CHEMICALLY CROSS-LINKED HYDROGEL HAVING HIGH MECHANICAL STRENGTH

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Abstract

The mechanically tough shape memory gel (SMG) was synthesized. The chemically cross-linked process was applied using a cross-linker named methylenebisacrylamide (MBAA). The SMG was prepared by N, N-dimethyl acrylamide (DMAAm) and stearyl acrylate (SA). The DMAAm is a hydrophilic monomer, whereas SA is a hydrophobic monomer. Due to the transparency, shape memory property, low friction, and high water content, the SMG is suitable for biomedical and optical applications. The physical property such as mechanical strength of most hydrogels is not good enough. However, the properties of these hydrogels are easily controlled by changing the polymer concentration, molecular weight and cross-linker concentrations. It is found that the swelling degree increases with respect to the DMAAm concentration. The mechanical properties of transparent shape memory hydrogel were investigated by the tensile, the compression and the dynamic mechanical analysis. The Young’s modulus gradually decreases with the increase of hydrophilic components. On the other hand, higher Young’s modulus is observed by increasing the high hydrophobic concentration. It is also seen that the mechanical stress decreases with respect to the temperature, indicating the loss of Young’s modulus. The result of dynamic mechanical analysis designates that the water swollen sample has both the elastic and viscous properties.

Keywords: Hydrogel, Shape Memory Gel, Mechanical Properties, Dynamic Mechanical Analysis (DMA), Viscoelastic

Introduction:

Hydrogel, a polymeric material is a combination of soft and wet state, attracts scientists due to its potential applications for the development of a wide variety of biomedical and biotechnological products such as surgical sealants, actuators, drug depots and tissue engineering etc. (Chia-Jung, 2011). Hydrogel composes with block copolymers and crosslinking agent, which builds internal cross-linked networks between the polymers. Hydrogel also contains a large amount of water contents. The properties of hydrogel are functioned by swelling-deswelling (Kabir, 2013), and external stimuli (Lendlein, 2002, Liu, 2007, Mather, 2009). However, the hydrogel with shape memory effect is a promising material in the application of biomedical science.

A large number of shape memory polymers (SMP) have been developed those are operated by external stimuli and have applied in the different fields (Miyata, 1999, Miyata, 2002). Prof. Osada was first developed shape memory hydrogel (Osada, 1995). The shape memory gel (SMG) has the ability to memorize the original shape and size. The SMG can deform to fix a temporary shape and can recall its original shape by applying an external stimulus such as heat.

Due to the large quantities of water content, most of hydrogels do not have sufficient mechanical strength. As a result, to find a suitable application of hydrogel is still a challenge. In order to improve the mechanical properties, the chemically cross-linked shape memory gel (SMG) was synthesized using N, N-dimethyl acrylamide (DMAAm) and stearyl acrylate (SA). The DMAAm is a hydrophilic monomer, whereas SA is a hydrophobic monomer. The photo polymerization process was applied in the preparation of SMG. The SMG has improved the mechanical strength because the covalent bond is formed due to the crosslinking as well as the crystallinity of the sample. By virtue of transparency, shape memory property, low friction, and high water contents, the SMG is suitable for biomedical and optical applications. However, the properties of SMG hydrogel can be easily controlled by changing the polymer concentration, molecular weight and cross-linker concentrations.

Sample Preparation

Materials:

A hydrophilic monomer *i.e.* N, N-dimethyl acrylamide (DMAAm) and a hydrophobic monomer *i.e.* stearyl acrylate (SA) were used as basic monomer. Methylenebisacrylamide (MBAA) was used as a cross-linker whereas benzophenone was used as a UV initiator. The materials used in this study are tabulated in table 1.

Table 1: The materials are used to prepare the SMG gel.

Chemical	Molecular weight (g/mol)	Ratio	(Unit)
N,N dimethyl acrylamide	99.13	0.75	mol
Stearyl acrylate	324.54	0.25	mol
Methylenebisacrylamide	154.17	0.05	mol%
Benzophenone	182.22	0.1	mol%

Synthesis of SMG:

The SMG was synthesized by simple bulk polymerization method. To make one mole solution, DMAAm and SA were taken in 3:1 ratio denoted as sample1. However, the concentrations of MBAA and benzophenone were 0.05 mol% and 0.1 mol%, respectively. The mixed solution was stirred for 30 minutes with N_2 bubbling gas to remove O_2 gas from the solution. The sandwiched two pieces of glass molds with the silicone rubber spacer was filled with the solution and was placed in the UV chamber (wavelength is 365nm) for several hours. Finally, the sample was swollen to an equilibrium state by dipping into pure water for several days. Besides sample1, two other samples were prepared by varying only the concentrations of DMAAm. In this case, the weight value of DMAAm is multiplied by two and three times to produce a molar ratio of 6:1 and 9:1, denoted as sample2 and sample3, respectively. However, crosslinking agent and photo initiator were remained constant.

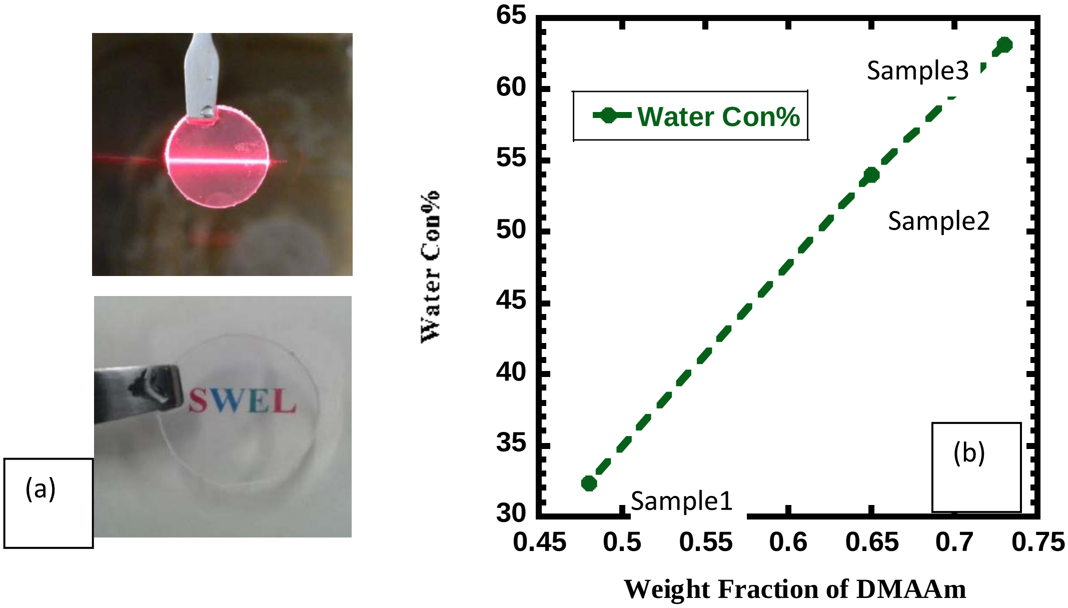

Fig. 1. Transparent shape memory gel, (b) Swelling degree of SMG as a function of weight fraction of hydrophilic monomer component (DMAAm).

Results and Discussion

Swelling Degree:

The SMG is a water-swollen hydrogel. The water content in the sample W_c (wt%) is defined by the percentage of the ratio between the weight of water in the gel and the total weight of the gel. Here we indicate the amount of water content as a swelling degree.

$$W_c = (weight\ of\ water)/(total\ weight\ of\ gel) \times 100\% \qquad (1)$$

Figure 1(a) shows the transparent SMG, the evidence of transparency. The samples were 2 mm thick. The material shows a unique property, which is called the shape memory effect. The detail of shape memory effect can be found in our previous work [2]. The swelling degree of SMG as a function of the weight fraction of hydrophilic monomer (DMAAm) is shown Fig.1(b). Here, the weight fraction of DMAAm is defined as the weight of DMAAm in the sum weight of DMAAm and SA [DMAAm/(DMAAm+SA)]. The weight fractions of DMAAm in the solution were 0.48, 0.63 and 0.73 for the sample1, sample2 and sample3, respectively. It is seen from this figure that the swelling degree increases with respect to the DMAAm monomer, indicates that the interstitial spaces in the internal network increases due to the large amount of hydrophilic components. The swelling ratio was also investigated with other solvent such as ethanol shown in Fig. 2. The solvent was prepared with the mixture of water and ethanol. The x-axis indicates the percentage of ethanol in the solution. The swelling ratio was defined as the weight of the swollen sample at a specific time divided by the weight of as-prepared sample. The swelling ratio increases with the increase amount of ethanol. The swelling ratio goes to more than 6 at 100% ethanol. Although the swelling ratio is very high with ethanol, but it is noticeable here that the SMG gradually became opaque, soft and sticky with respect to the amount of ethanol. The resulting material decreased its Young's modulus. For the application point of view, such as optical lenses as an alternative of soft contact lens, the opacity is not good. Therefore, we only considered the water-swollen sample for the investigation of mechanical strength.

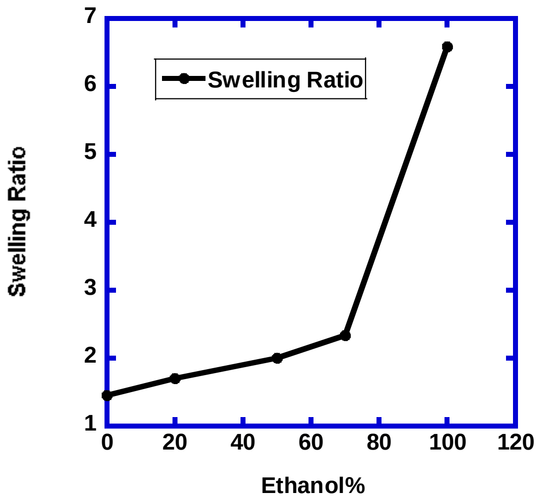

Fig.2. Swelling ratio as a function of the percentage of ethanol in the mixer of the solvent.

Tensile and Compression test:

The mechanical properties were investigated by the tensile test and the compression test by mechanical testing instrument STA-1150 (ORIENTEC Co., LTD, Japan). The samples were cut by dumbbell K6251-7 specimen for the tensile test. The size of the sample was 35mm long, 2mm width and 1mm thick while the crosshead speed was 100mm/min.

The tensile measurement was performed at room temperature. The Young's modulus of different samples is shown in Fig. 3. It is clearly seen that the Young's modulus decreases as a function of the DMAAm weight fraction. It indicates that the mechanical strength decreases with respect to the decrease of SA concentration in the solution. Therefore, SA concentration plays a significant role to increase the mechanical strength because the SA works as a side chain in the main networks. Due to the large amount of SA components in sample1, high mechanical strength is found. The stress vs strain of three samples is shown in the inset of Fig. 3. The maximum values are indicating the breaking stress and strain. The mechanical stress of sample 1 is higher than that of other samples. As we achieved higher mechanical stress in sample 1, so the other investigations were performed in the sample 1.

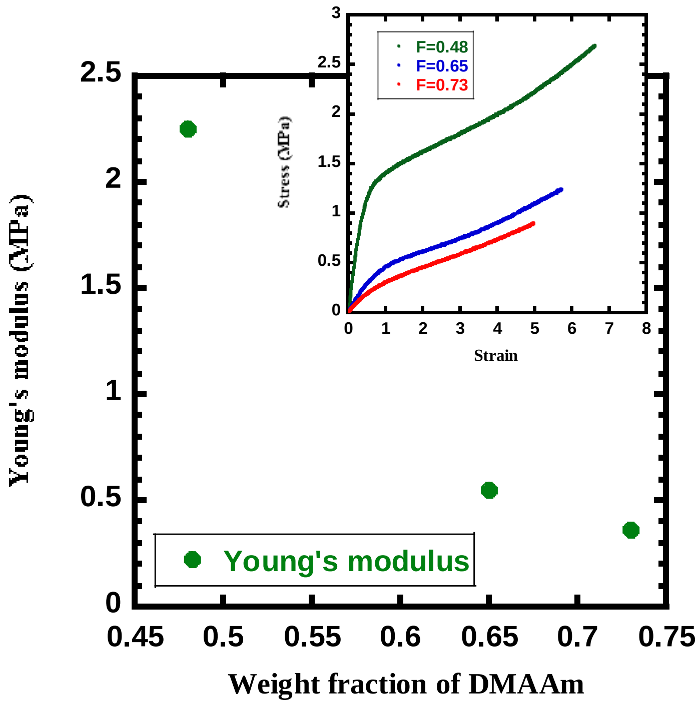

Fig. 3. The Young's modulus of different samples is calculated from the linear part of the stress-strain curve as a fraction of DMAAm concentration. In inset, the stress-strain curve of the corresponding samples.

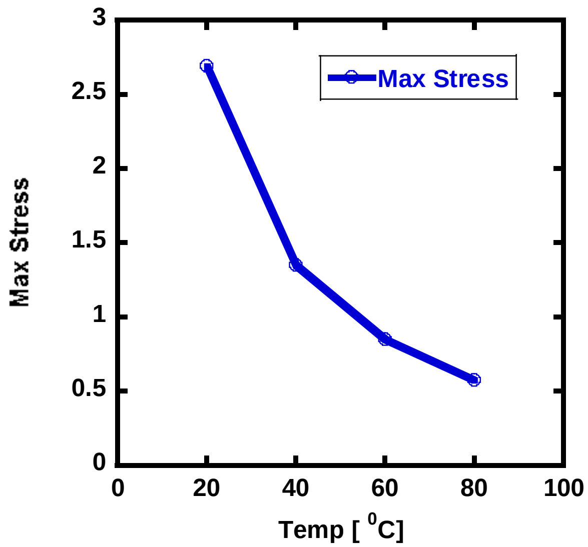

Fig. 4. The tensile stress of sample1as a function of temperature.

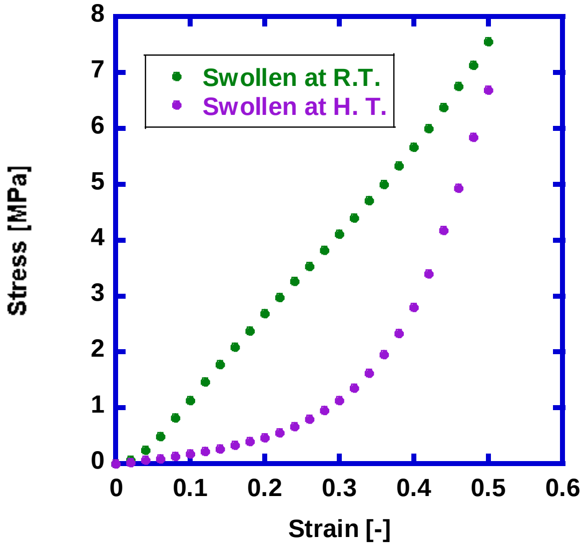

Fig. 5.The compression stress vs strain curve of sample1 at room and at high temperature (60˚C).

It was also investigated the temperature dependence of the mechanical stress. In this case, we customized the tensile STA-1150 equipment with a bathtub and a temperature sensor. Therefore, it is possible to adjust the desired temperature of the water in the tub. We measured the stress of the sample by varying the temperature as shown in Fig. 4. It is seen from this figure that the stress gradually decreases with respect to the temperature. This is because the SA component has a thermo responsive affinity. At room temperature SA behaves as a solid whereas the melting temperature of SA is 30˚C. This indicates that at high temperature the SMG becomes soft, loses the binding energy. As a result, the material decreases the Young's modulus.

We conformed that the transition temperature of sample 1 (F=0. 48) was 42.5˚C in our previous study (Kabir, 2013). The transition temperature is actually an order-disorder transition, in other words, hard-to-soft transition or *vice-versa*. The study was performed by laboratory dynamic light scattering (DLS) equipment. If the SMG is heated slightly above from the transition temperature, the gel becomes soft, loses its mechanical strength and is possible to deform easily. Therefore, we have found the trade-off characteristic between the mechanical stress and the temperature. Nevertheless, mechanical stress sharply decreases around 40˚C, suggests the merit of DLS result. It is noticeable here that we have observed one order of magnitude smaller mechanical stress than that of Y. Tanaka's observation with same amount of SA at 25˚C (Tanaka, 1996).

It was also investigated the mechanical strength of swollen SMG by compression test at room temperature and at high temperature (60˚C). The sample was cut with a cylinder shape of 5.5mm diameter. Figure 5 illustrates the stress-strain curve of compression test. It is pointed out here that the room temperature sample shows the linear relationship between the stress and strain. On the other hand, high temperature sample shows large elongation with a small amount of stress. It implies that at room temperature sample has a crystalline structure, whereas the crystallinity decreases at high temperature.

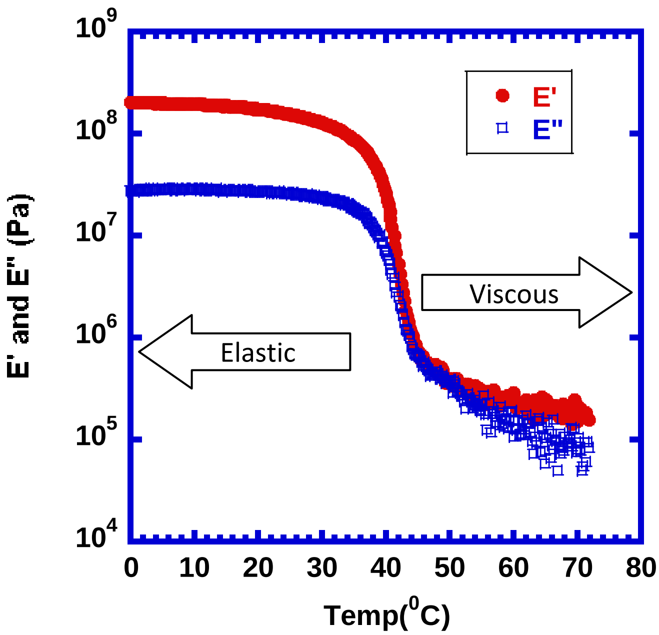

Fig.6. Storage and loss modulus of sample1 as a function of temperature.

Dynamic Mechanical Analysis:

The dynamic mechanical analysis (DMA) was done with TA instruments (Rheometrics Series RSA III) at a fixed frequency of 1Hz. The length, width and thickness of the sample 1 were 36mm, 6mm and 0.6mm, respectively. The measurement was carried out from 0 to 70˚C using a step of 1˚C/min. The sample was placed in an N_2 cooling chamber. The gap between sample holders was 25mm. The measurement was carried out on equilibrium-swollen sample to investigate the viscoelastic property of the sample. Before measurement the sample was wiped with soft tissue paper to remove the additional water from the surface of the sample.

The storage modulus E′ and loss modulus E″ of the DMAAm-co-SA network as a function of temperature is shown in Fig. 6. Both modules drastically decrease around the transition temperature (T_c). However, below the $T_{c,}$ there is a significant difference between them, whereas around the $T_{c,}$ they overlap each other. In addition, above the 45˚C, there is small difference can be seen where much fluctuation is occurred. This result suggests that the water swollen SMG has both the elastic and viscous properties. Below the $T_{c,}$ SMG shows the elastic property, whereas above the $T_{c,}$ the SMG shows the viscous phenomenon.

Conclusion

Transparent shape memory gel with high mechanical strength was synthesized and characterized by tensile, compression and dynamical mechanical analysis. The gel contains 30wt% - 60wt% water depending on the chemical compositions. The high Young's modulus is observed in the sample1 (F=0. 48) and it gradually decreases with the increase of DMAAm fraction, indicating that the amount of SA component plays the major role to increase the mechanical strength. The temperature dependence stress sharply decreases around the 42 - 45˚C suggested the merit of DLS result. Higher breaking strength is observed at room temperature sample than that of at high temperature sample reviled from the compression test. The DMA results demonstrate the elastic and the viscous nature of the water swollen SMG.

Acknowledgments

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