Modeling physico-mechanical properties of an individual photopolymerization-induced urethane-based microgel particle

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1. Introduction

Highly cross-linked materials have been used in different industries in order to design engineering products with high degree of quality. One of the most special types of these materials is a class of materials so called microgel particles. The crucial role of these polymeric materials in different high-tech applications such as drug delivery, wave attenuation, anticorrosive properties and electronic devices has been studied [1–4]. The microgel particles suspended in a liquid has been considered to assess polymer dispersions. From the view point of surface chemistry, the stabilization and the rheological properties of the microgel-based polymer dispersions are very significant to design the stimuli-responsive materials in recent years. Different procedures for the microgel formation have been reported in literature [5,6]. In situ-photopolymerization-induced microgelation process is one of the most attractive approaches to generate the microgel particles dispersed in a viscous-like matrix. This procedure has not been reported in this way to form the microgel particles.

However, the recognition of the microgel domains driven by the intermolecular cyclization has been demonstrated for the first time by Kannurpatti et al. [7]. They found that by using the photopolymerization process two dynamically extreme regions are formed namely microgel domain and pool of unreacted monomers. Several scientists have intended to study these two dynamically extreme regions on the basis of different techniques like dynamic mechanical thermal analysis and dielectric relaxation spectroscopy techniques [8–10]. Meanwhile, the separate characterization of these two dynamically extreme regions is lacking in literature. This may be because of the fact that the photopolymerization process is very complicated. In fact, the control of morphology through the photopolymerization process is not easy. Recently, Shukutani et al. [11] have reported a wide variety of morphologies with changing the monomer content and light intensity in ternary photo-curable mixture. On the other hand, characterization of an individual microgel particle dispersed in a viscous-like matrix can be so helpful to generate the products with different physical and mechanical properties. In our previous work [12], the importance of the microgel particle dispersed in a viscous-like matrix in control of the anticorrosive properties of the organic coatings has been investigated. We showed that the anticorrosive coatings containing microgel particles
exhibit a diffusion-limited behavior leading to better anti-corrosion performance. But, the viscoelastic behavior of an individual photopolymerization-induced microgel particle remains as an unsolved problem. This lack of a good understanding structure-property relationship makes it difficult to control the final performance.

The main aim of this work is to predict a series of the physical and dynamic relaxation properties of an individual photopolymerization-induced microgel particle. We tried to predict the cross-link density, hardness, cooperative length, dynamic fragility of an individual microgel particle using the dynamic mechanical results and the AFM phase images obtained for the mixed sample.

2. Experimental

2.1. Materials and synthesis procedure

A urethane acrylate oligomer (UA) was supplied from Eternal Company and used without any purification. 2-ethyl-phenoxycrylate (PEA) was also purchased from Eternal Company. Liquid benzophenone was utilized as the photo-initiator (supplied from Insight Company). 25 gr PEA was added to 75 gr UA to form a mixed sample. A 0.5 wt% of the photo-initiator was added to the mixed sample. To synthesize the individual microgel particle throughout the viscous-like matrix, the mixed sample was exposed to a 33 W/cm UV lamp which has a distinct peak at 365 nm for about 60 s at ambient temperature by using a homemade UV curing oven. This oven is formed from two different parts namely the illuminator and the sample holder box. To prohibit ageing process of the samples, the mechanical and morphological tests were immediately conducted after sample preparation.

2.2. Instrumental testing

The blocks of 1 mm thickness were prepared as the samples for instrumental analysis. A dynamic mechanical analyzer (Tritec 2000, America) was employed at a scan rate of 5 °C/min at four frequencies of 2, 3, 5 and 10 Hz. An initial strain of 0.2% was used for the start-up of the oscillation process. The stress-strain behavior of the mixed sample was characterized using a tensile machine (Giovanni XXIII 183, Italy). A rate of tension of 5 mm/min was used for this purpose.

A LEO 1455VP scanning electron microscope at an acceleration voltage of 10 kV was used to identify the individual microgel particle dispersed in the viscous-like matrix and measure the inter-particle distance. The fractured mixed sample was prepared by the breaking it in liquid nitrogen. An Ambios Technologies USPM atomic force microscope (Ambios Technologies, USA) was used in tapping mode to map the relative elastic modulus of the surface of the mixed sample. A silicon cantilever at a resonant frequency of 180 kHz was used for this purpose.

An IVIUM electrochemical impedance analyzer was used to measure the electrochemical data for the mixed sample of 30 micron thickness. The measurements were performed on the mixed sample with an area of 1 cm² at the OCP in the frequency range $10^{-2}$–$10^{6}$ Hz with a perturbation voltage of 10 mV. The electrolyte was aqueous NaCl (3.5% w/w). Z-View software was utilized for fitting the equivalent circuit to the raw data measured by EIS.

3. Results and discussion

3.1. Calculating the actual size of the individual microgel particle

An individual microgel particle embedded in a viscous-like matrix is illustrated in Fig. 1.

Fig. 1a shows the broad band wave image of the microgel particle. The size of this photopolymerization-induced microgel particle is found to be about 100 nm. The size measured form AFM broad band wave image is related to the diameter corresponding to the projected area of an individual microgel particle. The maximum roughness that is equal to the height of the microgel particle is measured to be about 20 nm. It means that the hill illustrated in AFM image is a part of an individual microgel particle embedded in the viscous-like matrix (Fig. 1b). By assuming the unit sphericity number for the microgel particle, the actual size of the individual microgel particle can be calculated using based on the simplest geometrical laws and it is given by the following expression:

$$ R = \frac{r}{\tan(\frac{\pi}{2} - 2 \arctan(r/R_0))} $$

in which $r$, $R_0$, and $R$ is the radius of the microgel particle obtained from AFM measurements, the height of hill and the actual size of the microgel particle, respectively (Fig. 2).

The accrual size of the microgel particle buried in the matrix was predicted to be 170. It may be possible that the change of operation conditions for instance temperature or resonant frequency of the AFM measurement leads to variation in the height of the microgel particle, for example, as a result of plastic deformation. However, herein, the temperature at which AFM results were measured was sufficient below the glass transition temperature of the microgel.
particle (see Fig. 5). It states that the AFM measurements were carried out while the microgel particle is in its glassy state. Another important operation condition was resonant frequency of the cantilever which was chosen to be much more ($1.8 \times 10^5$ Hz) than the relaxation frequency of the photopolymeric systems (from $10^{-2}$ to 10) reported in literature [13,19]. It means that the difference between the resonant frequency of the AFM tip and relaxation frequency of the network chain is quite much resulting in microgel particle is taken into account as a very rigid domain during measurements. In this circumstance, it is expected that the operation conditions (the test temperature and the resonant frequency) can not influence the microgel physical characteristics (the height and the size of the microgel particle).

The disparity between the diameter of the microgel particle and the maximum roughness achieved from AFM image may be due to the aggregation of some individual particles resulting in a coarser microgel domain. The micro-graph obtained from scanning electron microscopy technique is shown in Fig. 3.

Also, making comparison between the result obtained from AFM technique and the data achieved from SEM technique can be true because SEM samples were also prepared by breaking the films at temperatures much lower than their glass transition temperature (in liquid nitrogen) statically (not dynamically).

This SEM image can be used to observe the morphology of the microgel particle in the bulk. As observed in this image, the size of the microgel particles dispersed in the viscous-like matrix is very close to the its actual size calculated above. This can deny the possibility of the aggregation of the individual microgel particles to form the coarse particle. Actually, the photopolymerization-induced individual microgel particles embedded in a viscous-like matrix was formed with a 380 nm value of the interparticle distance. It is helpful to consider a model for characterization of the physico-mechanical behavior of the individual microgel particle. The incorporation of the individual microgel particles into a viscous-like matrix can be estimated by the introduction of some rigid nanoparticles into a flexible matrix with chemical interfacial interactions. This model is schematically depicted in Fig. 4.

### 3.2. Prediction of the cross-link density of the individual microgel particle

We would try to calculate the cross-link density of an individual microgel particle using the DMA results and stress-strain data obtained for the resultant mixed sample. The $\tan \delta$ vs. temperature curve of the pure pre-polymer and the mixed sample are plotted in Fig. 5.

The storage modulus vs. temperature plot of the mixed sample is also drawn in Fig. 5. As seen, the storage modulus in rubbery region which may be taken into account as a representative of the averaged cross-link density of the photo-polymeric system, increases with addition of a monomer.

The data corresponding to the pure pre-polymer network presents a distinct maximum peak of $\tan \delta$. The low width of this peak also reflects in a high dynamic homogeneity. The SEM micrograph
of the pure pre-polymer sample is also shown in Fig. 6.

No subsequent microgel particles exist in the bulk of the pure pre-polymer sample. The incorporation of the microgel particles into the pre-polymer network leads to appearance of a shoulder at higher temperature in the loss spectrum of the mixed sample. This shoulder can be due to the presence of the microgel particle inside the mixed sample. As seen in Fig. 5, two dynamically extreme regions appeared in form of a peak (at lower temperature) and a shoulder (at higher temperature) in the loss spectrum of the mixed sample. It is while that it was not the case for the pure prepolymer. Based on the studies have been reported in the literature [7–9], in multi-components photopolymerized networks, two domains including the microgel particle (stiff domain) and the soft matrix (flexible domain) can be considered. As a result, the dynamic feature appeared at higher temperature in a form of shoulder can correspond to the micro-gel domains.

The storage modulus in plateau rubbery region can be considered to calculate the cross-link density of the mixed network as below expression [14]:

\[ X = \frac{E'}{3RT} \]  

(2)

in which \( X \) is the averaged cross-link density of the mixed network, \( E' \) is the storage modulus in rubbery region, \( R \) is the global gas constant and \( T \) is absolute temperature. This calculated cross-link density is related to both microgel particle and viscous-like matrix. On the other hand, the equation for calculation of the elastic modulus of the mixed sample by incorporation of the microgel particles is the Einstein’s model and it is given by the following expression:

\[ E_{ms} = E_{vm} (1 + 2.5\varphi_{mp}) \]  

(3)

in which \( E_{vm} \) is the elastic modulus of the viscous-like matrix and \( \varphi_{mp} \) represents the number fraction of the microgel particle achieved from AFM measurements. By using AFM phase image the ratio of the elastic modulus of the microgel particle to that of the viscous-like matrix (\( \kappa \)) can be determined:

\[ \kappa = \frac{E_{mp}}{E_{vm}} \]  

(4)

The bimodal fitting of phase modulus data obtained from AFM technique is shown in Fig. 7. Through this figure, the \( \varphi_{mp} \) and \( \kappa \) parameters are calculated to be near 0.2 and 1.5, respectively.

By incorporation of equation (3) into equation (2) and rearrangement of the desired equation, the new expression is obtained as the below equation:

\[ E_{mp} = \frac{\kappa E_{ms}}{1 + 2.5\varphi_{mp}} \]  

(5)

On the other hand, the relationship between the elastic modulus of the microgel particle and cross-link density of the microgel particle can be considered according to Mark equation [15] and it is given by the following expression:
\[ E_{mp} = X_{mp}RT(1 - e) \alpha \]  

(6)

It is assumed that the sole parameter affecting the elastic modulus of the microgel particle is the cross-link density and the effect of the dynamic heterogeneity as another possible potential will be ignored. Although the dynamic heterogeneity may play a crucial role in dynamic mechanical behavior, the static mechanical behavior of the microgel particle at temperatures much lower than \( T_g \) does not depend on its dynamic heterogeneity [16]. Another possible reason of dynamic heterogeneity-independent behavior of the elastic modulus of the microgel particle can be the higher process temperature than \( T_g \) of the resultant microgel particle. In fact, when the photopolymerization process occurs at temperatures much higher than the \( T_g^{\text{max}} \) of the sample, the dynamic heterogeneity does not play a key role [16]. We considered the photopolymerization temperature of 100 °C to eliminate the effect of the dynamic heterogeneity on the static mechanical properties. On the basis of this procedure, the assumption of the cross-link density as only parameter influencing on the elastic modulus can be reasonable. By assuming the affine model for the microgel particle, the equation (5) can be estimated by the following expression:

\[ E_{mp} = X_{mp}RT(1 - e) \]  

(7)

With combination of (4) and (6) the below expression can be obtained:

\[ X_{mp}RT(1 - e) = \frac{kE_{ins}}{1 + 2.5\phi_{mp}} \]  

(8)

Here, by rearrangement of the equation (7), the cross-link density of an individual microgel particle can be predicted:

\[ X_{mp} = \frac{kE_{ins}}{RT(1 - e)(1 + 2.5\phi_{mp})} \]  

(9)

The dynamic and static data obtained for the mixed sample (\( k = 1.5, E_{ins} = 1.1 \text{ GPa}, \epsilon = 0.021, T = 298 \text{ K} \) and \( \phi_{mp} = 0.2 \)) were inserted in equation (9) and a 0.041 mol/cm³ value of cross-link density was achieved for the individual microgel particle. This value of the cross-link density shows that the microgel particle is counted as a highly dense domain. However, this calculated quantity of the cross-link density is somewhat large. It can be explained on the basis of this fact the only factor affecting the elastic modulus is cross-link density (as seen in equation (6)) while the magnitude of the elasticity of the photopolymeric networks can be influenced by other important parameters for instance dynamic heterogeneity, stress concentration around microgel particles and physical entanglements.

3.3. Characterization of cooperative relaxation properties of the individual microgel particle

The cooperative relaxation parameters in the \( \alpha \)-transition zone of the microgel particle are predicted based on the dynamic mechanical results. The \( \log r \) vs. 1000/T curve obtained from the dynamic results at various frequencies for the microgel particle is plotted in Fig. 7. The plots through the data constitute the best fits to the Vogel-Fulcher-Tamman (VFT) model [17–19]:

![Fig. 7. The \( \log r \) vs. 1000/T plot of the photopolymerization-induced microgel particle.](image-url)
\[ \tau = \tau_0 \exp \left( \frac{B}{T - T_\infty} \right) \]  
\[ (10) \]

in which, \( T_\infty \) represents Vogel temperature describing the temperature where relaxation time diverges to infinite values. \( B \) is a representative of the relaxation activation energy. And a value of \( 1 \times 10^{-14} \) sec is usually estimated for pre-exponential \( \tau_0 \) [20].

The linearity of the temperature dependence of the relaxation time regarding the microgel network is high indicating a low non-Arrhenius behavior and low dynamic fragility [21]. By considering these data and using the random walk model [22] the CRR size of the microgel particle (\( Z(T_g) \)) can be calculated. The temperature dependence of the relaxation time of the microgel network above and below relaxation temperature (\( T_c \)) is given by the following expressions:

\[ \tau = \tau_0 \left( \frac{\pi}{2(\alpha - 1)} \right)^{0.5} a^{(2a-3)/2(\alpha - 1)} \left( \frac{T_0}{\alpha} \right)^{(2-a)/2(\alpha - 1)} \exp \left[ (\alpha - 1) \left( \frac{T_0}{\alpha T} \right)^{a/(\alpha - 1)} \right] \quad T < T_c \]  
\[ (11) \]

\[ \tau = \tau_0 2^{(2a-1)/2(\alpha - 1)} \left( \frac{1}{\alpha} \right) \left( \frac{T_0}{T} \right)^{a/(\alpha - 1)} \exp \left[ (\alpha - 1) \left( 1 - 2^{-1/(\alpha - 1)} \right) \left( \frac{T_0}{\alpha T} \right)^{a/(\alpha - 1)} \right] \quad T > T_c \]  
\[ (12) \]

The intersection of two curves corresponding to two temperature regimes is counted as the temperature corresponding to the maximum flow nature of the microgel network [23] (Fig. 8).

According the Korus’s model [24] the size of CRR of the microgel particle can be calculated by the below equation:

\[ Z(T_g) = A^2 \left( \frac{T_c - T_g}{T_g - T_\infty} \right)^2 \]  
\[ (13) \]

A value of 0.1 for \( A/(T_g - T_\infty) \) is assumed for the microgel particle. The dynamic fragility index of the microgel network is calculated according to the expression which has been developed by Hodge [25]:

\[ m = \frac{d \log \tau}{d(T_g/T)} \bigg|_{T = T_g} = \frac{B/T_g}{\ln(10)} \left( 1 - \frac{T_\infty}{T_g} \right)^{-2} \]  
\[ (14) \]

A value of 18 for the dynamic fragility index of the microgel particle is calculated. The calculated dynamic fragility index of the microgel particle is astonishingly close to that of the strong systems reported in literature [26–28]. This high strong behavior of the

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**Fig. 8.** Temperature dependence of relaxation time of the mixed sample calculated based on RWM.
microgel particle is found to be in agreement with the high proportionality of the relaxation time of the microgel to the temperature shown in Fig. 7. The cooperative relaxation characteristics of the photopolymerization-induced microgel particle are tabulated in Table 1.

### 3.4. An electrochemical-based approach for measuring the apparent diffusion coefficient of an individual microgel particle

Electrochemical impedance technique is used to calculate the apparent diffusion coefficient of Cl⁻ ion through the microgel particle. In previous work [12], we showed that the photopolymeric networks containing the microgel particles exhibit a broadening trend in the direction of the real axis of the Nyquist plot. This broadening trend has been attributed to the presence of the microgel particles as the structurally dense domains inside the photo-polymeric network. The origin of this behavior was found to be the diffusion limited behavior of the structurally dense domains. So, we used EIS technique as a means of the characterization of the diffusion behavior of Cl⁻ through the individual microgel particle quantitatively. Fig. 9 shows the Nyquist plot of the mixed sample and the broadening effect is completely clear.

The raw data measured from EIS technique was analyzed based on an electrical equivalent circuit (EEC) shown in Fig. 9. Two crucial elements can be seen in EEC namely pore resistance (R_p) and finite length Warburg (FLW). The pore resistance defines the resistance against the penetration of the electrolyte species through the network without self-limiting effects. The FLW element can be considered as the transportation of the electrolyte specie through the network occurs difficulty [29]. This phenomenon is happened if the diameter of the penetrant and that of the conductive pathway is nearly the same. On the basis of this concept, the apparent diffusion coefficient of the Cl⁻ through the microgel particle can be calculated according to the below equation [29,30]:

\[
D_{app} = \frac{L^2}{T}
\]  

The apparent diffusion coefficient of the Cl⁻ through the microgel particle is calculated to be 10.34 μm²/sec.

### 3.5. Prediction of the hardness value of the individual microgel particle

To predict the hardness value of the microgel particle the load–displacement data obtained from nano-indentation technique was used. On the basis of our model for describing the behavior of the microgel particles dispersed in the viscous-like matrix, the indentation behavior of the microgel particle can be interpreted if the microgel particle can be touched by the indenter. A 150 nm diameter of the indenter was chosen.

The contact diameter of the indenter is near the size of the microgel particle and about two times larger than the interparticle distance (see Fig. 3). It would be expected that if the indentation measurements are carried out several times, the difference between the calculated hardness may be considerable because the indenter may touch the microgel particle or the viscous-like matrix. If the indenter touches the microgel particle, the calculated indentation hardness corresponds to the microgel particle. Four series of load-displacements data obtained from the nano-indentation technique for the mixed sample are plotted in Fig. 10. The values of 0.08, 0.08, 0.13, and 0.14 GPa of the nano-indentation hardness are calculated. Two first values are related to the viscous-like matrix and two last values are considered for the microgel particle. So, the highest calculated value (0.14 GPa) corresponds to the microgel particle. The ratio of the hardness of the microgel particle to that of the viscous-like matrix is found to be compatible with the elastic modulus ratio obtained from the AFM image of the mixed sample. To study the validity of this approach a mixed sample with high degree of microgelation was prepared by adding 50 weight percent of the monomer to the pre-polymer. The SEM image of this mixed sample is displayed in Fig. 11. As observed in this figure, the microgel particles are completely in contact with together. The hardness values are calculated from

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<th>T_m(K)</th>
<th>α</th>
<th>T_c(K)</th>
<th>Z(T_g)</th>
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</table>

Table 1

The cooperative relaxation properties of the photopolymerization-induced microgel particle.
the load–displacement data of this mixed sample. Three values of 0.15, 0.15 and 0.16 are measured for the hardness value. The difference among these three values is negligible. The area of the viscous-like matrix limited by the microgel particles can be calculated based on a simple geometrical approach illustrated in Fig. 12.

In this graphical model, the microgel particles are estimated by some perfect spheres embedded in a surface as the viscous-like matrix. The spheres are assumed to be in contact with each other. The viscous-like area limited by three microgel particles can be calculated based on the simplest mathematical laws and it is given by the following expression:

\[ A = \frac{\sqrt{3}}{4}R^2 \]  

The ratio of the limited area of the viscous-like matrix to the contact area is calculated to be 0.13. So, the limited area does not affect the data measured by the indentation process. In this case, the indentation data can correspond to the microgel particles. So, the nano-indentation hardness value of an individual microgel particle can be calculated by choosing the appropriate indenter diameter.

4. Conclusion

The physico-mechanical characteristics of an individual photopolymerization-induced microgel particle dispersed in a viscous-like matrix were studied. The microscopy techniques were used to demonstrate the embedment of the individual microgel particle in the viscous-like matrix. The stress-strain data and the

Fig. 10. Four iterations of Load-displacement data of the mixed sample.

Fig. 11. The SEM image obtained for the mixed sample containing the microgel particles with contact together.
results obtained from atomic force microscopy technique were used to predict the cross-link density of the individual microgel particle. The microgel network revealed a strong behavior with a value of 18 for dynamic fragility index. This low fragility index is assigned to the high dynamic heterogeneity of the microgel particle. The nano-indentation hardness of the microgel particle was calculated based on a simple geometrical model.

Fig. 12. A simple geometrical picture representing the area of the viscous-like matrix limited by three microgel particles.

References