Polymer Bulletin 61, 257–265 (2008)
DOI 10.1007/s00289-008-0948-0

Polymer Bulletin

Nanotailoring of Nanocomposite Hydrogels Containing POSS

H. Eshel, L. Dahan, A. Dotan (✉), H. Dodiuk, S. Kenig

Department of Plastics Engineering - Shenkar College of Engineering and Design, Ramat Gan, Israel
E-mail: adotan@shenkar.ac.il

Received: 27 February 2008 / Accepted: 30 April 2008

Summary

The development and commercialization of nanoparticles such as nanoclays, carbon nanotubes and polyhedral-oligomeric-sil-sesquioxanes (POSS) offer new possibilities to tailor hydrogels in the nanometer scale range. Due to the large surface area of the nanosize particles, only small amounts are needed to cause significant changes in hydrogels properties. Properties affected include swelling behavior and thermo-mechanical properties.
Experimental results showed that only small amounts of POSS (<5 wt%) were needed to enhance the storage modulus and the swelling ability compared with that of the pure Poly(N-vinyl-2-pyrrolidone\ itaconic acid) hydrogel. In the case of epoxy functionalized POSS incorporated into the hydrogel, the weight swelling increased by more than 120% while the volumetric swelling by 350% . In addition the storage modulus increased by 300% compared to the neat hydrogel.
The results led to the conclusion that the incorporation of functionalized POSS particles in hydrogels could improve the hydrogel properties.

1. Introduction

Hydrogels are hydrophilic polymer networks that are able to swell, retain large amounts of water and maintain three-dimension swollen structures due to chemical crosslink. The ability of hydrogel to absorb water is determined by the hydrophilic groups in the hydrogel network chains and the degree of cross-linking. In general, the amount of water absorbed by the hydrogel is at least 20% of its total weight. In the case of superabsorbent hydrogel water absorption is usually higher than 95% of the total weight. Due to the high water content and swollen structure the mechanical strength of the swollen hydrogels is poor. Hydrogels have been a topic of extensive research because of their unique bulk and surface properties [1]. The fast and high water absorbing properties of hydrogels offer many industrial applications in agriculture, horticulture, hygiene, construction, medical and biomedical fields. As most hydrogels absorb a large amount of water, they become mechanically weak to maintain their functions for long periods. Accordingly, it is desirable to formulate hydrogels having enhanced mechanical strength [2]. Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as new class of materials for preparing organic–inorganic nanocomposites [3-13]. A typical POSS molecule (Fig. 1) has the structure of octameric cage framework represented by the formula ($R_8Si_8O_{12}$) with an inorganic silica-like core (Si_8O_{12}) surrounded by eight organic corner groups, one or more of which is reactive or polymerizable [14]. Nonetheless, the effects of POSS on behavior of hydrogels remain largely unexplored [15].

In the present work, Trisilanol ethyl POSS, Trisilanol Isobotyl POSS, Trisilanol octavinyl POSS, 1(2-(3, 4-epoxycyclohexyl)-ethyl)-3, 5, 7, 9, 11, 13-isobutyl-pentacyclo-POSS (Table 1) were used in cooperation with Poly (N-vinyl-2-pyrrolidone\itaconic acid) hydrogel to yield a novel organic–inorganic hybrid hydrogels. In addition, the presence of POSS cages in hydrogel networks could act as nanosized hydrophobic microdomains, which could be favorable to improve the rates of swelling and deswelling of hydrogels [15].

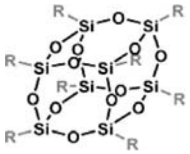


Figure 1. General structure of POSS.

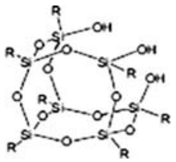
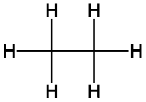
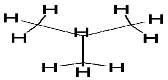
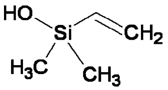
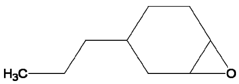


Figure 2. General Structure of Trisilanol POSS.

Table 1. POSS Constituents

Name	R
Trisilanol ethyl POSS	
Trisilanol Isobutyl POSS	
Trisilanol octavinyl POSS	
1(2-(3,4-epoxycyclohexyl)-ethyl)-3,5,7,9,11,13-isobutyl-pentacyclo-) POSS	

2. Experimental

2.1. Materials

The *N*-vinyl-2-pyrrolidone (NVP) and itaconic acid (IA) monomers were used in conjunction with ammonium peroxodisulphate (APS) that served as an initiator, and *N*,*N*-Methylene bisacrylamide (MBAAm), was utilized as a cross linking agent. The hydrogel was prepared from the appropriate monomers, initiator and cross linking agent, as given in Table 2 [16].

Table 2. Feed composition

Name	Amount(wt%)
IA	17.0
APS	9.6
MBAAm	9.6
NVP	25.3
Water	38.5

The aqueous solution was stirred for 5 minutes and then UV-induced cross-linking and polymerization were carried out with sunlight for 24 hour, or with a 1000 W UV source (wavelength: 365 nm).

The copolymer hydrogels were washed for 24 hours with distilled water, to remove the uncured monomers, dried in the open air for several days and dried again in a vacuum oven at 42°C for 8 hours [4].

The reaction is described in Fig. 3.

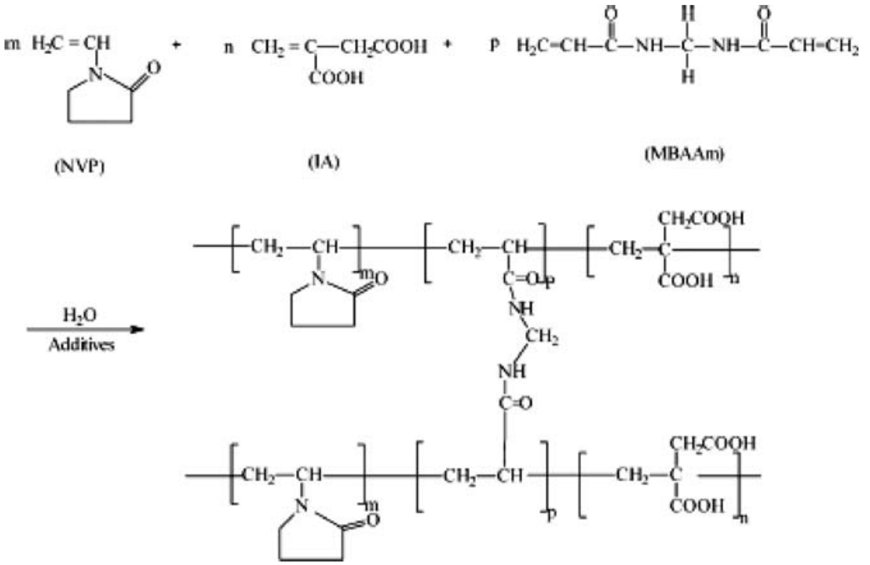


Figure 3. Poly(NVP/IA) copolymer hydrogel reaction [16].

POSS with four different types of functionalities, and in various loading levels: 1, 3 and 5 wt% have been included in the study. The POSSs were incorporated into the solution with intensive mixing.

2.2. Characterization of hydrogel nanocomposites.

The chemical structure of the copolymer hydrogels was determined by means of Fourier Transform Infrared (FT-IR) spectroscopy. The swelling was determined as follows: dried copolymer hydrogels were left to swell in distilled water at 25°C and their weight was followed until equilibrium was attained. The measurements were continued for 24 hours for each sample. The swelling ratio of each copolymer hydrogel was defined using Eq. (1); where Mt is the mass of swollen copolymer hydrogel at time t and M_0 the initial mass of the copolymer hydrogels [4]:

$$\text{Swelling (\%)} = ((M_t - M_0)/M_0) \times 100 \qquad (1)$$

The volume of swelling was determined as follows: dried copolymer hydrogels were left to swell in distilled water at 25°C and their volume followed until equilibrium was attained. The volumetric swelling ratio of each copolymer hydrogel was defined using Eq. (2); where V_t is the volume of swollen copolymer hydrogel at time t and V_0 the initial volume of copolymer hydrogels [4]:

$$\text{Swelling (\%)} = ((V_t - V_0)/V_0) \times 100 \qquad (2)$$

Dynamic mechanical analysis (DMA) was carried out on a DMA (Perkin Elmer), by three-point bending mode, at a frequency of 1.0 Hz and temperature range of 20 to 30°C. Sample bars of 1.5 x 4 x 15 mm were used.

3. Results and discussion

Nanopaticles are characterized by their inherent large surface area. Uniform dispersion and avoidance agglomeration of nanoparticles is essential to obtain fine nanocomposites. This can be achieved if the surface of the nanoparticle is functionalized to interact with the host polymer matrix. In this study the effectiveness of POSS containing a variety of functional groups was evaluated. Furthermore, different concentrations were studied. The effect of the POSS structure on the morphology, thermo-mechanical, and swelling behavior were investigated for adhesive systems by Dodiuk et al [17].

FTIR Spectroscopy

Figure 4 shows the FT-IR spectra of the epoxy POSS (a), poly(NVP/IA) copolymer hydrogel (b) and 5 wt% epoxy POSS reinforced poly(NVP/IA) copolymer (c). As can be observed, a new peak at 2953 cm^{-1} appears after the addition of the epoxy POSS to the polymer, indicating some level of chemical interaction between them. This change in the FTIR spectra was noticed only for the epoxy POSS and not for the trisilanol POSS.

Weight swelling

The hydrogel containing epoxy POSS reached the highest and fastest swelling level, as can be seen from Figures 5 and 7. This may be due to the extended epoxy groups which result in a relative large volume of the epoxy POSS. This steric effect keeps the

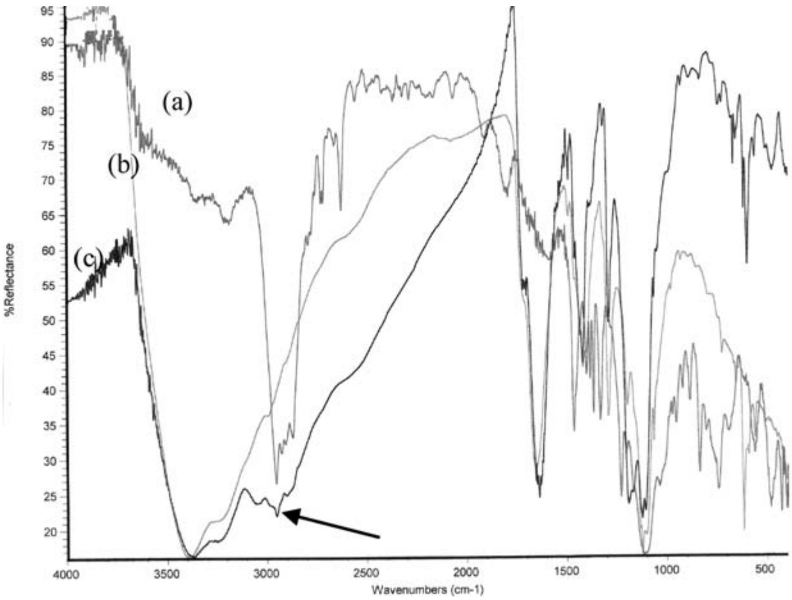


Figure 4. FT-IR spectra of 1(2-(3,4-epoxycyclohexyl)-ethyl)-3,5,7,9,11,13-isobutyl-pentacyclo) POSS (a), poly(NVP/IA) copolymer hydrogel (b) and 5 wt% 1(2-(3,4-epoxycyclohexyl)-ethyl)-3,5,7,9,11,13-isobutyl-pentacyclo-) POSS reinforced poly(NVP/IA) copolymer (c) in the regions from 4000 to 500 cm^{-1}.

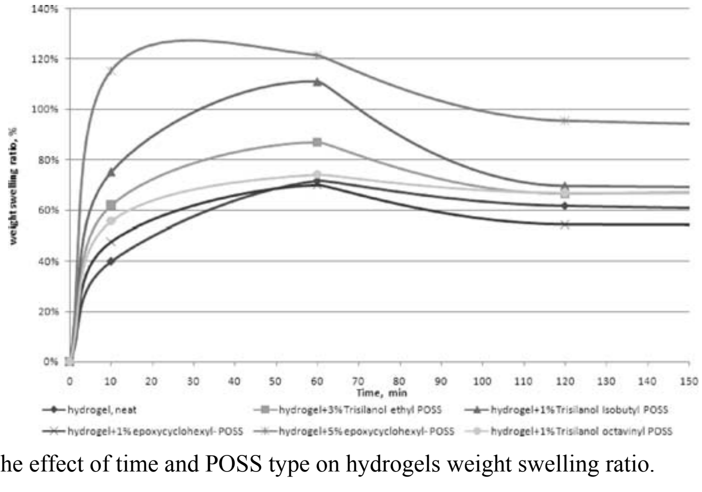


Figure 5. The effect of time and POSS type on hydrogels weight swelling ratio.

polymer chains apart and creates additional free volume for possible water absorption. It should be emphasized that in most cases the nanocomposites showed a high rate of diffusion. As times increased, the rate of diffusion decreased. Longer times (>24 hours) caused some weight losses. This may be attributed to extraction of small molecules that did not react during the curing reaction.

Moisture absorption by nanocomposite materials can be described by Fick's second law of diffusion, as expressed in Equation 3:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left| \frac{-D(2n+1)^2 \pi^2 t}{h^2} \right| \qquad (3)$$

where M_t and M_∞ are the moisture content at time t and the equilibrium or maximum moisture content, respectively. D is the diffusion coefficient and h is the sample thickness. At short times (initial absorption), Eq. 3 reduces to:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{h^2}\right)^{1/2} \qquad (4)$$

Eq. 4 can be rewritten as:

$$M_t = kt^{1/2} \qquad (5)$$

where k is a constant related to the diffusion coefficient.

Fig. 6 represents the results according to Equation 5. As can be seen the experimental results exhibit a linear relationship between the M_t and $t^{1/2}$ for the first hour in the case of the neat hydrogel. In the cases of nanocomposite gels the linear relationship takes place only for shorter times. The non-linearity could be related with the functionality of the POSS particles. The less reactive POSSs (Trisilanol ethyl POSS, Trisilanol Isobutyl POSS and Trisilanol octavinyl POSS) have demonstrated a higher degree of linearity. The loss of linearity was especially observed in the case of the reactive POSS. The deviation from linearity indicates that water sorption in nanocomposites is a complex phenomenon and maybe affected by molecular relaxation, void content, diffusion path, etc. The pure hydrogel showed the lowest swelling levels (Fig. 6). Volume swelling results are shown in Figure 7 and the swelling weight to volume

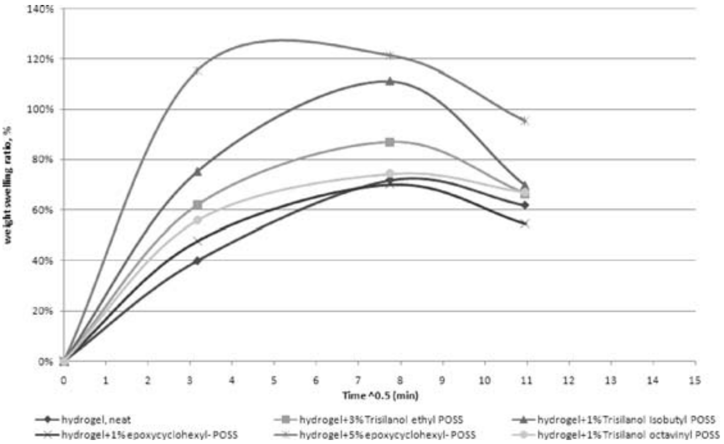


Figure 6. The effect of time and POSS type on hydrogels weight swelling ratio as a function of the square root of immersion time.

ratio in Figure 9. As can be seen the neat hydrogel and the hydrogel containing silanol POSS have a similar weight to volume swelling ratio. The epoxy POSS which exhibited the highest weight swelling showed the highest volume swelling ratio and the swelling increased with the POSS concentration (Fig. 8). Furthermore, the volume swelling ratio is much higher compared to the weight swelling ratio, indicating the hydrogel network had been highly expanded due to the chemical reaction between the epoxy functional group and the hydrogel constituents.

DMA results

The hydrogel containing epoxy POSS showed a significant increase in storage modulus at low concentrations, as can be seen from Figure 10, while at high concentrations the storage modulus decreased. Moreover, it can be observed that the neat hydrogel showed the greatest decrease in the storage modulus with increase in temperature. The hydrogels containing nano POSS particles exhibited higher temperature stability. Epoxy POSS demonstrated the best thermomechanical

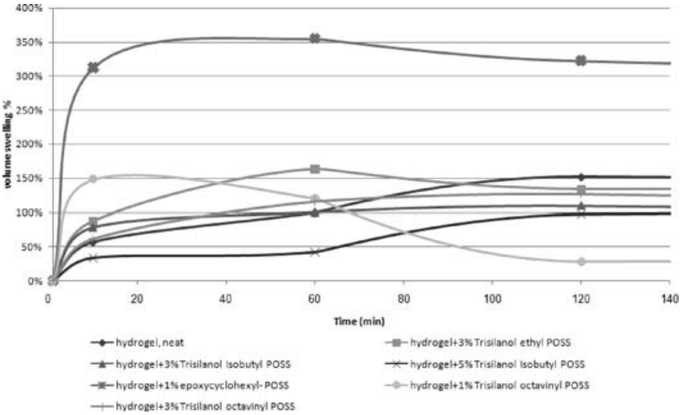


Figure 7. The effect of time and POSS type on hydrogels volume swelling.

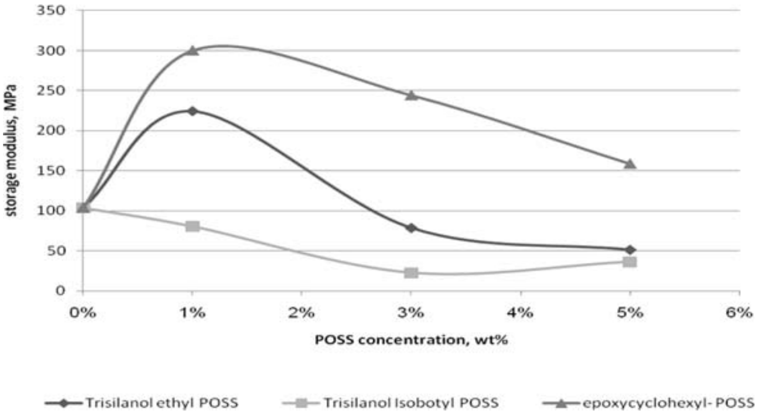


Figure 8. The effect of POSS type and concentration on weight swelling ratio.

properties. Fig. 11 depicts the effect of POSS type and concentration on storage modulus. As can be noticed a maximum in storage modulus was obtained at 1% POSS.

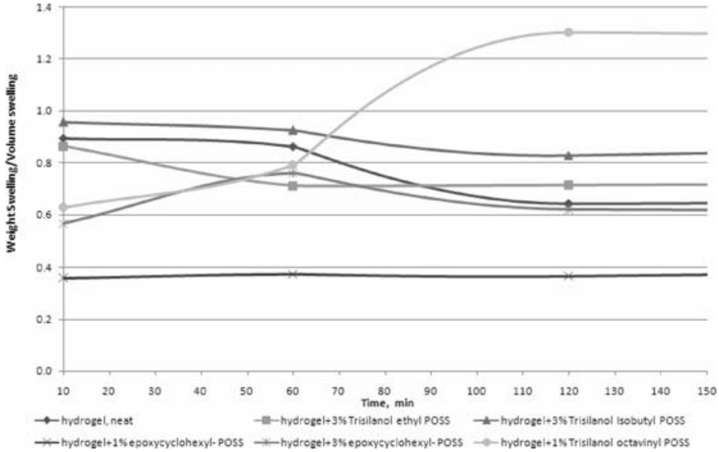


Figure 9. The effect of time and POSS type on weight-volume swelling ratio relationship.

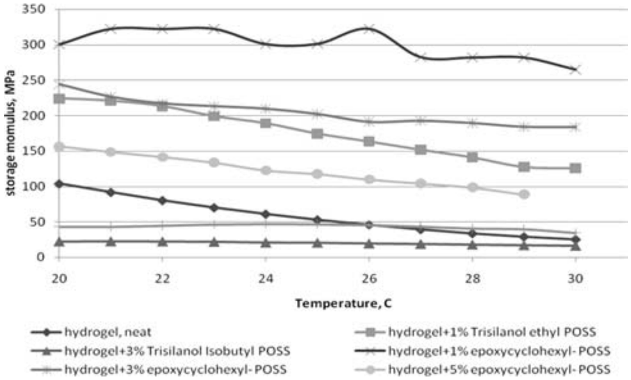


Figure 10. The effect of POSS type on storage modulus.

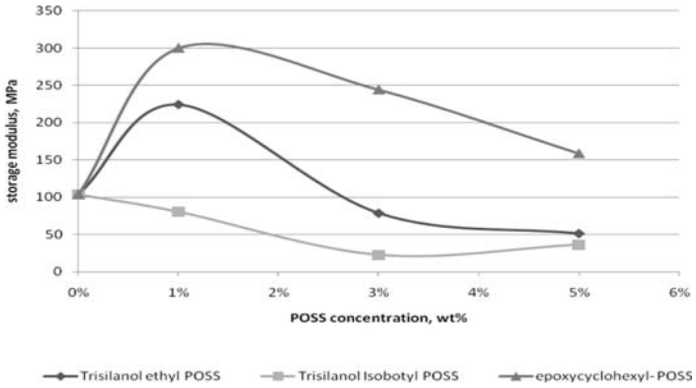


Figure 11. The effect of POSS type and concentration on storage modulus.

Conclusions

The addition of POSS nanoparticles increased the water swelling of the hydrogel studied. The hydrogel containing 5% of epoxy POSS showed the highest percentage of swelling due to interaction with the host polymer, as verified by the FTIR analysis. Furthermore the volumetric swelling compared to the weight swelling was the highest for the epoxy POSS containing hydrogels. In addition, the storage modulus of the nano-reinforced hydrogels was increased with the addition of POSS. Optimal concentration for reinforcement was 1%, above this level the storage modulus decreased. As was the case for swelling, the epoxy functionalized POSS exhibited the highest modulus and highest preservation of modulus with increased temperature. It was concluded from this study that functionalization of POSS is the decisive factor in nanostructuring of the molecular hydrogel network. Due to the large surface area of POSS, only relatively small amounts are needed to cause significant changes. Optimal concentration exists for each functional derivative. The type of the functional groups (reactive or nonreactive) of the POSS is the dominant factor in formation of the molecular network.

References

[1] Othmer, K., "Hydrogels" Encyclopedia of Chemical Technology. Vol. 13 p 729-759.
[2] Omidian, H., Qiu, Y. Yang, S., Kim D., Park, H., Park K., "Hydrogels having enhanced elasticity and mechanical strength properties" United States Patent No 6,960,617, (2005).
[3] Schwab, J.J., Lichtenhan, J.D., Appl. Organomet. Chem. 12 707, (1998).
[4] Li, G., Wang, L., Ni, H., Pittman C.U., J. Inorg. Organomet. Polym. 11 123, (2001).
[5] Feher, F.J., Wyndham, K.D., Baldwin, R.K., Soulivong, D., Lichtenhan, J.D., Ziller, J.W., Chem. Commun. 1289, (1999).
[6] Lichtenhan, J.D., Vu, N.Q., Carter, J.A., Gilman, J.W., Feher, F.J., Macromolecules 26 2141, (1993).
[7] Lichtenhan, J.D., Otonari, Y.A., Carr, M.J., Macromolecules 28, 8435, (1995).
[8] Haddad, T.S., Lichtenhan, J.D., Macromolecules 29, 7302, (1996).
[9] Choi, J., Harcup, J., Yee, A.F., Zhu, Q., Laine, R.M., J. Am. Chem. Sci. 123 11420, (2001).
[10] Choi, J., Kim, S.G., Laine, R.M., Macromolecules 37, 99, (2004).
[11] Liu, H., Zheng, S., Macromol. Rapid Commun. 26, 196, (2005).
[12] Ni, Y., Zheng, S., Chem. Mater. 16, 5141, (2004).
[13] Lichtenhan, J.D., Feher, F.J., Schwab, J.J., Zheng, S., US Patent 6933345, (2005).
[14] Bandi, S., Bell, M., Schiraldi, D.A., Macromolecules 38, 9216, (2005).
[15] Mu, J., Zhneg, S, Journal of Colloid and Interface Science Vol. 307, 2, 377, (2007).
[16] Chen, K., Ku, Y., Lin, H., Yan, T., Sheu, D., Chen, T., Lin, F., Materials Chemistry and Physics, Vol. 91, 2-3, 484, 2005.
[17] Dodiuk, H., Kenig, S., Belinsky, I., Dotan, A., Buchman, A., International Journal of Adhesion and Adhesives, Vol. 25, 3, 211, (2005).