textbf{(4.6)}$$

where *f* is the force acting per unit cross-sectional area of the undeformed gel specimen, and a is the deformation ratio (deformed length/initial length). Deformation ratio was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo) which was sensitive to displacements of 10^{-3} mm.

4.4 Pore Volume and Porosity Calculations

Total volume of the pores in a porous material (with an open-pore structure) can be estimated from the uptake of poor solvents. In the present work, the pore volume V_p of the networks was estimated through uptake of methanol of dry gels. Since methanol is a nonsolvent for BR, it only enters into the pores of the polymer networks while the polymer will not absorb the solvent. Thus, V_p (mL pores in one gram of dry polymer network) in the material can be estimated from the amount of the absorbed poor solvent as.

$$V_p = (m_M - m_{dry}) / (d_M\, m_{dry}) \quad \textbf{(4.7)}$$

where m_M is the weight of the network immersed in methanol after 2h and d_M is the density of methanol (0.792 g/ mL).

4.5 Texture Determination by Scanning Electron and Optical Microscop

The internal morphology of the gels was investigated by Scanning Electron Microscopy (SEM). The gels were dried by replacement of toluene with methanol (0→100 %) and were kept under vacuum at room temperature for one week. Thereafter, the dried gel samples were coated with gold using Sputter-coater S150B Edwards. JEOL JSM 6335F Field Emission Scanning Electron Microscope instrument was used for obtaining the SEM images of the dry gel samples.

The morphology of dry gels was also investigated by an optical microscope coupled with a PC and image analyzing system. An Olympus Biological Microscope Model CX31 was used to monitor the interior morphology of the organogels in their swollen state. For this purpose, the samples were first immersed into liquid nitrogen for 1 min and then, they were cut into thin slices of about 1 mm in thickness. After adding a few drops of oil for contrast enhancement, the measurements were conducted at various magnifications. Microphotographs taken from the gels were captured by Q Imaging Camera, MicroPublisher 3.3 RTV connected to PC, and analysed with software Image-Pro PlusVersion 6.0. The image analysing system used in the present work is shown in Figure 4.3.

Figure 4.3: Photograph of the image analyzing system. PC monitors (right), imaging camera (left).

5. PROCEDURE FOR OIL REMOVAL TESTS

Oil removal tests were conducted using organogel samples prepared in the form of cylindrical tissues of about 14 cm in diameter and 2 cm in thickness. Five mixtures were used to investigate removal of contaminants. These include gasoline, diesel fuel, crude oil, fuel oil, olive oil, whose characteristics are listed below:

1. Gasoline: BP super, 95 octane, lead-free, density = 0.720 – 0.775 g/mL, viscosity = 0.75 cP (38^{o}C),
2. Diesel fuel: BP ultimate diesel, setan number = 55, density = 0.85 g/mL, viscosity = 5.0 cP (25^{o}C),
3. Crude oil: From Ozan Sungurlu wells, Turkey. density = 0.89 g/mL, viscosity = 350 cP (25^{o}C),
4. Fuel oil: No.6 (Bunker C), density = 1.03 g/mL (15^{o}C), viscosity = 130 cP(25^{o}C)
5. Olive oil: From Kent Boringer, d = 0.918 – 0.923 g/mL, viscosity = 69 cP (25^{o}C). It is a mixture of saturated (11.4 %) and unsaturated fatty acids.

All tests were performed at 20 ±1^{O}C. The kinetics of the oil sorption process was determined by immersing 2 g of dry gel tissues into 500 mL of test solution and then monitoring the mass of the gel as a function of time. For this purpose, the gel was removed from the test solution at selected time intervals (30 s – 5 min) and weighed. The uptake capacity at time *t*, i.e., g of pollutants absorbed by 1 g of dry gel was calculated as:

$$(m_t - m_{dry}) / m_{dry} \qquad \textbf{(5.1)}$$

where m_t is the sorbent mass at time *t*.

The reusability of the gels as well as their continuous extraction capacities were determined by subjecting the gels to successive sorption-squeezing cycles under identical conditions. Dry gel samples were first immersed into 500 mL of test solution for 1 min and then, it was left to drip for 30 s. The saturated gel was weighed and then squeezed in the hand. The gel sample was then weighed again to calculate the amount of sorbed pollutant by 1 g of dry gel. This sorption squeezing

cycle was repeated 20 times to obtain the recycling efficiency and continuous extraction capacity of the rubber gels.

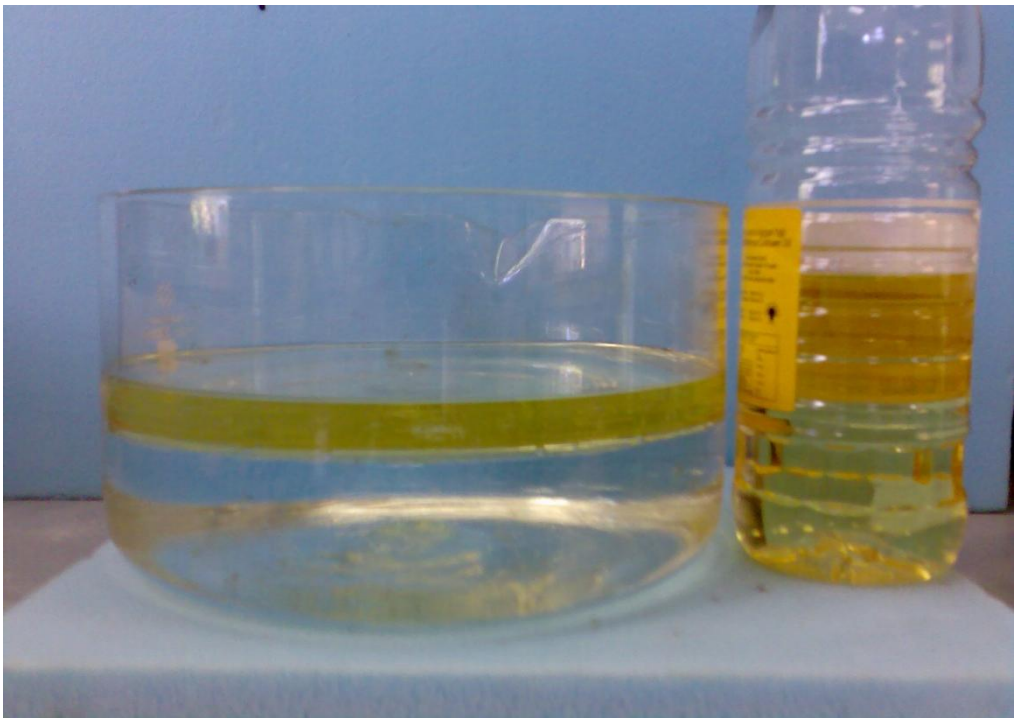


Figure 5.1: Eksperimental set up for the determination of the uptake capacity of the gels at time t = 2 min for pollutants spread on the water level.

6. RESULTS AND DISCUSSION

6.1 Effect of Crosslinker Concentration

In this section, the solution crosslinking of PIB1, PIB2, CBR and SBR in benzene using the crosslinker S_2Cl_2 was carried out at a temperature of -18^oC, which is about 23^oC below the bulk freezing temperature of benzene. We first investigated the crosslinking efficiency of S_2Cl_2 in a range of concentrations between 6% and 12%. Experiments conducted at a rubber concentration of 5% show that the gel fraction Wg, i.e., the amount of the crosslinked (insoluble) polymer obtained from one gram of rubber, is always close to unity (Wg > 0.98). This finding indicates that sulfur monochloride has high crosslinking efficiency even at very low reaction temperatures. This high efficiency is due to the high local concentrations of rubber and crosslinker in the unfrozen domains of the reaction system. As reported previously [5], when a 5% PIB solution was frozen at -18^oC, 14% of the benzene remained unfrozen in the frozen system. This means that, although the initial concentration of polymer was 5%, its concentration in the unfrozen liquid phase was approximately 36%. Thus, the reduced rate constant of the crosslinking reaction between sulfur monochloride and the vinyl groups at low temperatures is compensated for by the increased polymer concentration in the reaction zones.

The reason why benzene does not freeze completely at the reaction temperature that was below the bulk freezing temperature is likely due to a freezing point depression caused by the polymer. As benzene freezes, the polymer concentration in the liquid phase rises continuously so that successively greater osmotic pressure is required to keep the liquid phase in equilibrium with the pure frozen benzene phase.

The crosslinking reactions between the internal unsaturated groups of the rubbers via sulfur monochloride are believed to proceed in similar steps as in the reaction between ethylene and sulfur monochloride (Figure 6.1) [29,31].

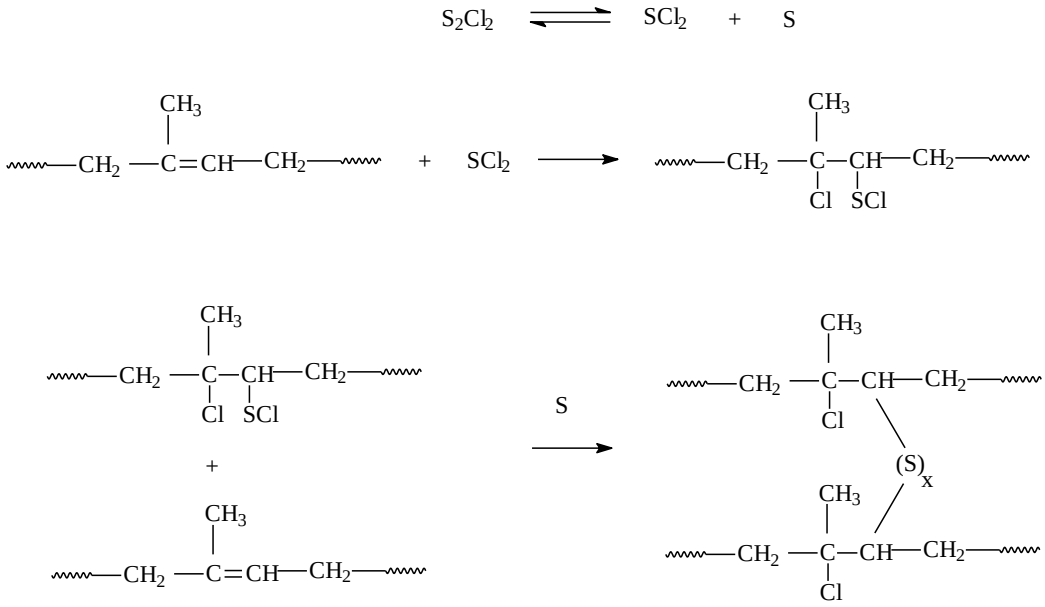


Figure 6. 1: Crosslinking reactions between the internal unsaturated groups of the rubbers via sulfur monochloride.

According to this scheme, attack of sulfur dichloride to the internal vinyl group of the polymer leads to the formation of pendant sulfur chloride groups on the chains, which act as potential crosslinking points. Reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective crosslinks. Assuming that the crosslinking reactions are complete, one may calculate the theoretical crosslink density, ν_{theo}, of the rubbers. In Table 1, the crosslinker ratio *X* (the molar ratio S_2Cl_2 / unsaturated group) and the corresponding ν_{theo} are shown for 6 and 12 % S_2Cl_2.

Table 6.1: Crosslink densities and sulfur contents of the cryogels formed at 5% rubber concentration and in the presence of 6% and 12 % S_2Cl_2. The degree of unsaturation of the rubbers is indicated. X = the crosslinker ratio, i.e., molar ratio S_2Cl_2/unsaturated group. ν_{theo} = theoretical crosslink density calculated from the amounts of S_2Cl_2 and internal unsaturated groups of the rubbers. ν_{chem} = chemical crosslink density calculated from the sulfur content (S %) of dry cryogels. The numbers in the parenthesis are standard deviations.

RUBBER	*X*		10^{-3} ν_{THEO} / MOL.M^{-3}		S %		10^{-3} ν_{CHEM} / MOL.M^{-3}	
	6%	12%	6%	12%	6%	12%	6%	12%
CBR (100 mol %)	0.040	0.080	1.4	2.8	3.0 (0.3)	3.3 (0.3)	1.8 (0.2)	2.0 (0.2)
SBR (86 mol %)	0.053	0.106	1.4	2.8	2.8 (0.3)	2.7 (0.2)	1.7 (0.2)	1.6 (0.1)
PIB2 (2.3 mol %)	1.8	3.6	0.38	0.38	< 1		< 0.6	
PIB1 (1.1 mol %)	3.8	7.6	0.18	0.18				

For both PIB1 and PIB2, the crosslinker S_2Cl_2 is in excess so that $\mathbf{\nu}_{theo}$ is determined by the number of unsaturated groups of the rubbers and, thus, $\mathbf{\nu}_{theo}$ is independent of the crosslinker concentration. However, for the rubbers with higher degrees of unsaturation, namely for SBR and CBR, the unsaturated groups are in excess and, therefore, $\mathbf{\nu}_{theo}$ increases with increasing concentrations of S_2Cl_2. To estimate the chemical crosslink density $\mathbf{\nu}_{chem}$ of the rubbers, the dried cryogel samples were

subjected to sulfur analysis after extraction. The results are shown in the fourth column of Table 1, where the sulfur contents S% (based on the dry mass) of the cryogels prepared at 5% rubber concentration are given. We see that the S% increases in the order PIB < SBR < CBR, i.e., in the order of the increasing unsaturation degree of the rubbers. From these sulfur content measurements, the chemical crosslink density $\mathbf{\nu}_{chem}$ was calculated as:

$$\nu_{chem} = \frac{2\,S\,d_2}{32\,x\,(100-S)} \qquad \textbf{(6.1)}$$

where S and d_2 are the sulfur content (S %) and the bulk density of dry rubber, respectively, and x is the number of sulfur atoms in each crosslink (Scheme 1). Assuming x = 1 and d_2 = 0.92, 0.94, and 0.93 g/mL for PIB, SBR, and CBR, respectively, the calculated results of ν_{chem} are shown in the last column of Table 1 for 6 and 12% S_2Cl_2. It is seen that at 6% S_2Cl_2, ν_{chem} is close to ν_{theo}, indicating that the reactions between the internal unsaturated group and the crosslinker S_2Cl_2 are complete after cryogelation. However, for both SBR and CBR, ν_{chem} does not show a substantial increase with increasing S_2Cl_2 concentration, which suggests that there was a reduced reactivity of the internal unsaturated groups available to the crosslinker molecule.

6.1.1 Equilibrium swelling properties of PIB gels

The swelling capacities of the rubber gels in toluene in terms of their equilibrium weights (q_w) and volume swelling ratios (q_v) are shown in Figure 6.1A and B for 6 and 12% S_2Cl_2, respectively. The gels were prepared starting from a 5% rubber solution. At 6% S_2Cl_2 (Figure 6.1A), the weight swelling ratios q_w of CBR and SBR gels were both approximately 40, which is about twice the swelling ratio q_w of PIB gels. Increasing S_2Cl_2 content decreases the swelling capacity of the organogels, especially those obtained from SBR and CBR. Further, the volume swelling ratios q_v of all gels were much smaller than their weight swelling ratios.

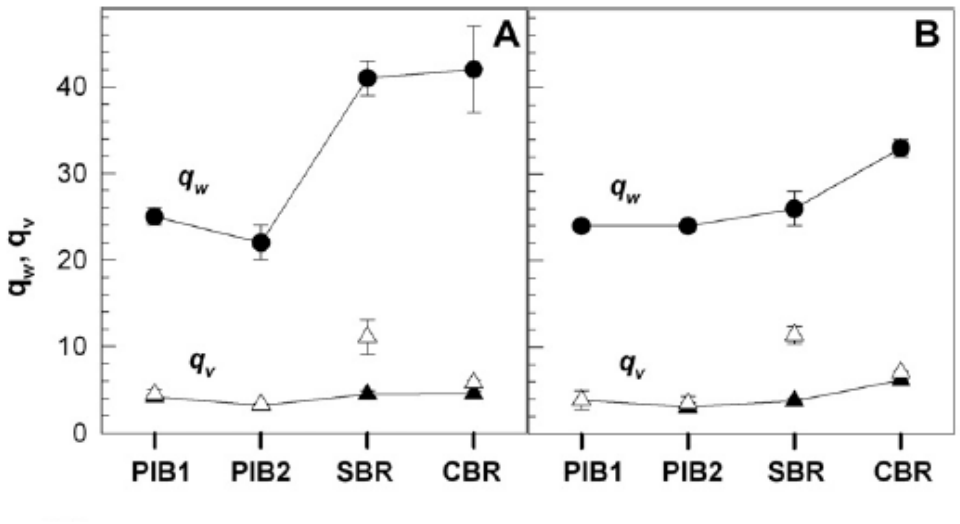


Figure 6.2: The equilibrium weight (q_w, circles) and volume swelling ratios (q_v, triangles) of cryogels formed at 6 (A) and 12% S_2Cl_2 (B). The values of q_v measured before and after drying the cryogels are represented by the filled and open symbols, respectively.

As mentioned in the literature [32], the porous structure of swollen gels may collapse during their drying process due to the instability of the pore walls. Such a process would lead to lower porosities in dry state and higher volume swelling ratios. To check this point, the volume swelling ratio q_v of cryogels were determined both before and after drying and, these values are indicated in Figure 6.1A and 6.1B by the filled and open triangles, respectively. An increase in q_v was observed for SBR cryogels after drying, suggesting a partial collapse of their porous structures.

According to the Flory-Rehner theory of swelling equilibrium, the effective crosslink density of gels is related to their volume swelling ratios [32]; the higher the effective crosslink density, the lower the volume swelling ratio of the gels. However, Figure 6.2A and B show that q_v slightly increases in the order PIB < SBR < CBR, which is in contrast to their chemical crosslink densities (Table 1), and needs some comments. Due to the low unsaturation degree of PIB rubbers, it is reasonable to neglect cyclization reactions during gelation, i.e., the formation of sulfur bridges between the unsaturated groups belonging to the same primary molecule. Increasing unsaturation degrees of PIB from 1.1% to 2.3% increased the effective crosslink density such that the cryogel formed from PIB2 swells less than that the cryogel from PIB1 (q_v = 3.2 versus 4.2 and 3.1 versus 3.9 for 6% and 12% S_2Cl_2, respectively). In contrast, CBR and SBR had higher degrees of unsaturation and promoted cyclization reactions due

to their local high concentration of internal vinyl groups in the gelation system, thus leading to increased numbers of elastically ineffective crosslinks and to higher swelling ratios. This explanation was also supported by the rubber elasticity of the cryogels. The cryogels derived from both SBR and CBR exhibit lower moduli of elasticity as compared to the PIB cryogels, demonstrating lower effective crosslink densities within the former gels.

6.1.2 Pore volume and porosity of PIB gels

The relative values of q_w and q_v provide information about the internal structure of macroporous gels because the weight swelling ratio includes the solvent located in both the pores and in the polymer region of the gel, while (assuming isotropic swelling) the volume swelling only includes the solvent in the polymer region. From the weight and volume swelling ratios of gels, porosities P_s can be estimated using the following equation [22]:

$$P_s\% = (1 - \frac{q_v}{(q_w - 1)d_2 / d_1}) \times 10^2 \qquad \textbf{(6.2)}$$

where d_1 is the density of the swelling agent (toluene). Using the densities of the rubbers together with d_1 = 0.876 g/mL, the calculated porosities P_s are shown in Figure 6.2A. Calculations are using the qv values determined prior and after drying the cryogels, which are represented by the filled and open symbols in Figure 6.3A, respectively. We see that all gels exhibit significant porosities; the average P_s is 86 ± 3% before drying, whereas it decreases in SBR cryogels after their drying.

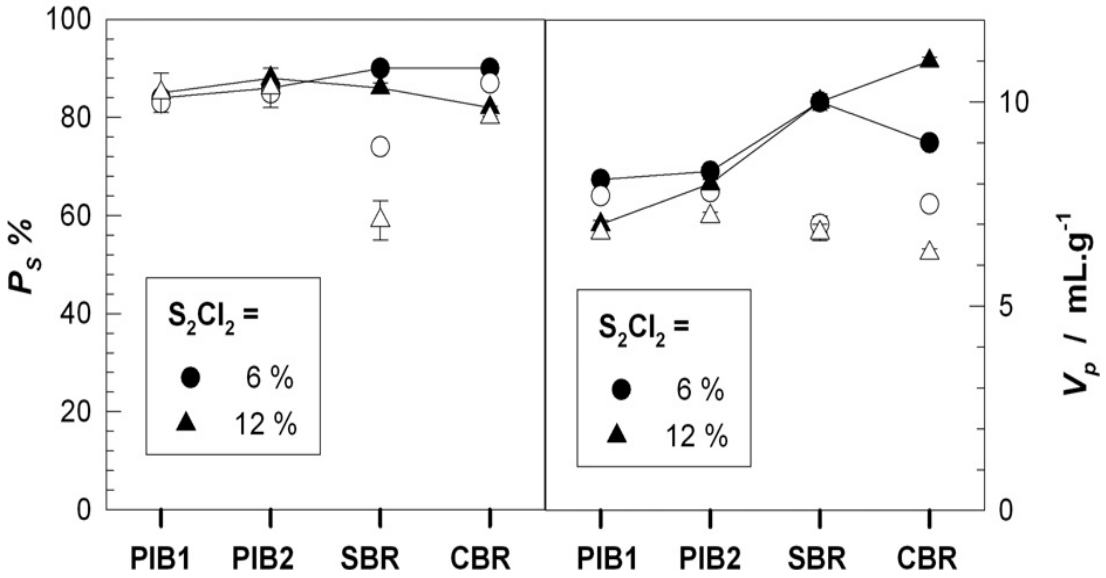


Figure 6.3: The calculated porosities P_s (A) and the total volume of the pores V_p (B) of cryogels formed at 6 (circles) and 12% S_2Cl_2 (triangles). C_p = 5%. P_s and V_p measured before and after drying the cryogels are represented by the filled and open symbols, respectively.

Figure 6.3B shows the total volumes of the pores, V_p, in the cryogels, which were estimated from the methanol uptake of the gel samples. The results are given for cryogels before (filled symbols) and after their drying (open symbols). In dry cryogels, V_p does not change much depending on the type of the rubber and the crosslinker concentration; the total pore volume in one gram of dry rubber is approximately 7 ± 0.5 mL, which enables the immediate penetration of the poor solvent, methanol, into the network structure. Moreover, the pore volumes of the cryogels derived from SBR and CBR are smaller after drying, which suggests that the pores partially collapse and/or the pore size decreases during the drying period of these gels. As will be seen later, the moduli of elasticity of SBR and CBR gels are much smaller than those of PIB cryogels. One may expect that, due to the weak network structure, the porous structure partially collapses during drying leading to smaller pore volumes.

6.2 Effect of the Polymer Concentration

The polymer concentration C_p during the gel preparation is known to be an important parameter affecting the swelling properties of gels [33,34]. Experiments conducted using PIB1 and PIB2 showed no gel formation at or below 2.5% rubber concentration. This is probably due to the low degree of unsaturation (1–2%) of the

PIB chains. However, organogels with complete conversion ($W_g \approx 1$) were obtained starting from the CBR and SBR polymers with unsaturation degrees of 100% and 86%, respectively. The sulfur contents of the CBR and SBR cryogels were found to be independent of C_p, indicating that the chemical crosslink density does not depend on the polymer concentration.

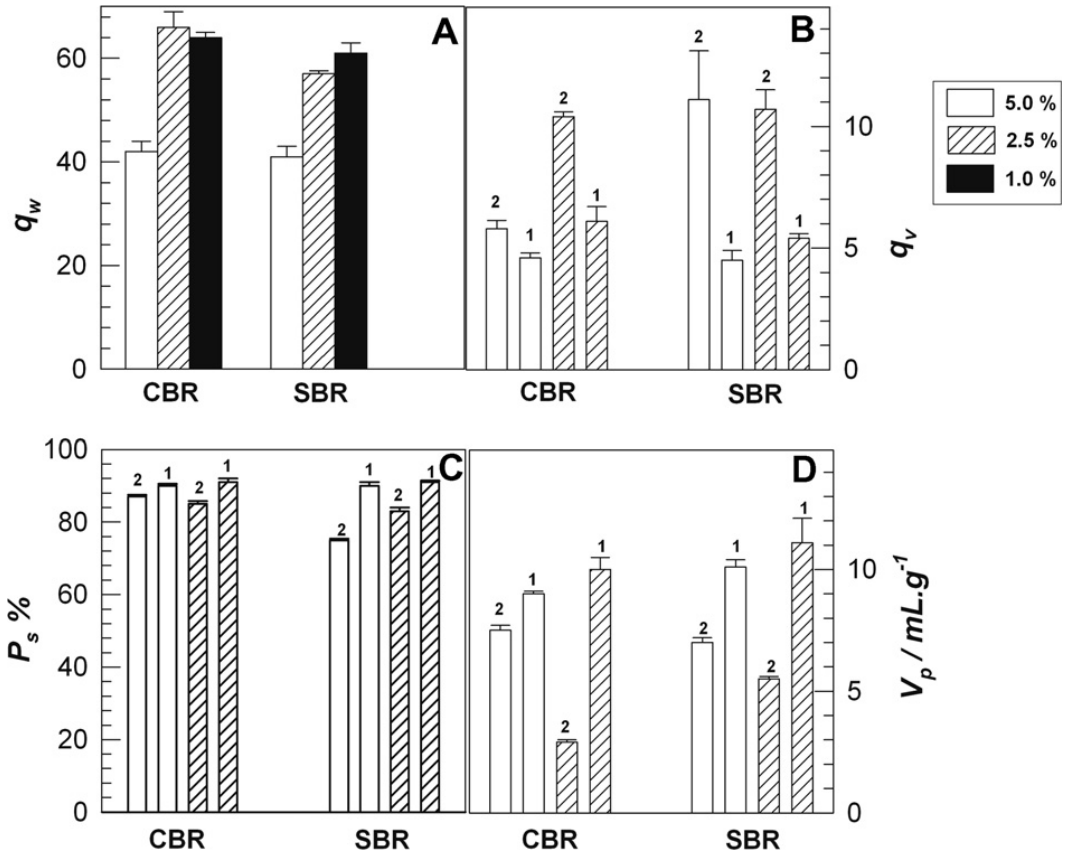


Figure 6.4: q_w (A), q_v (B), P_s% (C) and V_p (D) of cryogels formed at the indicated rubber concentrations, C_p. Crosslinker (S_2Cl_2) concentration = 6%. The numbers 1 and 2 on the bars in B–D denote the data measured before and after drying the cryogels, respectively.

Figure 6.4 shows the swelling ratios q_w and q_v, the porosities P_s and the pore volumes V_p of CBR and SBR gels formed at various polymer concentrations C_p. The numbers 1 and 2 on the bars in Figure 6.4B–D denote q_v, P_s and V_p data measured before and after drying of the cryogels, respectively. Highly swollen CBR and SBR gels with qw values around 60 and porosities above 80% were obtained at C_p 6 2.5%. The total volume of the pores in these cryogels was approximately 10 mL/g, which decreased significantly after drying due to the collapse of the weak pore structure that formed. The decrease in the pore volume of the cryogels formed at C_p = 2.5% was also evident from the collapse of the gel samples upon drying, which led to an increase in the volume swelling ratio q_v from 5 to 10. Moreover, the gels formed at 1% rubber

concentration were too weak to carry their own weight so that their diameters, and thus their volume swelling ratios, could not be measured.

6.3 Morphology of PIB Gels

To visualize the pores in the organogels, the morphologies of dried gel samples were observed by scanning electron microscopy (SEM).

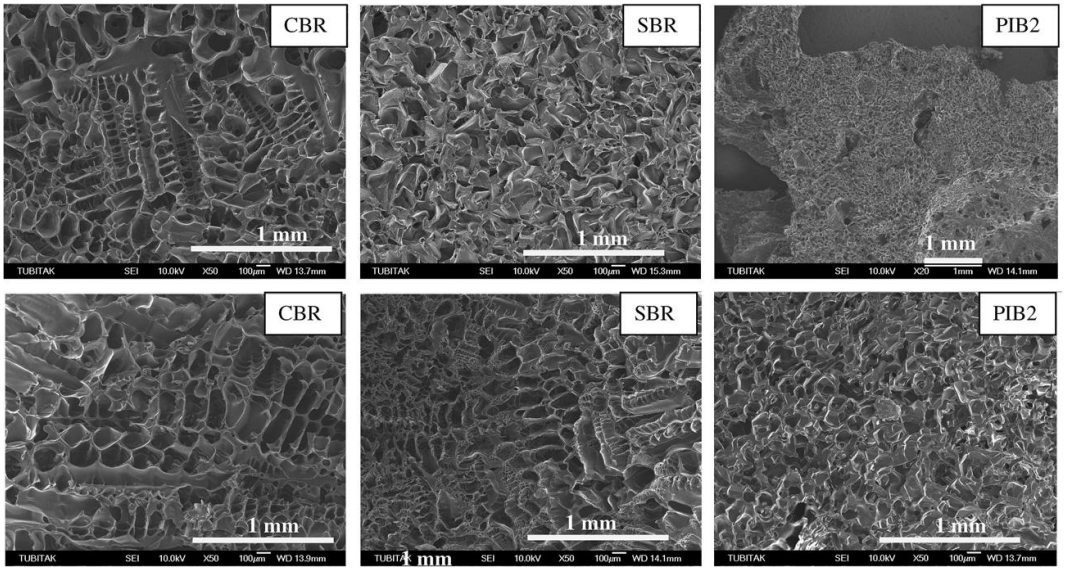


Figure 6.5: SEM of the gel networks formed from the indicated rubbers. Rubber concentration = 5%. Crosslinker (S_2Cl_2) concentration = 6% (upper panel) and 12% (bottom panel).

Figure 6.5 shows SEM images of the gel networks formed at C_p = 5% w/v. The crosslinker concentrations are 6% and 12% in the upper and bottom panels, respectively. The gel networks formed from CBR and SBR exhibit an aligned porous structure consisting of regular pores with sizes 10^1–10^2 μm, separated by polymer domains (pore walls) of 10–20 μm in thickness. Figure 6.5 shows SEM images of CBR and SBR networks formed at C_p = 2.5%, which reveal that by decreasing rubber concentration C_p, an increase in the regularity of the porous structure occurs.

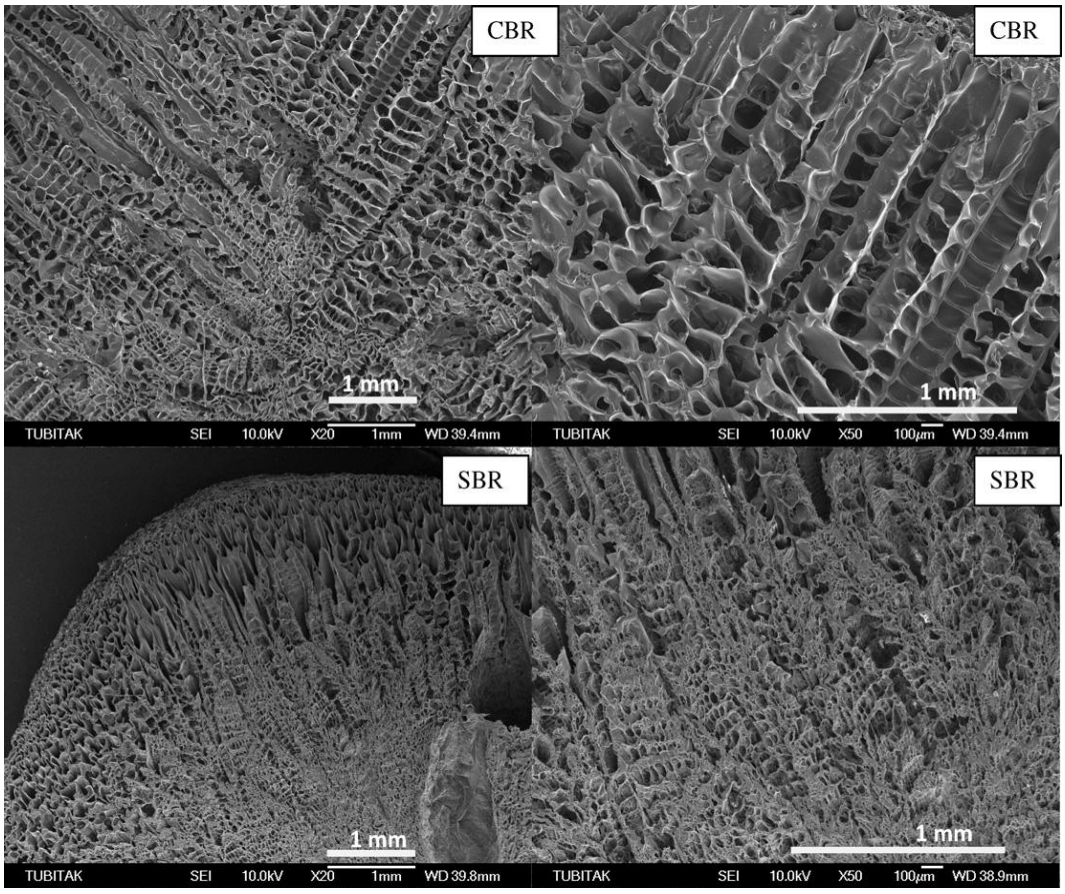


Figure 6.6: SEM of CBR and SBR networks formed at a 2.5% concentration. Crosslinker (S_2Cl_2) concentration = 6%.

Previous works indicate that the regularity of the pore structure formed by the cryogelation technique increases with decreasing freezing rates of the reaction solution [6]. The pore structure regularity can also be increased by conducting the cryogelation reactions under isothermal conditions [35]. Isothermal conditions facilitate homogeneous nucleation of solvent crystals such that the polymer network that forms exhibits monodisperse pores [36]. In the present case, gelation occurs non isothermally during the initial cooling period of the reaction solution from 20^{o}C to -18^{o}C, which takes place 5 min. Because decreasing polymer concentration also decreases the rate of the crosslinking reactions [5], the gel point is shifted toward longer reaction times as C_p decreases, such that gelation occurs isothermally in the frozen system. This leads to the formation of more regular pores. In contrast, gel networks formed from either PIB1 or PIB2 exhibit broad size distributions of irregular pores of μm to mm sizes. Thus, the use of PIB1 or PIB2 in the gel preparation destroys the regularity of the porous structures in the organogels.

In order to explain the differences in the morphologies of the organogel networks, homogeneous gels were prepared at room temperature, and they were subjected to swelling measurements in benzene at various temperatures extending down to the freezing temperature of benzene. The results are collected in Figure 6.7 where the normalized weight swelling ratios m_{rel} of PIB2, CBR and SBR gels in benzene are plotted against the swelling temperature. Both CBR and SBR gels exhibit temperature-independent swelling behavior, and, thus, benzene is a good solvent for these polymers over the whole range of temperatures investigated. This indicates that CBR and SBR remain in solution during the initial cooling period of the gelation reactions such that only the cryogelation mechanism is responsible for the formation of the pores in these networks. Thus, in these gelation systems, although there is no phase separation during the network formation process, the frozen zones of the reaction system act as inert diluents during gelation; the frozen solvent can easily be removed from the gel by thawing, and the process leads to the formation of a macroporous structure [9,15-16,37].

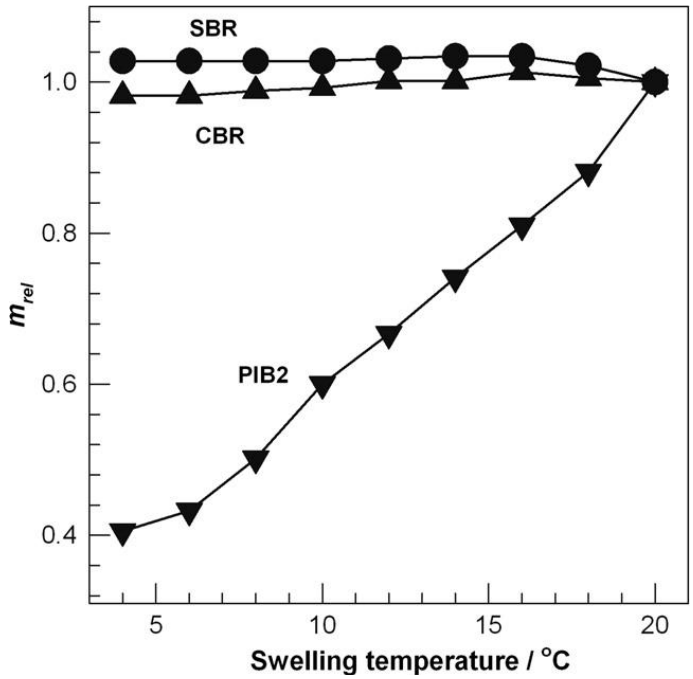


Figure 6.7: Normalized weight swelling ratio mrel of the organogels based on SBR, CBR and PIB2 in benzene shown as functions of the swelling temperatures. The gels were prepared at 20^{O}C in the presence of 12% S_2Cl_2.

The aligned porous structure of these networks is, therefore, a result of the directional freezing of the benzene crystals in the direction from the surface to the interior of the reactor, i.e., in the direction of the temperature gradient. In contrast, the swelling capacity of the PIB2 gel strongly depends on the temperature (Figure 6.6); the gel continuously deswells as the temperature is decreased and as benzene becomes a poor solvent at low temperatures. Thus, PIB chains are not only expelled from the solution due to the freeze induced concentrations, but they also undergo cooling-induced phase separation to form agglomerates of various sizes. Accordingly, both cryogelation and cooling-induced phase separation mechanisms govern the formation process of the pores in PIB networks. Formation of mm-sized large pores also support the hypothesis that two mechanisms are operative in the formation of the porous structures in the PIB1 and the PIB2 networks.

6.4 Mechanical Properties of PIB Gels

The mechanical properties of equilibrium swollen rubber gels in the form of rods were investigated by compression tests. Typical stress–strain data of the gels in the form of f versus ($\alpha - \alpha^{-2}$) plots are shown in Figure 6.8A.

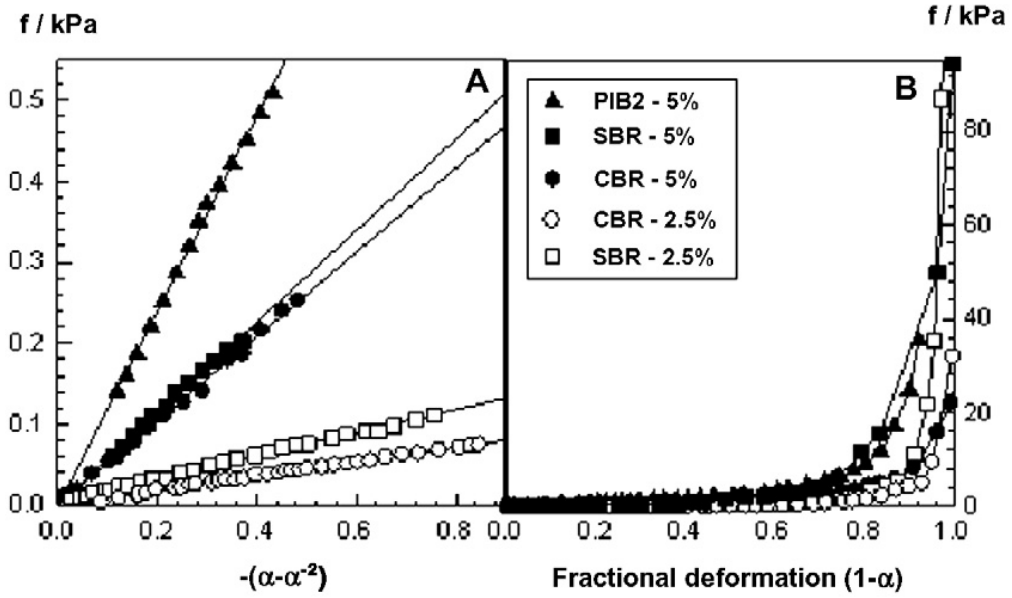


Figure 6.8: Typical stress–strain data of rubber gels as the dependence of *f* on $\alpha - \alpha^{-2}$)(A) and $1 - \alpha$ (B). S_2Cl_2 = 6%. Types of rubber and the rubber concentrations used during gel preparation are indicated.

PIB gels formed at a 5% rubber concentration exhibited moduli of elasticity of 1200 ± 200 Pa, which is about twice the moduli of CBR or SBR gels (540 ± 20 Pa). The lower elastic moduli of CBR and SBR gels as compared to the PIB gels is in accordance with their high volume swelling ratios in toluene (Figure 6.2A). Thus, although the degrees of unsaturation in SBR and CBR are much larger than in PIB, PIB undergoes more efficient crosslinking reactions with sulfur monochloride. Further, CBR and SBR gels formed at 2.5% rubber concentration exhibited elastic moduli of approximately 110 ± 30 Pa. We have to mention that all the gels were very tough and could be compressed up to about 100% strain without any crack development. This behavior is shown in Figure 6.8B where the stress–strain curves in the form of f versus $1-\alpha$ (fractional deformation) plots are given. No rubber gels broke even at a strain of 100%.

Photographs in Figure 6.9 also demonstrate how the SBR gel sustains a high compression. The gel remains mechanically stable up to complete compression, and, after the release of the load and the addition of toluene, the sample immediately recovers its original shape.

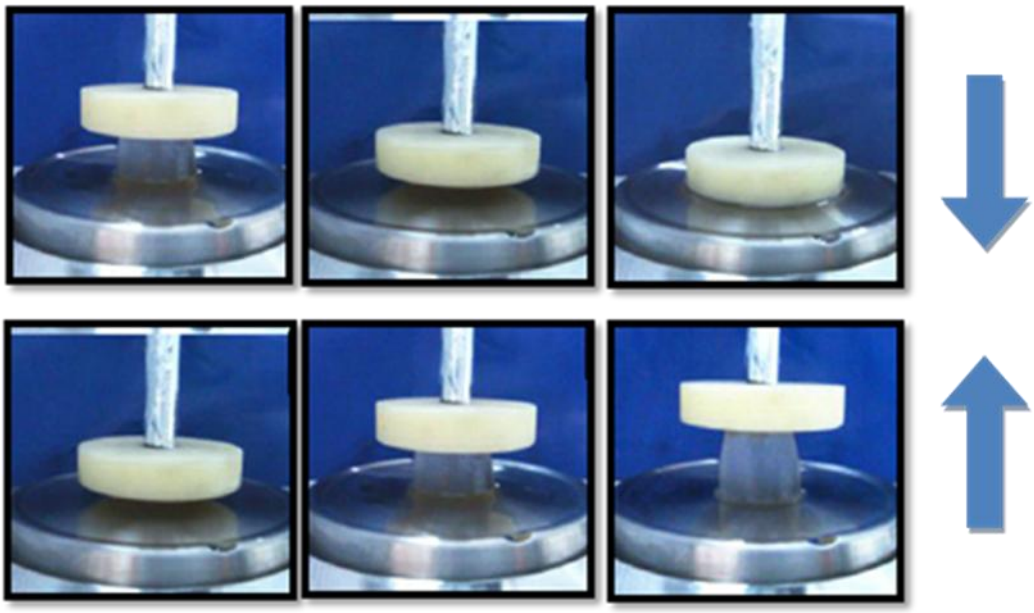


Figure 6.9: Photographs of the SBR gel formed at 5% rubber concentration during the compression test. After compression of the gel, addition of toluene converted the gel back to its initial state. S_2Cl_2 = 6%.

6.5 Removal of Crude Oil, Petroleum Products And Olive Oil From Waters

The sorption tests using organogels prepared in the present thesis were conducted for various pollutants mentioned in Experimental Section. The tests were carried out using the gel samples prepared in the form of cylindrical tissues of 14 cm in diameter. Pictures given in Figure 6.10 were taken from SBR gel samples before the sorption tests. The sorption properties of gels were first analyzed by immersing dry gel samples in oil media until attaining the swelling equilibria.

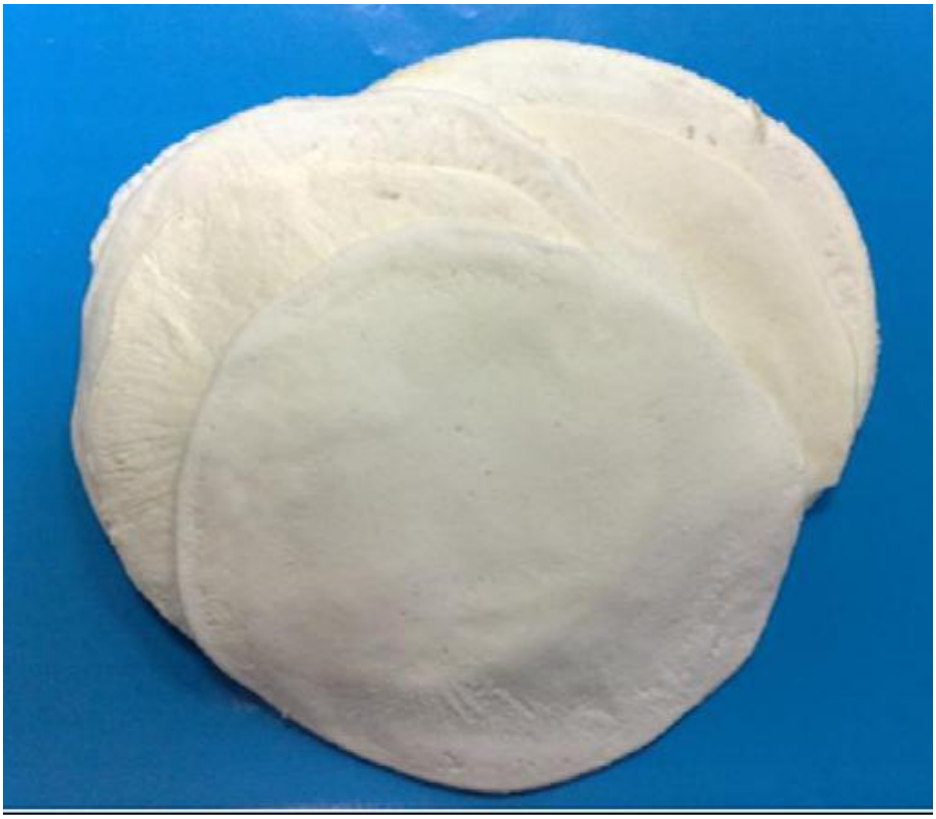


Figure 6. 10: Photographs of the SBR gel formed at 5% rubber concentration in the form of tissues. S_2Cl_2 = 6%.

The results of the sorption kinetics of the organogels in contact with various pollutants are shown in Figure 6.11, in which the sorbed amount of pollutants is plotted against the contact time. The crosslinker content of the organogels was 6%, while the rubber concentrations during the gel preparation were 5% (filled symbols) and 2.5% (open symbols). The sorption rates of all gels were very rapid and absorption of the pollutants occurred in less than 10–20 min. The fast sorption rate is due to the interconnected pore structure of these materials (Figure 6.5 and 6.6); the pollutants are sorbed through the micrometer-sized pores by convection, which is much faster than the diffusion process that dominates nonporous gels. Fig.6.10 also

shows that CBR and SBR gels prepared at C_p = 2.5% exhibit the highest sorption capacities. Moreover, PIB gels exhibit the fastest uptake rate for the pollutants, probably due to their large pores that were formed by phase separation.

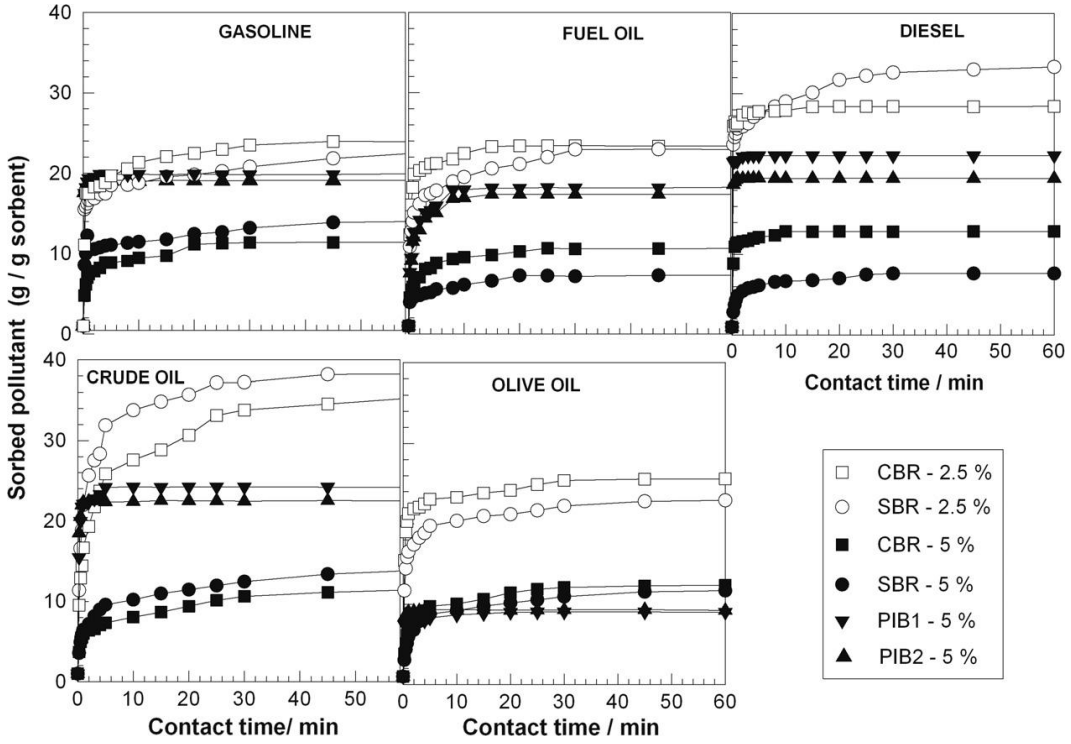


Figure 6.11: Sorption capacities of the organogels versus contact time with various pollutants. Crosslinker concentration = 6%.

Figure 6.11 demonstrates that the sorption capacity of cryogels greatly varies depending on the type of rubber used. Among the cryogels prepared at C_p = 5%, the uptake of crude oil and its derivatives is much higher for cryogels derived from PIB than the uptake seen in CBR- or SBR-based cryogels. Furthermore, a reverse situation is observed for the uptake of olive oil; in this case, CBR and SBR cryogels exhibit higher uptake capacities compared to the PIB cryogels. These results can be explained by examining the solubility parameters of the liquid components and the rubbers.

According to the Hildebrand theory [17], the solvating (swelling) power of a polymer solvent medium can be estimated from $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. The solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized, i.e., when the solubility parameters of the two components are most closely matched. δ_1 of vegetable oil is 18–19 $MPa^{1/2}$ [18,19], which is close to δ_2 of CBR and SBR (18.0 and 18.1 $MPa^{1/2}$,

respectively [20]). As a consequence, vegetable oils are good solvents for both rubbers and, therefore, cryogels derived from these rubbers exhibit large uptake capacities. Thus, favorable interactions between the olive oil and CBR or SBR increase the adherence of oil onto the surface of the polymer such that more oil is retained within these cryogels. However, δ_2 of PIB is much lower (16.5–16.8 $MPa^{1/2}$ [31,18]), but is close to the δ_1 of aliphatic and some aromatic hydrocarbons such that the uptake of crude oil and its derivatives is much higher for PIB cryogels.

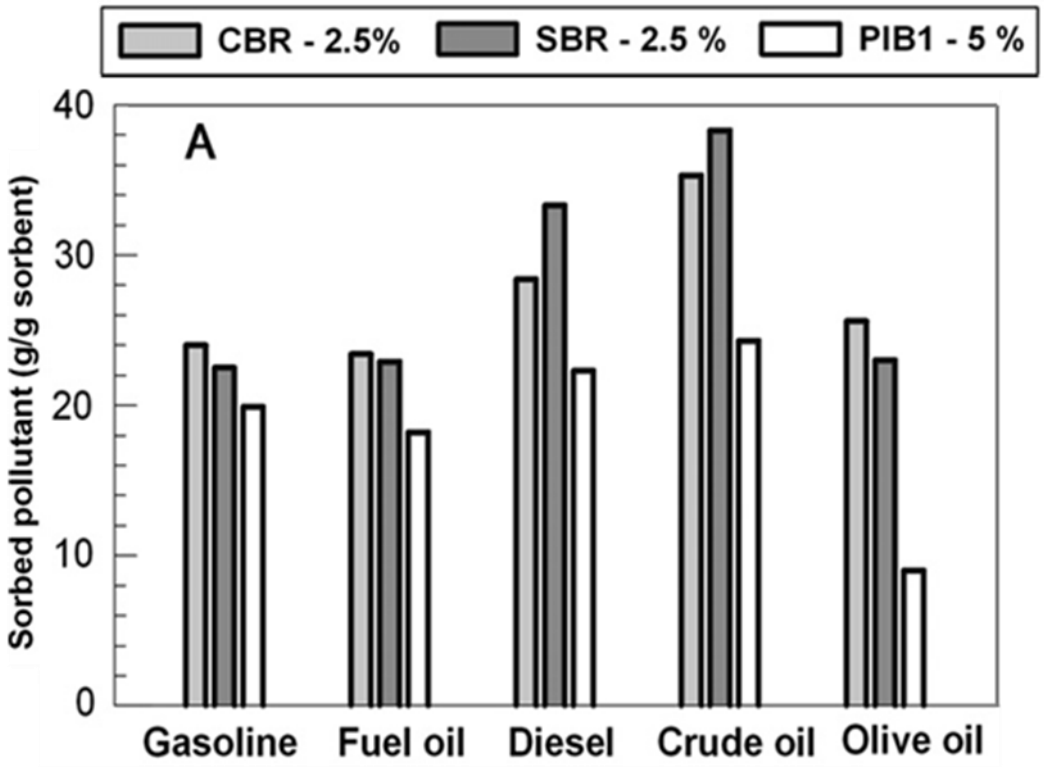


Figure 6.12: Maximum sorption capacities of the organogels for various pollutants. Crosslinker concentration = 6%. Amounts of sorbed pollutants are shown on the bars.

In Figure 6.12, the maximum sorption capacities of the best rubber sorbents, namely CBR and SBR formed at Cp = 2.5%, and PIB1 are compared for various pollutants. One gram of SBR or CBR sorbs 35–38 g crude oil or 23–26 g olive oil as compared to 23 g/g and 9 g/g, respectively, obtained using the PIB1 gel. One should also compare these values with those of commercial oil sorbents. The widely-used oil sorbents based on polypropylene have sorption capacities for both crude oil and olive oil of about 15 g/g [14]. Thus, SBR and CBR gels have sorption capacities that are about twice the capacity of the commercial oil sorbents.

Another result gleaned from Figure 6.12 is that the sorption capacity of the organogels is the highest for crude oil, i.e., for the pollutant with the highest viscosity. This implies that, although increased viscosity of the pollutant decreases the rate of sorption, favorable hydrophobic interactions between the crude oil and the hydrophobic polymer dominate the sorption process so that more oil is retained within the rubber gels. The reusability of the sorbents and the recoverability of the pollutants are important aspects within oil spill cleanup procedures [2]. Commercial oil sorbents are not reusable, thus they form a solid waste after the cleanup procedure [14]. However, all organogels prepared in this work can be squeezed completely to give up the pollutants without any crack developments (Figure 6.8). The reusability of the organogels and their continuous sorption capacities were checked by repeated sorption–squeezing cycles. The sorption– squeezing cycles were repeated 20 times to obtain the recycling efficiency and continuous extraction capacity of the organogels.

The results are shown in Fig. 6. 9 in which the uptake capacity of the organogels in each cycle for various pollutants is plotted against the number of sorption squeezing cycles.

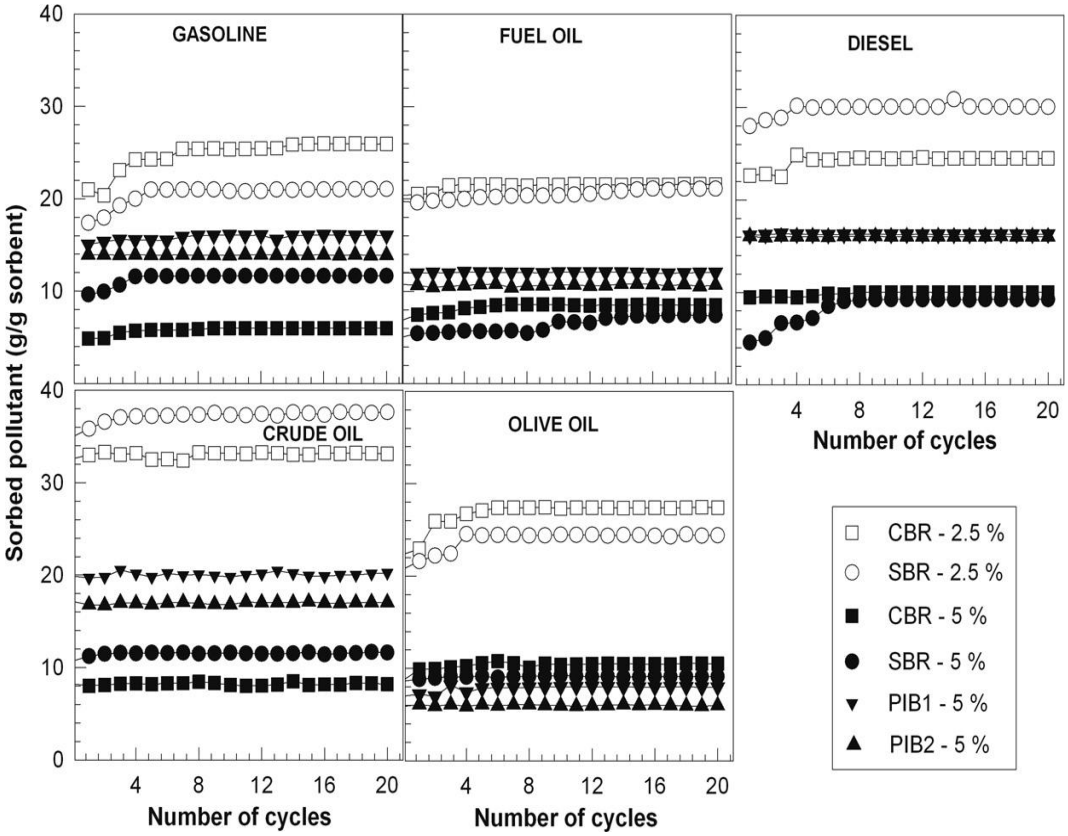


Figure 6.13: Continuous extraction capacities of the organogels for various pollutants as a function of the number of cycles. Crosslinker concentration = 6%. C_p = 5%

It is seen that the amount of pollutant sorbed in each cycle is almost constant for all cycles larger than 6. For example, the amount of pollutant sorbed is equal to 37.5 ± 0.1 g/g and 24.4 ± 0.1 g/g for SBR gels formed at C_p = 2.5% in contact with crude oil and olive oil, respectively.

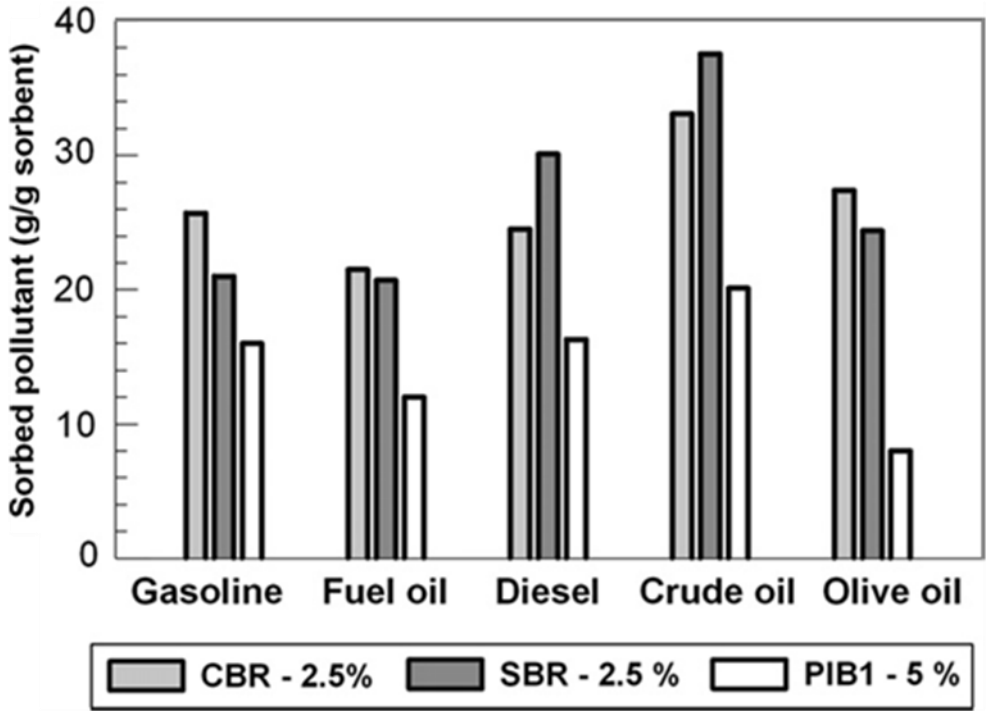


Figure 6.14: The continuous extraction capacities of the best sorbents.

The average sorption capacities, i.e., the continuous extraction capacities of the best sorbents, are reported in Figure 6.14. These results demonstrate that the continuous capacity is close related to the maximum capacity of gels, indicating the high reusability of all organogels and high recoverability of the crude oil, petroleum products and olive oil. Sorption tests were also conducted using pollutants that spread in water, as described in the literature [14]. Similar results as those given in Figure 6.14 were obtained. The fact that 37.5 g of crude oil could be recovered by the SBR gel in each cycle means that about one ton of crude oil could be separated from the surface waters through the use of 1 kg of SBR gel networks over 25 cycles.

7. CONCLUSIONS AND RECOMMENDATIONS

The present work was carried out to prepare an ideal gel defined as a soft material exhibiting both a high degree of toughness, i.e., a mechanical stability up to about 100 % strain and a fast response rate against the external stimuli. For this purpose, macroporous organogels were prepared from frozen solutions of PIB, CBR and SBR in benzene at -18^{O}C using sulfur monochloride as the crosslinker. The conclusions that can be drawn from the experimental results can be summarized as follows:

i. The pores in CBR and SBR networks are regular and oriented along a common direction, whereas those in PIB networks are irregular with broad size distributions from μm to mm sizes.

ii. It was shown that the regular morphology of CBR and SBR networks is due to the fact that benzene is a good solvent for CBR and SBR chains such that pores are only generated by the cryogelation mechanism.

iii. Sorption tests conducted using the organogels demonstrate that they are efficient materials for the removal of crude oil, petroleum products and olive oil from surface waters.

iv. The most important feature of the rubber gels is their reusability after simply being squeezed; the continuous sorption capacities of CBR and SBR gels for crude oil and olive oil are 33–38 and 24–27 g/g, which are two to three times the capacity of the gels derived from PIB.

v. The measured sorption capacities of all organogels are also much higher than those of commercial oil sorbents, suggesting that the rubber gels are a better alternative to the widely used polypropylene sorbents because of their improved efficiency for oil sorption and their reusability.

For the future studies, different solvents suitable for the solution crosslinking of these rubbers at subzero temperatures may be investigated to highlight the effect of the freezing point as well as of the crystal structure of the solvent on the gel properties. Furthermore, polymer-clay nanocomposite systems exhbiting extraordinary mechanical properties may also be investigated by selecting butyl rubber as the polymer component and, by conducting the reactions in a frozen state of the system.

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