Characterization of Mechanical Property Change in Polymer Aerogels Depending on the Ligand Structure of Acrylate Monomer

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Abstract: In an effort to overcome the weakness of aerogel, polymer aerogels have been prepared by copolymerizing the different types of monomers through sol-gel process. Polymerizing the successive phase of a high internal phase emulsion, which has interconnected porous structure, porous polymer aerogel can be manufactured. In this paper, we use the styrene/divinylbenzene chain as a basic monomer structure, and additionally use 2-ethylhexyl methacrylate (2-EHMA) or 2-ethylhexyl acrylate (2-EHA) as monomers for distinguishing the visible mechanical properties of synthesized polymer aerogel. We can observe the different tendency of polymer aerogels by kinds of monomer or ratio. Flexibility and microstructure can be changed by the types of monomer. EHA polymer aerogel shows high flexibility and thin microstructure, and EHMA polymer aerogel shows high hardness and thick microstructure. EHA/EHMA polymer aerogel shows the intermediate nature between them. By utilizing the mechanical properties of three types of polymer aerogels to adequate situation or environment, polymer aerogels could be used as drug agent, ion exchange resin, oil filter and insulator, and so on.

Keywords: high internal phase emulsion, polymer aerogel, flexible, radical condensation, sol-gel process

1. Introduction

Aerogels are mesoporous materials which have a lot of nanopores inside.1,2) Porous structure can be made by supercritical drying of crosslinked wet-gel prepared by sol-gel process and their porosity is up to 99%.1-3) Aerogels have been considered as promising porous materials since they have high surface area, low thermal conductivity (0.013-0.04 W/mK) and low density (0.003-0.1 g/cm³).4) Because of these properties, their applications are diverse and they can be used in thermal, electronic, and catalytic field, so aerogels have led significant attention as future material.4-6) However, aerogels are very fragile and brittle so they can be easily destructed when they undergo external force or mechanical stress.1,7) Their low mechanical strength is a big problem in terms of wide application of aerogels. In an effort to overcome their weakness and expand the application of aerogels, some solutions have been brought up such as aerogel blanket8) and composite aerogel, which can be made by combining aerogel with mechanically strong material just like a metal, fiber, carbon compound and organic material.2,4,5,7)

As one of these solutions, polymer aerogels have been researched as alternative materials which can keep good properties and relieve the problems of aerogels for several years.1,9) Through this research, high internal phase emulsion (HIPE) has been considered as one of the useful materials.9) By polymerizing the successive phase of a high internal phase emulsion, porous polymers with interconnected porous structure can be manufactured.10) HIPE is also called high concentrated emulsion or gel emulsion since it is like a jelly in stable state.11) HIPE is a dispersed phase with a volume fraction of more than 74.05% and up to 99% emulsion system.11,12) These kinds of polymer are also known as polyHIPE.12) It is made by emulsion polymerization and radical condensation with phase reversion. By these processes, less than 10 µm size pores are made inside.11-14) Therefore, it is also called as polymer aerogel because aerogel also has many pores inside. Also, polyHIPE has various applications such as drug agent,12) blood absorbent,15,16) ion exchange resin,17-19) oil filter12,20) and insulator11,12) so it can be used for diverse situation and environment.

Styrene/divinylbenzene monomer chain is the most researched polyHIPE structure.10) And polyHIPE materials which have specific properties can be made from emul-
sions mixed with specific materials\textsuperscript{21,22}. Good example material is 2-ethylhexyl acrylate (2-EHA) because it has low glass transition temperature ($T_g$) around 223 K.\textsuperscript{23} So, introducing this EHA to emulsion is more general route for increasing flexibility. Materials with high quantities of 2-EHA exist as rubbery plateau.\textsuperscript{24} On the other hand, the similar monomer, 2-ethylhexyl methacrylate (2-EHMA), has non-linear relationship with EHA polymer\textsuperscript{21,23} because it has relatively high $T_g$ around 263 K.\textsuperscript{23} So materials with high levels of EHMA are relatively hard. Based on the facts that properties of finished product can be changed by the kind and $T_g$ of component material, three types of polymer aerogel using different monomer or ratio were prepared by radical condensation with sufficiently high temperature. The volume percent of monomer was adjusted to 60\%, and mechanical properties, chemical bonding, and surface morphology of samples were studied.

## 2. Experimental Details

### 2.1. Materials and methods

Styrene, divinylbenzene (DVB, crosslinker), 2-ethylhexyl acrylate (2-EHA), and 2-ethylhexyl methacrylate (2-EHMA) were used as monomers for making polymer aerogel. The volume percent of monomer in the sample is 60\%, and using different monomer or ratio, three types of polymer aerogels were prepared and they were named as EHA polymer aerogel, EHMA polymer aerogel, EHA/EHMA polymer aerogel, respectively. EHA polymer aerogel followed the ratio of styrene:DVB:2-EHA = 1:0.56:4. The ratio of EHMA polymer aerogel was as follows as styrene: DVB:2-EHMA = 1:0.56:4. EHA/EHMA polymer aerogel’s ratio was as styrene:DVB:2-EHA:2-EHMA = 1:0.56:2:2.

And free radicals, for radical condensation between monomers, were provided by potassium persulfate. It was dissolved in calcium chloride aqueous solution used for good dispersion and acting as electrolyte. This solution consists of calcium chloride and distilled water. For mixing the monomers and aqueous solution, sorbitane monooleate (span 80) was employed in these mixtures.\textsuperscript{7} Teflon mold is also used for embodiment.

### 2.2. Preparation of polymer aerogel

Styrene, DVB and 2-EHA or 2-EHMA or 2-EHA/2-EHMA were introduced to long-necked beaker. Span 80 was also added as a surfactant\textsuperscript{7} and all of them were mixed by overhead stirrer at 400 rpm. During stirring, calcium chloride aqueous solution containing potassium persulfate were added dropwise to mixture in the long-necked beaker. Then two different mixture were mixed and its color was gradually changed to white. After all aqueous solutions were used up, kept stirring for 30 mins to yield high internal phase emulsions. After that, emulsions were introduced in sealed teflon mold and it is bathed in large beaker filled with water. While it was kept at 65°C for 2 days, emulsions were polymerized and slightly high temperature catalyzed the rate of polymerization. Once they had formed solid phase polymer, it was pulled out from mold and kept in cold water flow for 2 days, for extracting surfactant in polymer by capillary action. Through aging in sufficient quantity of acetone for more than 3 days followed by drying in 80°C oven for more than 48 hrs, EHA polymer aerogel, EHMA polymer aerogel and EHA/EHMA polymer aerogel were finally prepared.

### 2.3. Analysis method about sample

Mechanical properties could be expected by the results obtained with BET surface area, pore volume, pore size using a multipoint Brunauer-Emmett-Teller (BET) surface analyzer (Quantachrome autosorb iQ) and Barrett-Joyner-Halenda (BJH) method (TriStar 3000 V6.05 A) because of microstructural dependent mechanical behaviors. Porosity of polymer aerogels is calculated using mass and volume of polymer aerogel samples. For verifying the presence of monomers in polymer aerogel samples, Fourier transform infrared (FT-IR) spectroscopic studies of the polymer aerogels were carried out using Perkin Elmer (Model no. 760) IR spectrophotometer in 500-4000 cm\(^{-1}\) range for chemical bonding structure. The surface morphology of polymer aerogels was analyzed using a scanning electron microscopy (SEM; JEOL, JSM 7001F).

## 3. Result and Discussion

Polymer aerogels were synthesized by sol-gel process as Fig. 1, which forms sol by dispersion of colloid particle, and forms gel by unstabilization of sol phase.\textsuperscript{25} In organic phase solution, including monomers and surfactant, aqueous initiator solution was added as droplet during stirring. These all matters were mixed and hydrolyzed, and formed the sol phase HIPE. Aqueous phase and organic phase existed independently because of the difference of polarity. After condensation in adequate temperature, monomer-condensed gel phase polyHIPE could be prepared. Lastly, mesoporous polymer aerogel was formed after ambient drying.

The monomers in organic solution could be condensed by free radicals. These free radicals were made by peroxide...
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or persulfate which have unstable oxidation number. By heating or light, it can be easily divided and creates free radicals. These free radicals attacked the monomers and because of that, two monomers could be connected by newly created single bond and formed a polymer. The procedure of formation process is defined as three-step condensation reaction - initiation, propagation, and termination reaction. This process is summarized in Fig. 2.

By experimental, three types of polymer aerogel could be prepared and its chemical structure is like as Fig. 3. And the flexibility of polymer aerogels depends on the kind of monomer. The polymer aerogel which consists of styrene, DVB and 2-EHA is flexible so it can be easily bent just like rubber as shown in Fig. 4(a). Flexible polymer aerogel has high bending property and ductility. And another polymer aerogel, made of styrene, DVB, and 2-EHA/2-EHMA, is little hard but little flexible. So it is regarded it has intermediate nature of 2-EHA and 2-EHMA. But unlike this aerogel, polymer aerogel which is made of styrene, DVB and 2-EHMA is completely hard so it is possible to be broken when external forces are applied.
to it. It has low flexibility so it has been divided eventually just like styrofoam. By bending the polymer aerogel samples, visible flexibility can be confirmed as Fig. 4.

Figure 5 shows the FT-IR spectra of polymer aerogels. Some characteristic absorption peaks were observed in the range from 500 to 4000 cm$^{-1}$ indicating the existence of monomers as component in the polymer aerogel samples. The several absorption peaks, observed at 1400 cm$^{-1}$ and from 3000 to 2500 cm$^{-1}$, were due to bending and stretching modes of C–H bonds of monomers. The strong peaks observed at 1700 cm$^{-1}$ proved the presence of C=O bonds, and C-O-C peaks are also seen at from 1300 to 1000 cm$^{-1}$. These peaks came from carbonyl group and ether group of 2-EHA monomers and 2-EHMA monomers. The reason why the wavenumber of C-O-C peak of EHMA is lower than EHA is caused by one more methyl group of EHMA. Because of this methyl group, electron density of EHMA is lower than EHA. So, bonding strength of EHMA is lower than EHA and C-O-C peak of EHMA appeared in a little low wavenumber. At 700 cm$^{-1}$, the strong peaks were observed and it means long-chain band of CH$_2$ groups of 2-EHA and 2-EHMA. And some weak peaks of C=C bonds were seen around 1500 cm$^{-1}$ and these peaks are originated from vinyl group and aromatic group of monomers. The reason why transmittance of C=C
bonds was little is C=C bonds of monomers were condensed by free radicals. So they formed C-C bonds by radical condensation and C=C bonds decreased. From the FT-IR spectra, it is known that some C=C bond residues of monomers were observed.

The surface morphology of polymer aerogels has been determined by the SEM image as Fig. 6. It is shown that there are a lot of uniform pores in the polymer aerogels. From these images, it is clear that polymer aerogels formed interconnected network by radical condensation and the vacancies of surfactant and water were remained as many pores. This porous structure is similar with porous aerogel, so it can become an evidence of the reason why polymers are also called polymer aerogel. But there are some structural differences among the three polymer aerogels. EHA polymer aerogel has the thinnest structure, EHA/EHMA polymer aerogel is second, and EHMA polymer aerogel has the thickest structure among them. These structural difference is caused by the Tg of monomers. 2-EHA has low Tg so its liquidity is high and it has relatively rare chance to contact and react with other monomers. So it forms relatively thin structure. Compared to 2-EHA, 2-EHMA has relatively high Tg so its liquidity is also low. So it has a frequent chance to contact and react with other monomers and forms a thick structure. And 2-EHA/2-EHMA mixture shows intermediate nature between 2-EHA and 2-EHMA. And the methyl group of 2-EHMA can become the cause of structural difference. The difference between 2-EHMA and 2-EHA is existence of one more methyl group and because of this, polarity of them is also different. 2-EHMA is relatively nonpolar, so it can easily contact with the nonpolar part of other monomer, which can become a part of radical condensation. So it can form a sturdy polymer structure and structural thickness of EHMA polymer aerogel is higher than EHA polymer aerogel. And 2-EHA/2-EHMA mixture has intermediate nature so its thickness looks higher than EHA polymer aerogel, but lower than EHMA polymer aerogel.

By the BET surface area analysis, the pore size and pore volume are measured and porosity using mass and volume of polymer aerogels is calculated. Table 1 shows that BET surface area, pore size, pore volume and calculated porosity of polymer aerogels. Porosity of three kinds of aerogels is sufficiently high, and satisfies the condition as aerogel. Small pore size and pore volume also prove that they can be utilized as other porous materials, and their surface area can be used in proper situation. By utilizing this porous structure, polymer aerogels could be used as drug agent, ion exchange resin, oil filter, insulator, and so on.

**4. Conclusion**

Using styrene/divinylbenzene as a basic monomer structure, polymer aerogels could be obtained using 2-EHMA or 2-EHA or 2-EHA/2-EHMA monomer by radical condensation. Depending on a kind of monomer, mechanical properties of polymer aerogels are different. The polymer aerogel containing 2-EHMA has low flexibility, and the polymer aerogel containing EHA has relatively high flexibility. EHA/EHMA polymer aerogel shows intermediate nature between EHA polymer aerogel and EHMA polymer aerogel. The FT-IR spectra showed the presence of various carbon bonds of monomers such as carbonyl group, ether group, and so on. Surface morphology could be confirmed by SEM images and it showed the porous inside of polymer aerogels. By the properties of monomer, there are some structural difference in terms of thickness. EHMA polymer aerogel shows the thickest structure, and EHA polymer aerogel shows the thinnest structure. By applying these three polymer aerogels to adequate situation or environment, polymer aerogels could be used as drug agent, ion exchange resin, oil filter and insulator.

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**Table 1. BET surface area, pore size, pore volume, and porosity values of polymer aerogels**

| Sample               | BET surface area (m²/g) | Pore size (nm) | Pore volume (cc/g) | Porosity (%) |
|----------------------|-------------------------|----------------|--------------------|--------------|
| EHA polymer aerogel  | 8.07                    | 3.82           | 0.078              | 80.11        |
| EHMA polymer aerogel | 6.13                    | 4.32           | 0.014              | 70.23        |
| EHA/EHMA polymer aerogel | 6.82                | 3.42           | 0.024              | 74.66        |

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