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COMPOSITE OF SiO_2 AND HYDROGEL HAVING MICROPHASE SEPARATED STRUCTURE: PHYSICAL PROPERTIES DEPENDENCE ON pH

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Key Words: Sol-Gel Process, Hydrogel, pH, Hydrophilic Domain, Depolymerization

ABSTRACT

Organic-inorganic composite gel was prepared by using PEG-modified urethane acrylate (PMUA) gel and tetraethoxysilane (TEOS). PMUA gel was prepared by the phase-inversion emulsion polymerization of PMUA emulsion. The gelation of PMUA emulsion using this method enables PMUA gel to swell with H_2O, TEOS, and ethanol. Hydrolysis and condensation reaction rates of the sol-gel process are strongly influenced by the pH controlled by catalysts such as HCl and NH_4OH. Additionally, the morphology on the cross section of composite and the amount of silica ingredient incorporated into the composite gel were dependent on solvent, the molar ratio of H_2O to TEOS, as well as the pH value.

As the silica content increased, due to hydrogen bonds interacting between PMUA gel and SiO_2, particles, the tensile strength of composites considerably increased, whereas the elongation at break decreased. The incorporation of silica ingredient in PMUA gel/silica composites was verified with FTIR/ATR and SEM. The amount of the silica component in the composite was indirectly investigated by using TGA thermal analysis.

INTRODUCTION

In recent years, the various types of sol-gel process have been extensively studied to improve or modify the process of making organic-inorganic glasses [1-6]. The sol-gel process was ordinarily investigated to avoid the high-temperature fusion procedure and save considerable energy loss. However, the sol-gel process has been recently studied to obtain synergistic effects to produce materials that have an optimized combination of the merits of polymers with the better properties of inorganic materials [7, 8]. Inorganic materials are brittle, but display a number of beneficial properties such as heat resistance and transparency, and physical properties such as tensile strength and modulus. On the other hand, organic polymers have merits such as good flexibility and low density.

As one method of applications of these sol-gel processes, organic-inorganic composites are prepared by swelling metal alkoxide, water, catalyst, and solvent into the membrane having microphase-separated structure and converting the absorbed species to an oxygen bridging network consequently [9, 10]. In this method, the morphology and physical properties of the final product are strongly influenced by the swelling degree of the organic network in aqueous solution. Mauritz and coworkers [11, 12], for instance, incorporated an aqueous solution into an organic membrane by using the principle that perfluorosulfonic acid makes micro-domains due to ionic crosslinking. Ordinarily, hydrogels containing ionic groups such as carboxyl and sulfonyl groups swell in external solution due to electrostatic repulsion or hydrogen bonding. In addition, it is also influenced by the pH of the external solution [13, 14]. However, a non-ionic hydrogel consisting of hydrophilic segments, and hydrophobic segments is not influenced by the pH of aqueous solution. Therefore, the non-ionic hydrogel can be efficiently used to define the relationship between physical properties and the pH changes in the sol-gel process using the swelling method above. Additionally, the pH, among factors such as solvent, molar ratio of H_2O to metal alkoxide, and temperature, primarily has an influence on the reaction rates of hydrolysis and condensation in the sol-gel process [15, 16].

In our previous studies [17-20], in the process of soap-free emulsification of PMUA, polyoxyethylene chains orient into the water phase, while hydrophobic segments aggregate to form their domains such that microphase separation between hydrophilic and hydrophobic segments of PMUA occurs. Because droplet coalescence and polymerization of a PMUA emulsion happen simultaneously, microphase separation between both segments can be maintained during gelation of PMUA emulsion.

In this study, PMUA gels having a hydrophilic moiety were prepared by the phase-inversion emulsion polymerization of PMUA emulsion, and then SiO_2 particles were incorporated into a network of gels by using *in situ* sol-gel process. FT-IR/ATR and EDS were used to verify the incorporation of silica into PMUA gel. Also, the morphology of the cross section of the composite was verified by SEM [21]. By surveying the amount of char yield after TGA thermal decomposition, silica contents incorporated in the PMUA gel/silica composites was verified. In order to investigate the relationship between pH change and physical properties, tensile strength and elongation at break were measured.

EXPERIMENTAL

Reagents

In the synthesis of PEG-modified urethane acrylate (PMUA) gel, polytetramethylene glycol (PTMG, Mw=1000, Hyosung BASF) and polyethylene glycol (PEG, MW=600, Junsei Chemical Co.) were dried and degassed at 60°C under vacuum. 2,4-Toluene diisocyanate (TDI, Junsei Chemical Co.) was purified by filtration. 2-Hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.) and potassium persulfate (KPS, Shinyo Pure Chemicals) were used. In the preparation of the composite, tetraethoxysilane (TEOS, 95%, Aldrich Chemical Co.), concentrated hydrochloric acid (HCl, Junsei Chemical Co.), and ammonia water (NH4OH, 28%, Junsei Chemical Co.), and ethanol (EtOH, Lancaster Synthesis) were used without further purification.

Preparation of PMUA Gel

PMUA resin was synthesized by three-step processes and the reaction mechanism was reported previously [17, 18]. PMUA emulsion was prepared using a phase-inversion emulsification process without using an external surfactant. PMUA (10 g) was placed in a 100 mL beaker and then vigorously stirred at room temperature. At first, DDI water was added very slowly until viscosity was increased (Weisenberg effect), and the remaining water was added gradually to reduce viscosity. PMUA emulsion was gelled by KPS initiating at low temperature. Sheet type gel was prepared by the molding emulsion mixture between glass plates surrounded by a 2 mm-thickness of silicon rubber. After this, the PMUA emulsion was gelled in an oven at 45°C and the gel was freeze-dried at -50°C. As the final step, gels were cut into dumbbell-type samples for the measurement of tensile strength and elongation at break.

Preparation of PMUA Gel/Silica Composites

PMUA gel/silica composite was prepared by swelling the PMUA gel in aqueous solution followed by *in situ* sol-gel process. Aqueous solution was prepared with DDI water and ethanol. The acid and base conditions depend on the amount of HCl and NH_4OH added, respectively. PMUA gels of dumbbell type were swollen in this aqueous solution at ambient temperature up to the equilibrium state, for 4 hours. After, PMUA gels were removed from the solution and washed with EtOH several times. Consequently, these gels were put into a solution of TEOS/EtOH for 2 hours. Since H_2O:TEOS molar ratio influences the amount of silica ingredient incorporated, the amount of water was controlled from 1 to 6 g with the conditions of 26.04 g of TEOS and 22.11 g of EtOH. The formulation for these composites is explained in Table 1. In order to evaporate the solvent, excess water, and residual reagents, composite gels were dried first at 45°C for 12 hours, and then dried at 70°C. These two drying steps were adopted to minimize the shrinkage of the resulting composite gel [22].

Swelling Ratio Measurement

For the preparation of composite gels, hydration time was determined as 4 hours. This condition was established by measuring the swelling ratio of the PMUA gels. The pre-weighed PMUA gel was immersed in a solution of DDI water, ethanol and catalyst such as NH_4OH or HCl at room temperature. After the excess surface water or organic solvent was removed, the weight of a swollen gel was measured. This procedure was repeated until no weight change was observed. The swelling ratio is determined by the equation as follows :

$$\text{Swelling ratio}(\%) = \frac{M_s - M_0}{M_0} \times 100$$

where M_s : Weight of swollen gel

M_0 : Weight of dried gel

TABLE 1. Formulation for the Preparation of Pmua Gel/Silica Composites

Samples	H_2O [a] (g)	H_2O:TEOS molar ratio	H_2O [b] (g)	TEOS (g)	EtOH (g)
PU 2	20	-	-	-	-
PUSI 2-1	20	1	13.5	26.04	22.11
PUSI 2-2	20	2	9.0	26.04	22.11
PUSI 2-4	20	4	4.5	26.04	22.11
PUSI 2-6	20	6	2.25	26.04	22.11
PU 3	30	-	-	-	-
PUSI 3-1	30	1	13.5	26.04	22.11
PUSI 3-2	30	2	9.0	26.04	22.11
PUSI 3-4	30	4	4.5	26.04	22.11
PUSI 3-6	30	6	2.25	26.04	22.11

a : The amount of water used during preparation of PMUA emulsion.

b : The amount of water used during preparation of PMUA gel/silica composite.

Measurements

To verify the precipitation of silica in PMUA gel/silica composites, attenuated total reflectance spectra (ATR, Nicolet Model 5-DX), and energy dispersive X-ray spectra (EDS, Philips C. XL-30) were measured. Scanning electron microscopy (SEM, Philips C. XL-30) was used to investigate the morphology of a cross section of the composite. Thermogravimetric analysis (TGA, Perkin Elmer TGA-7) was used to measure indirectly the amount of silica in the composite gels at 10°C/min heating rate. The physical properties of the composite gels were measured with an Instron (series 4400, INSTRON LTD.) at room

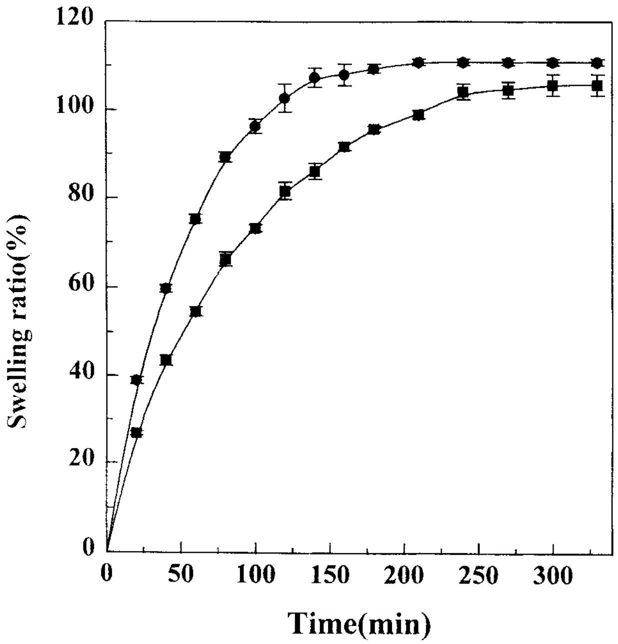


Figure 1. The change of swelling ratio of PMUA gels in H_2O/EtOH/catalyst solution as a function of time.

(-■-) PU 2, (-●-) PU 3

temperature using crosshead speed of 20 mm/min and head load cell capacity of 100N.

RESULTS AND DISCUSSION

Preparation of PMUA Gel and Swelling Behavior

As reported previously [17, 18], PEG-modified urethane acrylate (PMUA) emulsion was polymerized using the water-soluble initiator, KPS. Droplets coalesce and polymerization of PMUA emulsions happen at the same time in the course of gelation with an increase of the temperature, so it is assumed that PMUA gels, which maintain the microphase separation between hydrophilic and hydrophobic segments are obtained. PMUA gel was freeze-dried so as to maintain these hydrophilic micro-domains. As a result, the silica component is precipitated in these porous micro-domains. When samples PU 2 and PU 3 were swollen in the solution of H_2O and EtOH, the swelling ratios of these PMUA hydrogels reached

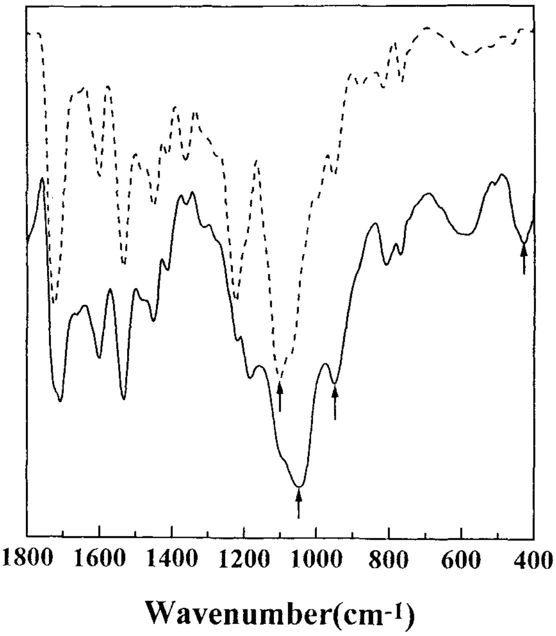


Figure 2. The comparison of PMUA gel and PMUA/silica composite gel prepared at pH 1.0 using FT-IR/ATR spectroscopy.
(—) PUSI 3-2, (----- PU 3

equilibrium after 3 and 4 hours, respectively. The swelling ratios of PU 2 and PU 3 in H_2O/EtOH/caltalyst solution are illustrated in Figure 1.

PU 3, using 30 g of water during preparation of PMUA emulsion, incorporated a large amount of aqueous solution during the initial 150 minutes, and then achieved a swelling ratio of 110% at 3 hours. On the other hand, sample PU 2 contained much more hydrophobic moiety than PU 3. PU 2, using 20 g of water during preparation of PMUA emulsion, swelled slowly and reached the equilibrium state, with a swelling ratio of 105% at 4 hours.

Qualitative Analysis

FT-IR/ATR was measured to verify the incorporation of the silica ingredient in PMUA gel/silica composites. The subtraction spectra of PMUA gel and the composite gel are illustrated in Figure 2.

The subtraction spectra for PU 3 and PUSI 3-2 appeared different from each other in the important fingerprint region, 1120-800 cm^{-1}. The C-O band that occurs due to asymmetric stretching vibration of carboxyl group, composing of PMUA gel, appeared at 1112 cm^{-1}. The Si-O-Si asymmetric stretching vibration, v_{asym} (Si-O-Si), being the signature of bridging oxygen, was an intense peak around at 1050 cm^{-1}. This band is known to be composed of two components arising from groups in linear and cyclic configurations [22]. However, because PUSI 3-2 was prepared to produce the mostly linear type, the spectrum of PUSI 3-2 showed only one peak of energy absorption. Also, the peak corresponding to the Si-O-Si bending mode, appeared at 435 cm^{-1}. In addition, because the PMUA hydrogel contains a slight amount of residual hydroxyl groups in free water in spite of the freeze-drying procedure, these hydroxyl groups in the PMUA gel by swelling in aqueous solution separated again into hydrophilic domains. Many peaks of hydroxyl groups from 1000 cm^{-1} to 820 cm^{-1}, therefore, occurred in one peak (949 cm^{-1}). Another method to verify the presence of silica in the cross section of resulting composites is the EDS measurement, which is attached to SEM. The k_{α}^{1} and k_{β}^{1} transition energy peaks of silica appeared at 1.740 and 1.832 KeV, respectively.

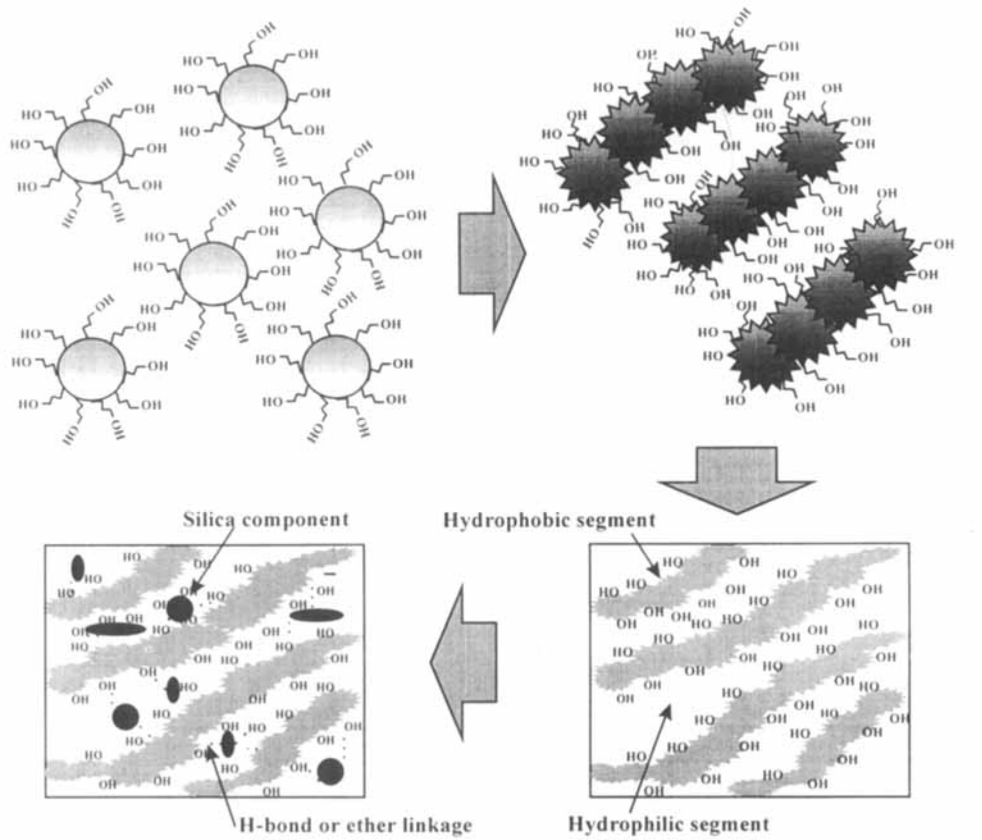
Morphology

The morphology of composites depends on amphiphilicity of hydrogel and pH changes. Because PMUA gel, prepared by phase inversion emulsification, contains hydrophilic and hydrophobic domains, the morphologies of these gels are subject to phase separation and appears rough in cross section. The mechanism of organic-inorganic composite formation using the amphiphilic properties of PMUA is illustrated in Scheme 1.

The reaction rates of hydrolysis and condensation in the sol-gel process are dependent on the pH. Though pH 7 ordinarily separates the acid region and the base region, pH2 appears to be a critical point in the sol-gel process. This point is close to the point of zero charge (ZPC) of silica at which the net repulsion force is zero. Therefore, the amount of silica in the cross section of the composite decreased with increasing pH. In addition, because the porous hydrophilic domains of the hydrogel occupy a larger volume fraction in the PU 3 than in the PU 2, the former composite contains more silica than the latter. Figure 3 shows SEM micrographs of cross sections of samples which vary in pH and hydrophilic domains.

Quantitative Analysis

TGA was measured to estimate the amount of silica in PMUA composite gel [24]. PMUA gel completely decomposes at 450°C. In this work, the composite gels were heated above 550°C. At this temperature, the organic materials in composite gel are decomposed, but the silica component is not decomposed at all.



Scheme 1. The Schematic Representation for the Formation of the PMUA/Silica Composite Gels.

Thus, the relative amount of silica in PMUA composite gels could be determined by measuring the residual weight of char yield. TGA thermograms of PMUA gel/silica composites are illustrated in Figure 4.

The residual hydroxy groups on the silica particles were more condensed by the thermal factor, and converted to by-products such as ethanol and water. Additionally, these materials, boundary water, and TEOS were vaporized below about 350°C. The rest of the organic materials were nearly decomposed under 550°C. Also, the sol-gel process, consisting of hydrolysis, condensation, and depolymerization reactions, is dependent on the pH value. Especially, depolymerization reaction containing alcoholysis and re-esterification reaction strongly affects the sol-gel process. In addition, the depolymerization reaction rate at high pH is

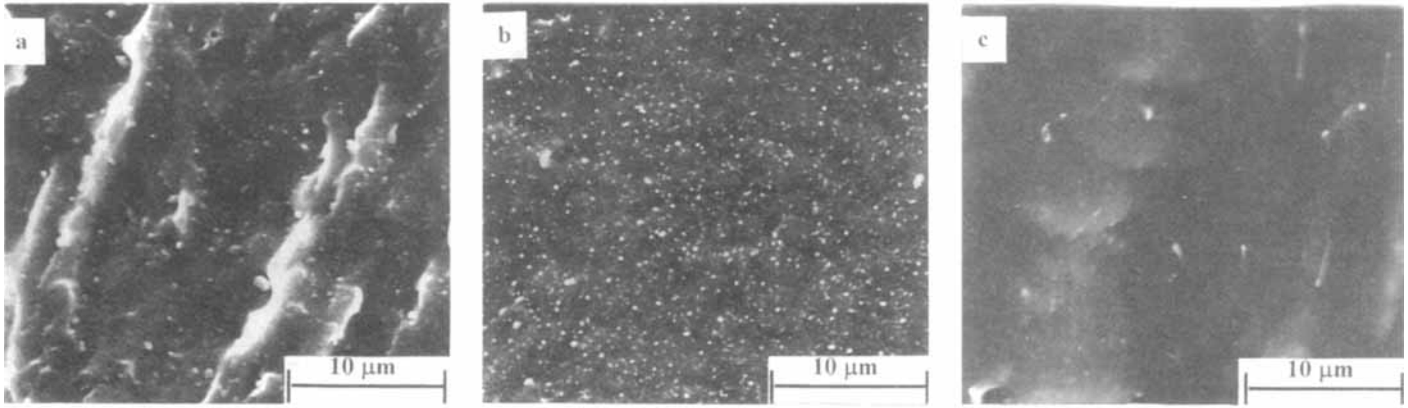


Figure 3. SEM micrographs of PMUA/silica composite gels with the amount of water used during preparation of PMUA emulsion and pH value.
(a) PUSI 2-6 at pH3.0 (b) PUSI 3-6 at pH3.0 (c) PUSI 3-6 at pH9.0

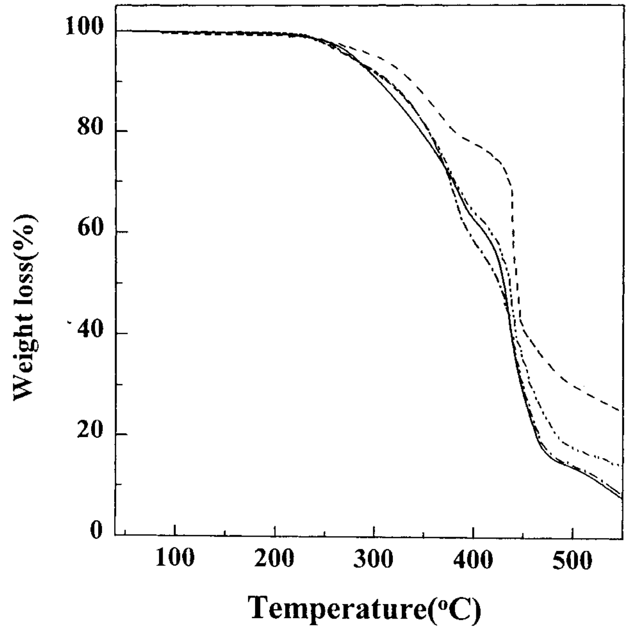


Figure 4. TGA thermograms of PMUA gel and PMUA/silica composite gels formed at different pH values.
(——) PU 3, (- - - - -) PUSI 3-2 at pH1.0, (- ·· — ·) PUSI 3-2 at pH7.0,
(-· — · —) PUSI 3-2 at pH11.0

much larger than at low pH. The depolymerization reaction is unlikely to occur at low pH, because the TEOS involved is hydrolyzed to prepare the silica gel sequentially. On the other hand, at high pH, because incorporated TEOS is hydrolyzed to prepare the silica sol, the depolymerization reaction occurs at a considerable rate. The amount of char yield prepared at low pH was much more than that of the char yield at high pH due to the reverse reaction mentioned above. Hydrogen bond formation, which affects thermal decomposition, necessitates the presence of hydrogen bond acceptors in the PMUA gel and on the silica particles. In addition, hydrogen bond acceptors such as oxygen and nitrogen in the PMUA gel, and ether groups in the composites can add hydrogen bond. Because the silica content was proportional to hydrogen bond energy between PMUA gel and SiO_2 particles, the PMUA gel/silica composite prepared at low pH was decomposed at a higher temperature than the composite prepared at high pH. These results are shown in Table 2.

TABLE 2. The Char Yield Contents and Decomposition Temperature of TGA

Samples	PU 3	PUSI 3-2 (pH1.0)	PUSI 3-2 (pH7.0)	PUSI 3-2 (pH 11.0)
Char yield [a] (wt %)	7.924	25.121	14.286	8.485
Decomposition temp [b] (°C)	435	445	440	437

a : The weight percent of char yield resulting from TGA decomposition at 550^{0}C.

b : The temperature where 1st derivative(%/min) occurs at TGA.

Physical Property Measurements

Generally, the microphase separation improves the physical properties. Domains separated into hydrophilic and hydrophobic segments interact with each other by hydrogen bonding or hydrophobic interaction. In the case of PMUA gel, hydroxyl groups in hydrophilic domains have a weak hydrogen bonding strength, so, tensile strength was relatively low. In PMUA gel/silica composites, hydroxyl groups on the silica particles interact with hydroxyl groups of the hydrophilic domains in PMUA matrix, so that tensile strength of these composites is largely improved. The tensile strength and elongation at break of composite gels are illustrated in Figure 5.

As mentioned in the TGA measurement, the silica content of the composite was more at low pH than at high pH. Accordingly, many more Si-O-Si network structures were formed at low pH. Specially, near the point of zero charge (ZPC) where there is no electrostatic repulsion on the particles, the growth and aggregation processes occurred together and might be distinguishable. Therefore, by forming a large number of Si-O-Si network bonds at pH2, the tensile strength of composites formed at pH2 was 70N, 12 times as much as that of PMUA gel itself. On the other hand, elongation at break varied inversely as the tensile strength.

CONCLUSION

PMUA gel/silica composite was prepared by using a swelling procedure followed by a sol-gel process. Because the swelling behavior of PMUA gels is

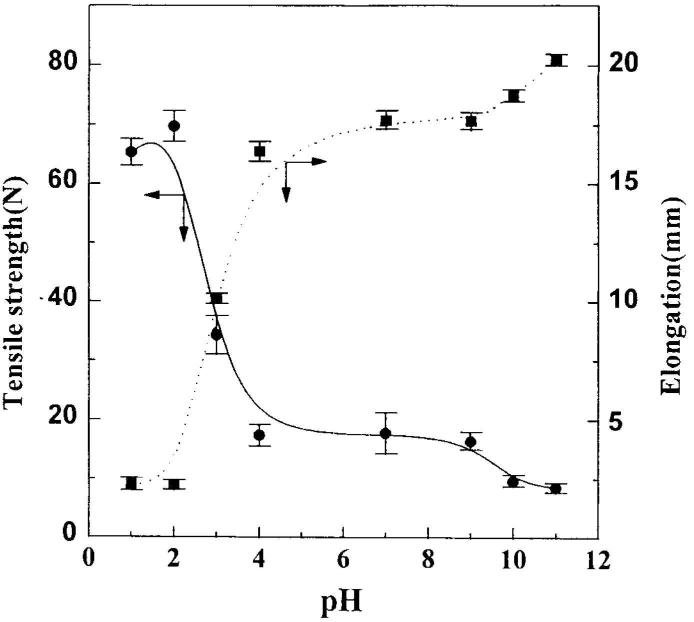


Figure 5. Tensile strength (-■-) and elongation at break (-●-) of PMUA/silica composite gels (PUSI 3-2) as a functional of pH.

dependent on the volume fraction of hydrophilic domains in PMUA hydrogel, PU 3 composed of many hydrophilic domains swelled more reagent materials such as H_2O, TEOS and ethanol than PU 2 with less hydrophilic domains. From the results of FT-IR/ATR and EDS analysis, it was verified that silica was incorporated with the composite itself. Many properties of PMUA gel/silica composites such as morphology, thermal analysis, tensile strength and elongation at break were influenced by the pH value at which they were formed. At high pH, because the re-esterification and alcoholysis reaction occur at the same as rate of forward reaction, the amount of silica in composite is much less than the amount of silica in composite formed at low pH. Because the amount of silica particles incorporated was proportional to hydrophilic volume fraction, the tensile strength of composite was improved rather considerably at low pH in comparison with high pH.

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