

A study on the bonding Characteristics of Inorganic/Organic Composite by Measurement of the Glass Transition Temperature(Tg)

Dong-a Lee¹, Goo-dae Kim, Hyun-min Kim

Korea Institute of Science and Technology, Seoul 136-791, Korea

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유리전이온도(Tg) 측정에 의한 무기/유기복합체의 결합특성에 관한 연구

이동아¹ · 김구대 · 김현민

한국과학기술연구원

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요 약. 졸-겔법에 의해 무기-유기 복합체를 합성하였으며, 복합체의 결합특성을 알아보기 위하여 DMTA(Dynamic Mechanical Thermal Analyzer)를 이용하여 유리전이 온도(Tg)를 측정하였다. HCl 과 물의 양이 증가될수록 Tg는 고온으로 진행됨으로부터 복합화가 더 잘 일어남을 알 수 있었다. 그러나 반응시간에 따른 Tg의 변화는 관찰되지 않았다.

Abstract. Inorganic/organic composite was synthesized by using sol-gel process, and the bonding characteristics of composite was investigated with glass transition temperature(Tg), measured by DMTA(Dynamic Mechanical Thermal Analyzer). It was found from shift of Tg to higher temperature that composite reaction was proceeded better with the amount of HCl and water. But Tg was not varied with reaction time.

Key Word : Inorganic/organic composite, glass transition temperature(Tg), DMTA(Dynamic Mechanical Thermal Analyzer)

1. Introduction

Ordinary glass will soften at a temperature well below its melting point, and this softening point is referred to as Tg, the glass transition temperature. There is a close similarity between polymers and inorganic glasses regarding their glass transitions,

therefore the same is also applicable in case of polymers. At Tg, a dramatic change occurs in the local movement of polymer chains, which leads to great changes in a host of physical properties. These properties, in addition to many other general properties, include density, specific heat, mechanical modulus, mechanical energy absorption, and,

their dielectric and acoustical equivalents, rate of gas or liquid diffusion through the polymer. But, none of these properties can be used, at least in a crude manner, to determine the T_g , since T_g of polymer is frequently sensitive to other variable parameters. Hence T_g as a mean to get an information of the bonding characteristics of polymer should be researched in terms of all the factors having an effect on it. These factors are considered to be polymeric structure, crystallinity, molecular weight, thermal history, pressure, and so on. In case of some polymers, T_g is said to be independent to molecular weight¹⁾.

The classical method for T_g measurement discussed by Flynn, Peyser, Richradson, et al^{2,3,4)}, is quite insensitive for some polymers like highly crosslinked polymers, and modern method for T_g measurement is involved with imposing an oscillating energy on the polymer, and measuring the absorbed energy and a phase shift by this absorbed energy. If this energy is mechanical one, we are in need of a DMTA type instrument which determines the modulus as well as a $\tan \delta$ peak value. This is because, at T_g , there often occurs an order of magnitude change in the modulus and a large maximum in $\tan \delta$.

An onset point, a mid point, or a change in modulus by a certain amount have all been used to determine the glass transition temperature. The maximum of $\tan \delta$, however, clearly and obviously specifies a T_g in using the method of curve analysis, but T_g must be independently determined since there appear many other transition points on a data from DMTA type instrument. Moreover, in a $\tan \delta$ type analysis of T_g , other variables are generally introduced into the measurement, namely the frequency in the measurement with which T_g increases. But it is possible to measure the maximum of $\tan \delta$ at constant temperature while the frequency is being scanned, and there is an inverse relationship between temperature and frequency. It can be

easily found that there is a correspondence between a classical T_g measured at a low programmed temperature rate (1 deg/min), and T_g earned by $\tan \delta$ measurement at a low frequency of measurement (1 Hz). However, even at a reasonably low frequency (10 Hz), a T_g of maximum $\tan \delta$ can easily be 20 ~ 30°C greater than the classical one. This correspondence between two methods has not been extensively studied yet.

Recently, pure oxide gels have been modified by the incorporation of organic groups to improve the ductility. This process can be carried out by forming network chain through dispersing organic polymer into inorganic glass network. These materials are named as ORMOSIL (Organically Modified Silicate) or 'Ceramer'. ORMOSILs are less brittle, furthermore show a tendency of not-easy-fracture, because some of the bonds are terminated by organic side groups^{5,6)}.

The basic 'construction principles' for inorganic polymers with the case of glasses are network forming units like $[\text{SiO}_4]^{4-}$ tetrahedron or analogous components linked to three-dimensional network by sharing corners. The properties defined by means of this principle are well known; hardness, brittleness, high temperature processing, high T_g values, and low free volumes. But, almost the opposite can be observed in organic polymers which are linked together with polymeric chains through chemical (not melting) process, and in this case, a linear chain is formed in the first step, which are crosslinked to get three-dimensional networks. As a result, the polymer are usually soft and the low temperature processing is possible. For these, intended or desired elastic or thermoplastic properties can be possibly achieved. In these products, high free volume is observed due to the organic chain movement, and T_g is generally low⁷⁾.

For the first attempt to fabricating inorganic/organic composite, tetraethoxy silane (TEOS) was used as the inorganic component. This was mainly

due to its controllable hydrolysis reaction rate, which could assist the possibility of incorporating oligomeric species into the system. Silanol-terminated poly(dimethyl siloxane) (PDMS) was chosen as the oligomeric component because of the similarity of its backbone structure(-SiO-) with the sol-gel glass matrix of TEOS and because of its good thermal stability⁹⁾. While these kinds of network defects and poorer mechanical properties of PDMS would contribute to the lower tensile strength, the silica backbone provides mechanical strength and an amorphous structure with possible transparency in the visible spectrum⁹⁾.

At the beginning of the reaction, all silanol groups present extend from the PDMS, hence the self-condensation would be favored, which results in a chain extension of the PDMS with promoting some phase separation. The Tg for these phase-separated siloxane region would be close to that of the siloxane rubber near -100°C. However, the silanol groups from the hydrolysis reaction would be increased with time, therefore the condensation of the silanol-terminated PDMS and the hydrolysed TEOS would gradually become the dominant in the reaction of system¹⁰⁾.

As a result, compared with the phase separated region, the Tg behavior is shifted to higher temperature. In other words, as oligomeric species are well distributed into the matrix of TEOS network, higher thermal energy is required for the onset of their backbone motion. It is believed that this shift to higher temperature is due to the end point restrictions of oligomeric locked into overall sol-gel network. Comparatively it is also noted that, at the temperature near -90°C, a small peak is observed in $\tan \delta$ which is believed to be related to rich phases of the siloxane component. In this reaction, if the hydrolysis of the alkoxide is not sufficiently rapid, self-condensation of the functionalized oligomers leads to chain extension and molecular weight build-up, and finally result in

poor dispersion of the oligomeric component¹¹⁾.

In this study, sol-gel process was used, which was intended to formed self-condensation in the first place and cocondensation in the second. With the variation of the amount of water in hydrolysis reaction, changeable results were investigated by using DMTA, and with the results from DMTA that indicates Tg at maximum $\tan \delta$, differences of bonding state was investigated as a function of the concentration of HCl used as a catalyst, amount of solvent, and reaction time. And in order to refine the results from DMTA and to confirm whether this instrument is a useful tool of explaining that organic material dispersed into inorganic network or not, SEM, IR were also used as the additional instruments.

2. Experiment

2.1 Sample preparation

Previously an appropriate amount of deionized water and hydrochloric acid were poured into a round-bottom flask, following the addition of 2-propanol and THF, and the solution was mixed thoroughly. Then a certain amounts of TEOS and PDMS(M.W.=1700) were simultaneously added into the solution and mixed for 20 min with a fast agitation stirrer. In this step, the reaction system was placed in a water bath with the temperature of 80°C. This reacted solution was maintained in a teflon-coated Petri dish covered with parafilm until forming a gel products. After several hours at room temperature, all of the samples gelled and dried at room temperature and 100°C.

The compositions of starting materials used in sample preparation with this method was shown in *Table 1*.

2.2 Instrument and conditions for analyzing

Glass transition temperature, Tg, was measured by using MKII DMTA(Dynamic Mechanical

Table 1. Various Composition for Preparing ORMOSIL.

Sample No.	H ₂ O/TEOS (mole ratio)	IPA/TEOS (mole ratio)	HCl/TEOS (mole ratio)	Reaction Time(min)	M.W. of PDMS	PDMS/TEOS	Reaction Temperature
1	1.0	4.0	0.30	20	1700	40/60	80°C
2	2.0						
3	3.0						
4	4.0						
5	7.0						
6	2.0	4.0	0.05	20	1700	40/60	80°C
7			0.10				
8			0.15				
9			0.20				
10	2.0	2.0	0.20	20	1700	40/60	80°C
11		4.0					
12		6.0					
13		8.0					
14	2.0	4.0	0.20	20	1700	40/60	80°C
15				60			
16				100			
17				280			

Thermal Analyzer, PL-Co.), in order to get an information about the distribution of oligomeric species of PDMS in the matrix of the TEOS network. The measurement was performed in the frequency range of 10~100Hz and temperature range of -200~300°C with the heating rate of 2~4°C/min.

In the region showing decrease of storage modulus, the value of $\tan \delta$ would increase. In this study, FT-IR was also measured to investigate the bonding state of each sample, and the microstructure observed by SEM.

3. Results and Discussion

The cocondensation of the silanol terminated PDMS and the hydrolyzed TEOS would gradually become the dominant reaction of the system. We measured Tg to know occurrence of reaction and homogeneity of incorporating oligomeric species into

the TEOS system. As the reaction system proceeds to well dispersion state, the glass transition temperature increases due to the higher inorganic contents. Exactly, with the dispersing of polymeric silane into inorganic network, Tg shifts to higher temperature^{1,2)}.

To know how to react PDMS with TEOS, as the amount of water increased from 1 mole to 4 mole, Tg was measured and the results were shown in Fig. 1. With the amount of water, Tg of composite shifts to higher temperature. With this result, reaction was promoted with water and silane dispersed into TEOS network homogeneously. For the case of 4 mole, measurement of Tg was impossible.

In the measurement by using DMTA, however, variation of temperature at maximum $\tan \delta$ peak was to be observed, that can be calculated as the ratio of storage modulus(E) and loss modulus(E*). As the storage modulus decreased, $\tan \delta$ peak

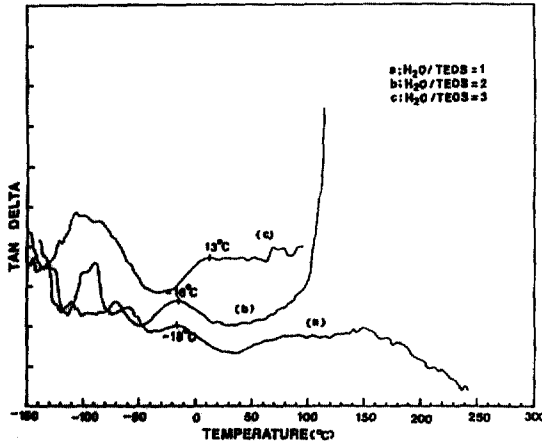


Fig. 1. Effect of H₂O/TEOS mole ratio on the tan δ behavior.

increased abruptly at a certain point. The first point showing higher tan δ peak at the temperature near $-80\sim 100^\circ\text{C}$ was believed to be T_g of the siloxane component. After continuous decreasing storage modulus, another maximum tan δ peak is found, which is believed to be the T_g of composite material.

It can be defined that glassy state of composite transformed into a rubbery state at this T_g point. Considering in the respect to polymer, the addition of inorganic material would have an effect on structure stabilization. This meaning of stabilized structure includes not only the higher T_g, but chemical property which decrease molecular motion of organic polymer.

Through SEM and FT-IR, reasonability of observation by T_g was investigated and these results were shown in Fig.2 and Fig.3. In Fig.2, it is surely observable that a mass of large particles interconnected one another(a), and with the amount of water, its structure transformed into a form of small particle dispersion (Fig. 2. (a), (b)), thereafter with more amount of water, structure was changed into a dense one. These illustrate that, in hydrolysis

reaction between TEOS and PDMS, cocondensation of each composition of TEOS and PDMS would be dominant with small amount of water, resulting in the large spherical particles of silica gel surrounded by the layer of the copolymer. But in Fig. 2(a), (b), it is found that hydrolysis and condensation take place simultaneously, and then the network was densified with one another (Fig.2(d)).

Especially, in these case, it was thought that the length of the chain was very short because of higher copolymerization. The IR result was shown in Fig. 3. This result shows, that as the amount of water increased, the ratio of $-\text{Si}-\text{O}-\text{Si}-$ bonding peak to methyl group peak that bonded with organic silane was also increased. In this case, formation of composite can be known from the peak near 1100 cm^{-1} , showing the bonding between $-(\text{OH})$ in TEOS and PDMS, which is thought to be the bonding between Si- of the inorganic TEOS and organic PDMS. In order to get an crude information about the change of composite formation with the amount of water, the ratio of peak height was calculated with the peak near 1100 cm^{-1} and one near 1250 cm^{-1} for methyl group of having PDMS¹³⁾. Up to 3 mole from 1 mole of H₂O/TEOS, this ratio was increased, and then in the case of variation to 7 mole, the ratio was abruptly decreased. This was thought to be resulted from the situation that an excess of water facilitated concurrent hydrolysis and condensation of TEOS, which inhibit the probability of bonding between TEOS and PDMS.

From the results above, we can quite sure that measurement of T_g is appropriate method to study the bonding of Si-OH in TEOS with PDMS. In Fig. 4, the variation of T_g was shown as a function of the concentration of hydrochloric acid used as a catalyst. With variation of concentration of hydrochloric acid from 0.05 to 0.2 mole, T_g of the composite was increased from -5.294 to 1.009°C . Even this variation was trivial in comparison with

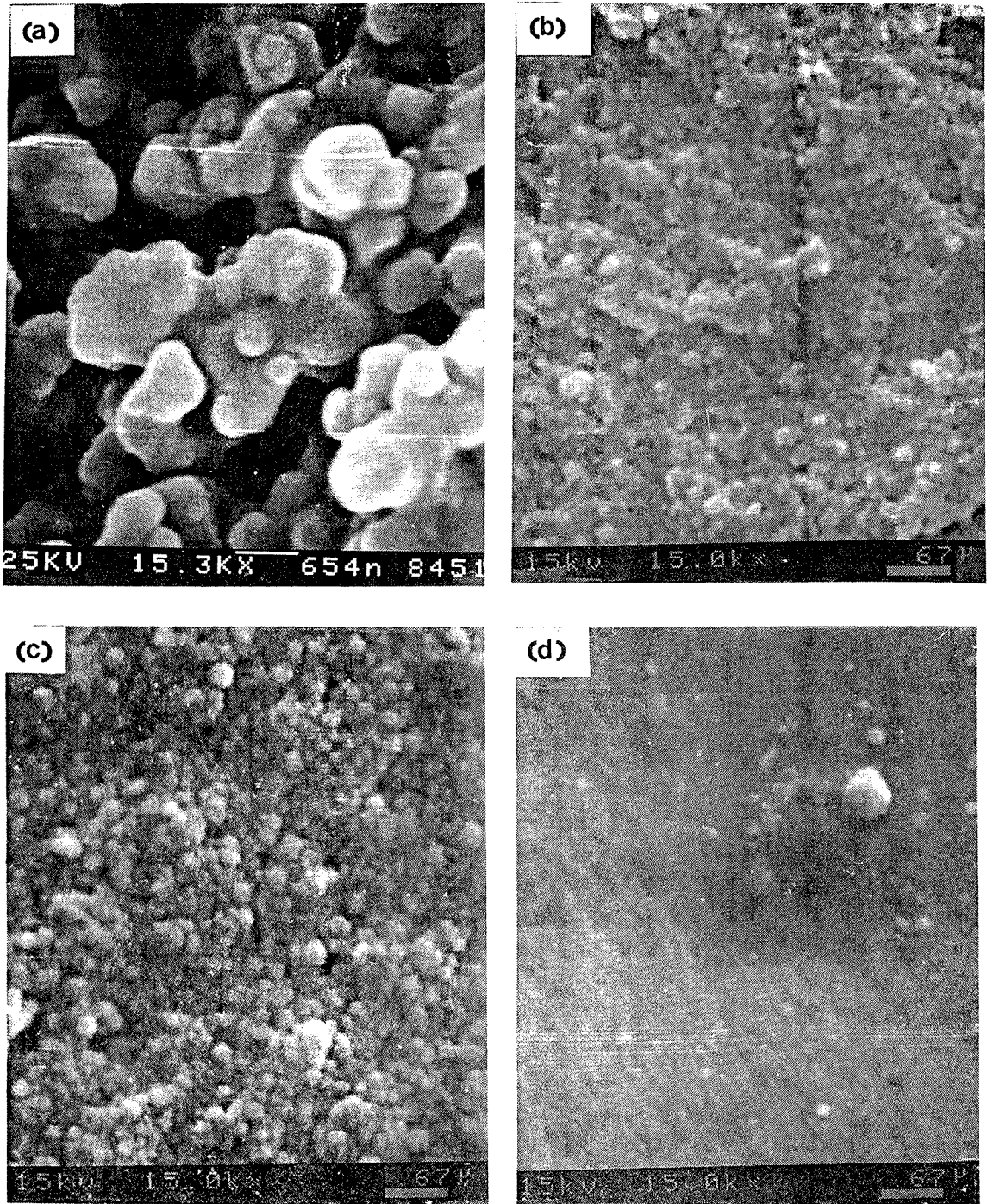


Fig. 2. SEM photographs of ORMOSIL with change of H₂O/TEOS ratio.

- (a) 1 mole (b) 2 mole
(c) 3 mole (d) 4 mole

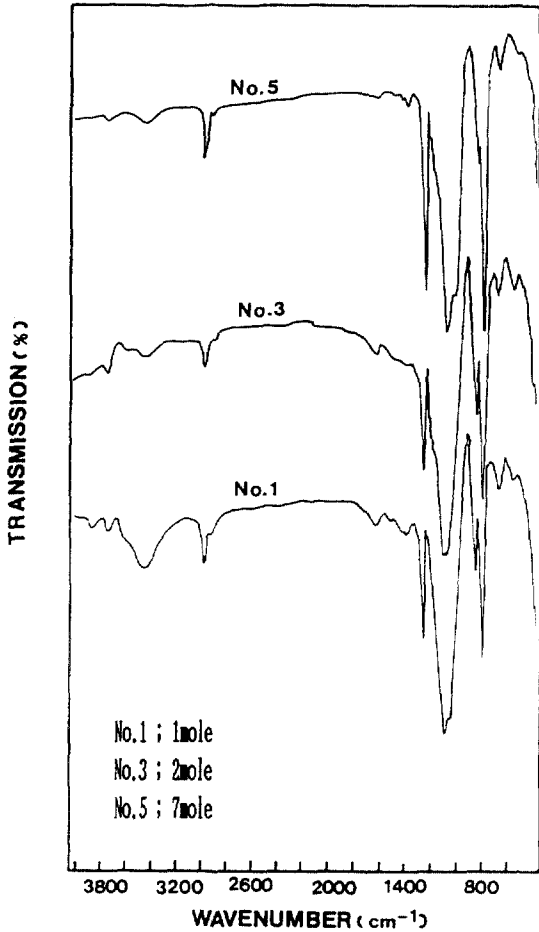


Fig. 3. Change of IR spectra with various H₂O/TEOS mole ratio.

the result revealed by amount of water, it was confirmed that organic polymer uniformly dispersed into inorganic network when the concentration of HCl was increased. The result with the amount of solvent is demonstrated in Fig. 5., and this shows whether the system reacted well or not. As the amount of IPA of solvent was increased, shift of T_g was observed. In the case with the molar ratio of IPA/TEOS, 2 (Fig. 5(a)) and 4 (Fig. 5(b)) of the ratio of IPA/TEOS, due to small amount of solvent, meaning high concentration of the system,

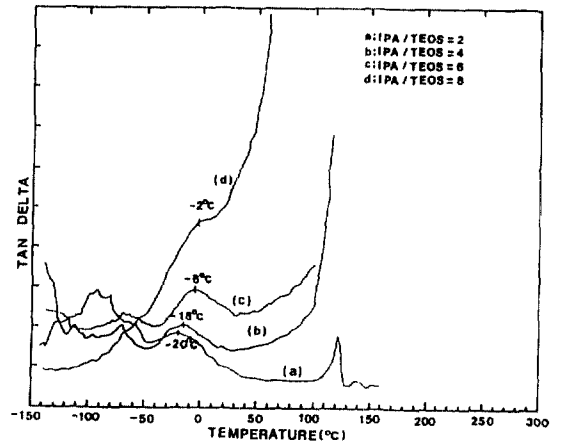


Fig. 5. Effect of IPA/TEOS mole ratio on the tan δ behavior.

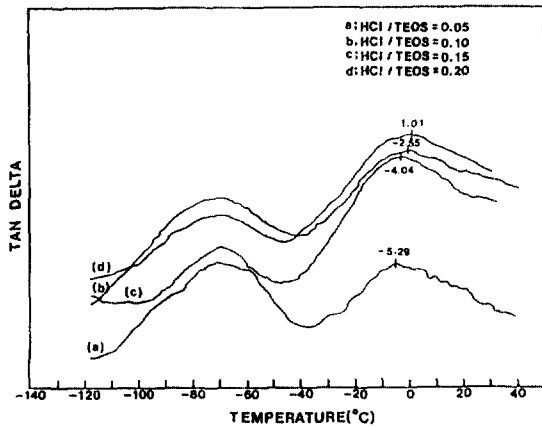


Fig. 4. Effect of HCl/TEOS mole ratio on the tan δ behavior.

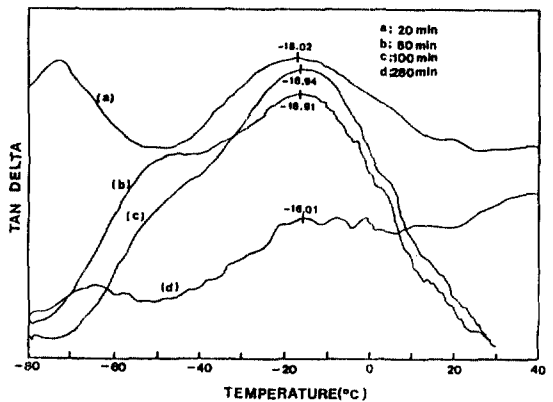


Fig. 6. Effect of reaction time on the tan δ behavior.

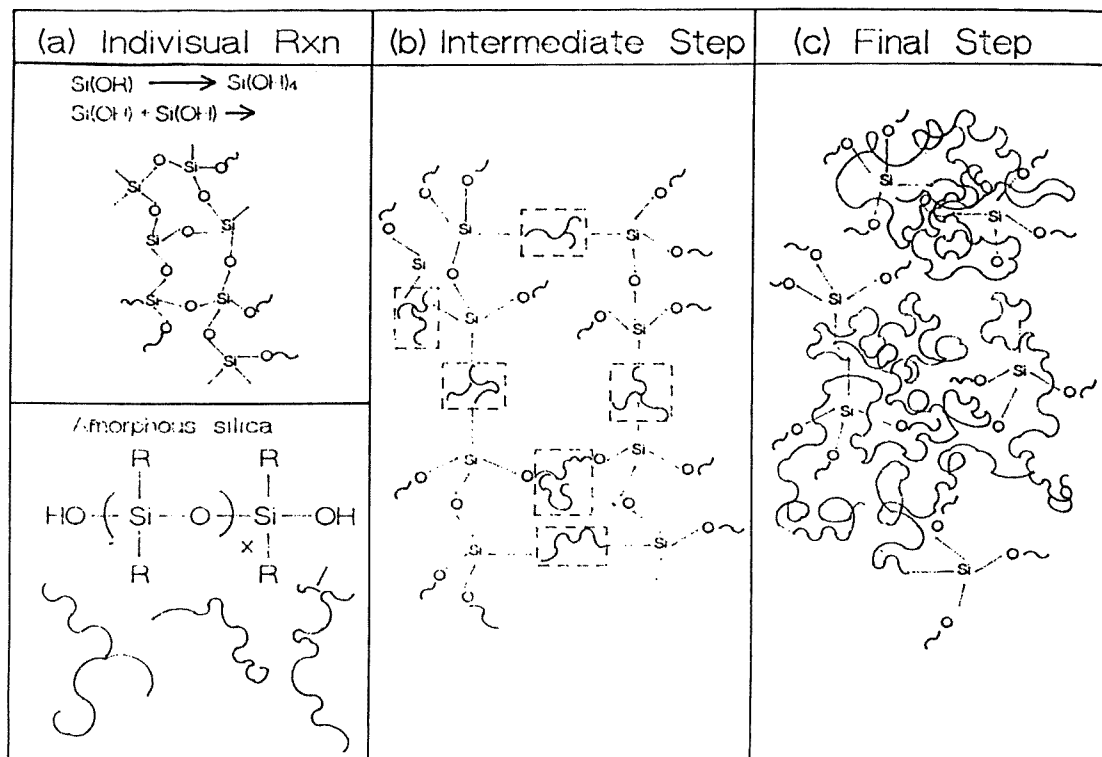


Fig. 7. Modeling of cocondensation between TEOS and PDMS.

copolymerization reaction proceeded well, but T_g showed low value for locally occurred reaction. This is probably due to the low mobility, a collision for linkage would be decreased. Subsequently as organic groups of the system had high mobility, probability of the collision was increased and the shift of the T_g to higher temperature progressed gradually (Fig. 5(c), (d)).

T_g graph shown in Fig. 6 is the result obtained from long conserved reaction time at 80°C in No.2 (standard). Considering the foundation modeling shown in Fig. 7, this result shows a good correspondence. Namely reaction time affect hardly on the shift of T_g to higher temperature, which resulted from the dispersion of organic polymer into inorganic network. The structure change of the

system from Fig. 7(a) to (c) did not show that the dispersion form of system structure, but shows that inorganic group was piled one on same form when changed, and so did organic groups, therefore total system is suggested to perform curing and aging.

4. Conclusions

By using DMTA, the bonding characteristics of inorganic/organic composite was investigated into the measurement of T_g , the maximum point $\tan \delta$, and the conclusions are as follows,

1. The facilitation of condensation reaction between inorganic/organic precursor was found from the T_g shift of composite to higher temperature with

increasing amount of HCl and water.

2. Tg shift to higher temperature was also found with increasing the ratio of IPA/TEOS, and from this, it was suggested that reaction of the system was increased, i.e. the collision probability between reaction groups, which caused from the mobility of system.
3. No influence on Tg was found by reaction time as a single factor in composite reaction, which was suggested that only the structure of system was changed by reaction time with no effect on the bonding of inorganic/organic composite.

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