

Effect of Nano-sized Silicas in HPDLC Based on PUA

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Abstract

Diffraction modes of holographic grating were fabricated with polyurethane acrylates (PUA). Two types of silica (AEROSIL 200 and AEROSIL R812) were added to reduce the shrinkage of polymer matrix. It was founded that shrinkage of PUA composite film was reduced with the addition of silica. HPDLC based PUA/silica composite also showed high diffraction efficiency. The morphology of the resultant gratings was analyzed by using scanning electron microscopy (SEM) and Tg of the polymer matrix by dynamic mechanical thermal analysis (DMTA).

1. Introduction

HPDLC is micrometer film containing liquid crystal and photoreactive prepolymer that is exposed to a coherent interference pattern generated by a laser¹. During photopolymerization, volume of polymer matrix is reduced upon polymerization, this is commonly known as polymerization shrinkage². The conversion of monomer molecules into a polymer network is accompanied by close packing of growing polymer chains and a subsequent reduction in volume. The shrinkage effect can significantly change the performance of HPDLC. The shrinkage of polymer results in nonuniformed grating and low diffraction efficiency. So, we have been made to minimize polymerization shrinkage by altering the filler load. Filler is used to modify mechanical behavior and bulk density³. Most of the fillers are played an important role to take up volume and polymer neighbored filler is represented different property of another region polymer. Filler is very important to disperse uniformly to contact all to nothing polymer and surface of filler. At this aspect, it is important that free surface energy degree of polarity on combination of polymer matrix and filler. Also, impact strength is enhanced because energy is uniformly spread at filler surface. In our experiment, hydrophilic and hydrophobic silica as filler is used.

The addition of silica increased the viscosity, the storage and loss moduli of silica-PUA composite. Also, addition of silica did not modify the glass transition temperature.

2. Experimental

Polypropylene glycol (PPG, Mn=400, Korea Polyol) was dried at 80 °C, 0.1 mmHg for several hrs until no bubbling was observed. Then, nano-size hydrophilic silica (aerosil 200) with average particle size of 12 nm and nano-size hydrophobic silica (aerosil R812) with average particle size of 7 nm are blended with PPG for 6 hr at 500 rpm. Chemical reagents of hexamethylene diisocyanate (HDI), hydroxyethyl methacrylate (HEMA) were used without further purification. PPG, HDI and DBTDL (0.03 wt% based on base PUs) were mixed and reacted at 80 °C for 3 hrs to obtain NCO terminated prepolymer. The reaction mixtures were then cooled to 45 °C before HEMA was added to obtain HEMA capped urethane acrylate oligomers⁴. The basic formulation is shown in Table 1.

Table 1. Formulation to prepare HPDLCs

Oligomer/ NVP	Type of silica	LC content (wt %)	Rose Bengal (wt %)	NPG (wt%)
3/1	No-silica			
	Aerosil 200	25 30		
2/1		35	0.3	1.8
1/1	Aerosil	40		
	R812	45		

The films used for this study were prepared using a homogeneous prepolymer syrup consisting of a

urethane acrylate oligomer, the nematic LC(E7), and the monofunctional monomer, viz. ethyl hexyl acrylate(EHA), and N-vinylpyrrolidone (NVP). The use of monofunctional monomer is essential to reduce the viscosity of LC/oligomer mixture to ensure the starting mixture is homogeneous. was fabricated through the preferential formation of photoproducts in the region of constructive interference arising from the overlap of two laser beams, called object and reference beams. The holographic recording system is schematically shown in Figure 1. The cell was constructed by sandwiching the resin/LC mixture between the two indium-tin-oxide(ITO) coated glass plates. The prepolymer mixtures with various structures have been irradiated with Ar-ion laser(514nm) at $90\text{mW}/\text{cm}^2$ with exposure time of typically 150s.

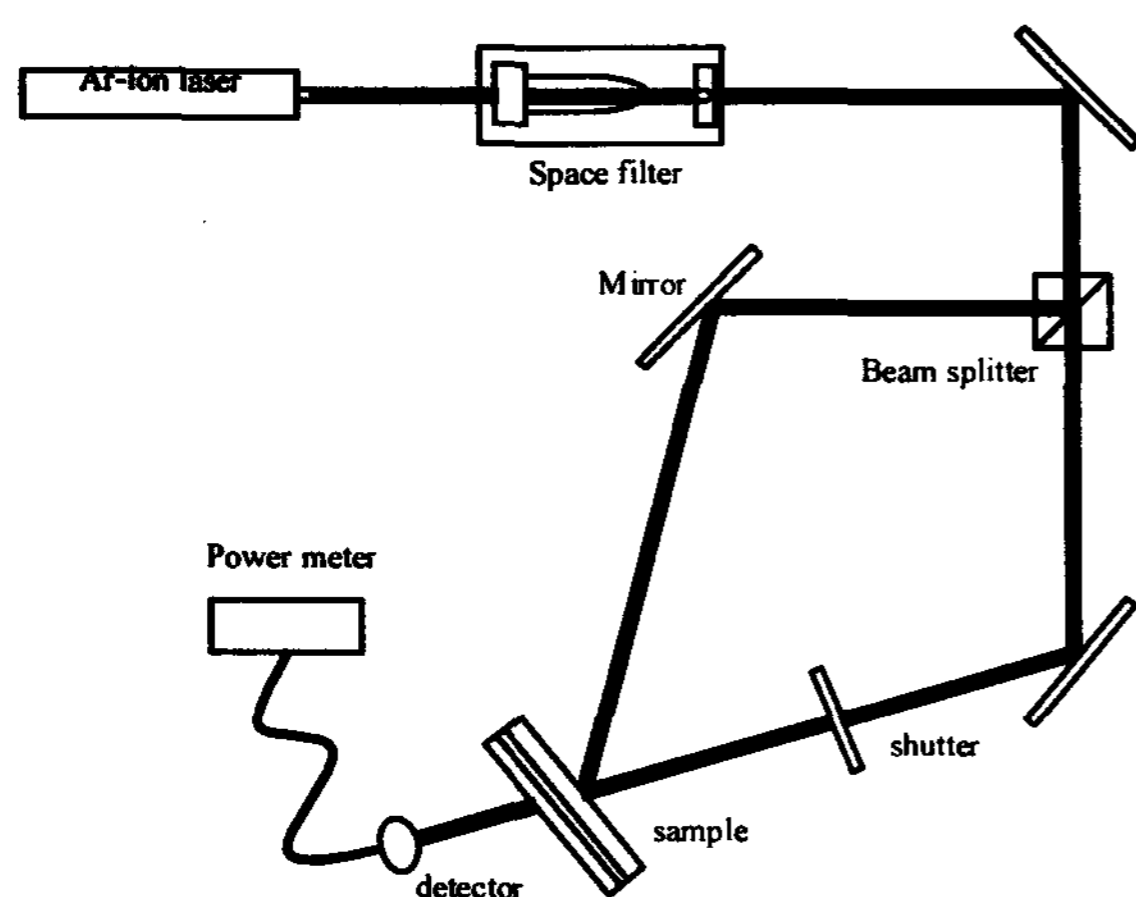


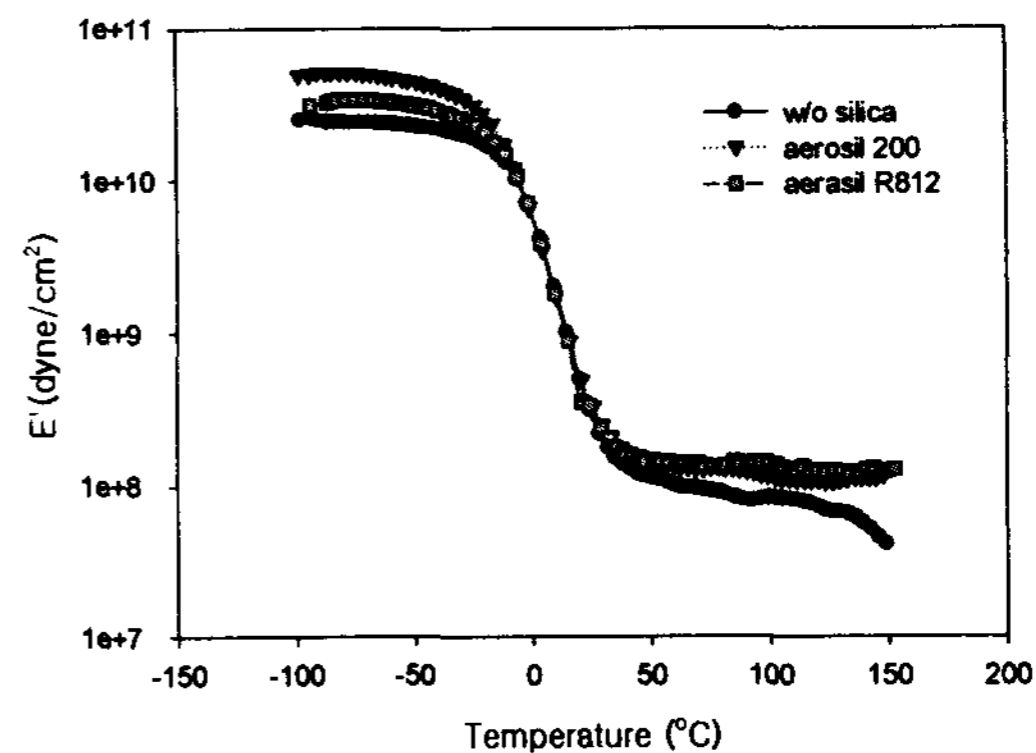
Figure 1. Experimental setup for transmission mode HPDLCs.

Dynamic mechanical properties of PUA films were measured using a Dynamic Mechanical Thermal Analyzer(Rheometry Scientific DMTA MK III) with a tensile mode at a heating rate of $4^\circ\text{C}/\text{min}$ and 10Hz. SEM(scanning electron microscopy) morphology of the gratings were obtained upon extracting the LC molecules in methanol.

3. Results and discussion

Typical dynamic mechanical behavior of the PUA films are shown in Figure 2 for a specific composition of oligomer/reactive diluent=3/1 without and with

different types of silica. Regardless of types of silica $\tan\delta$ curve shows a single peak(Figure 2b).



(a)

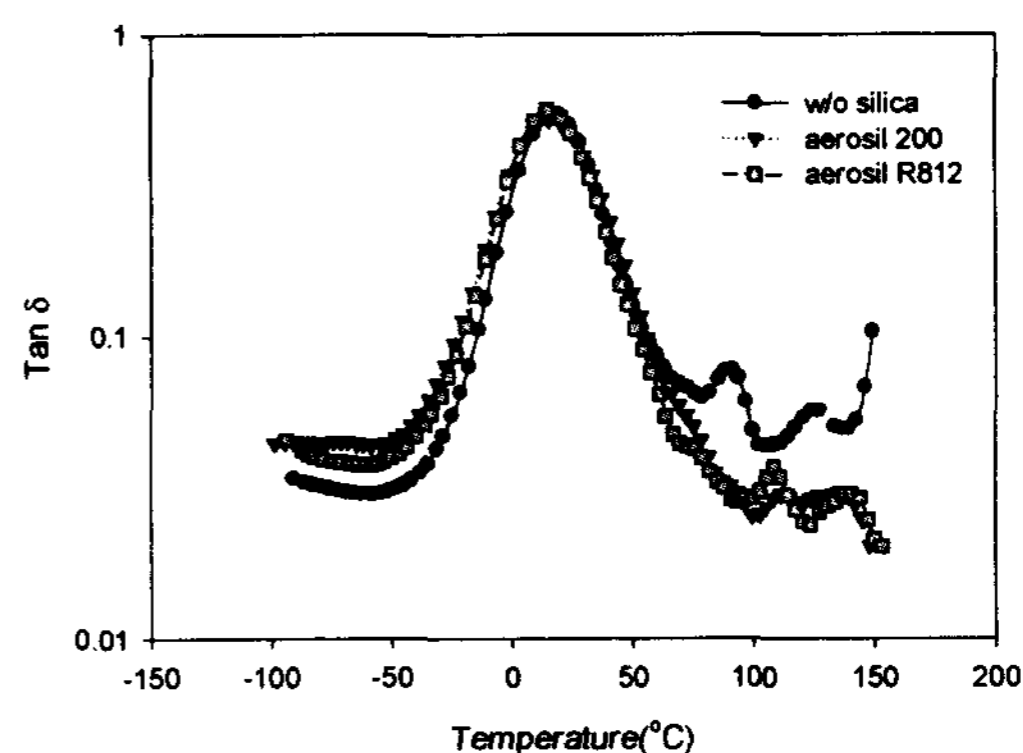


Figure 2. Storage modulus(a) and $\tan\delta$ (b) vs. resin with and without silica (oligomer/EHA=3/1).

This indicates that urethane and acrylate or NVP segments of the PUA are phase mixed at segment level. When two of the segments are immiscible generally two $\tan\delta$ peaks are obtained. On the other hand, the addition of silica does not affect the glass transition temperature of PUA. This is because combination of silica and resin is not chemical coupling but only mixing by shear. The elasticity of silica composite film is a bit higher than that of neat PUA film due to increasing density as silica is added. Following the ideal rubber theory⁵ rubbery modulus(G_N°) is given by

$$G_N^\circ = \frac{\rho RT}{M_c}$$

where ρ , R , T , and M_c are density, gas constant, absolute temperature, and molecular weight between crosslinks. The elasticity of urethane acrylate polymers which can be expressed in terms of elastic modulus of rubber is directly related to hooping stress⁶. This hooping stress squeezes LC molecules out of the polymer phase. It contributes to an increase in elasticity of the polymer phase giving rise to rapid squeezing of LC molecules. However, when the squeezing actions of the networks are too strong, LC molecules are squeezed out so quickly and are subject to coalescences to give larger droplets and smaller droplet density, giving rise to a bit decreased diffraction efficiency⁷.

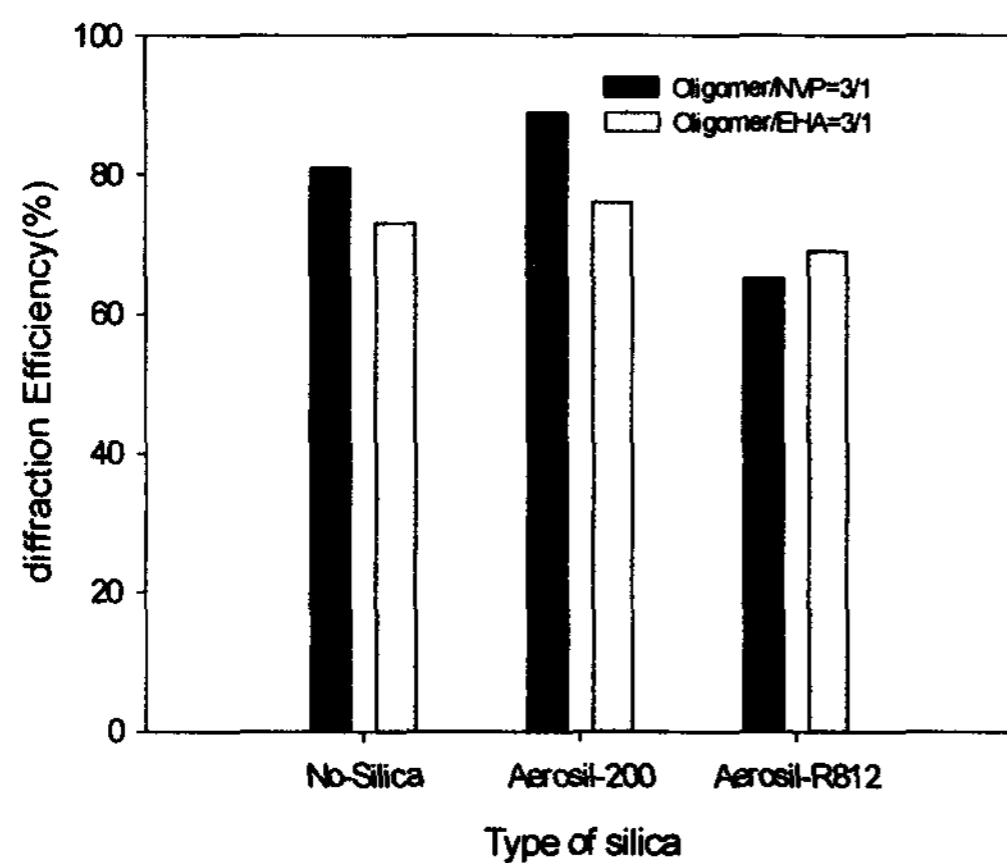


Figure 3. Diffraction efficiency vs. resin with and without silica(35wt%LC, 90mW/cm²).

Diffraction efficiencies of the HPDLC films with different types of silica and without silica are given in Figure 3. Diffraction efficiency increases along aerosil R812<w/o silica<aerosil 200. With the added silica, elasticity of polymer matrix increased(Figure 2a). High elasticity (aerosil 200) seems to squeeze LC molecules out of the polymer matrix and extracted LC forms LC-rich straits in the holograms. However, in spite of great elasticity, PUA with aerosol R812 has low diffraction efficiency as compared with that of PUA having no silica. This is probably due to low rate of phase separation by high viscosity of the prepolymer syrup. Earlier works⁸ showed higher obtained modulus and Tg for NVP-based PUA than EHA-based PUA. Therefore, diffraction efficiency of NVP-based PUA is generally higher than that of EHA-based PUA.

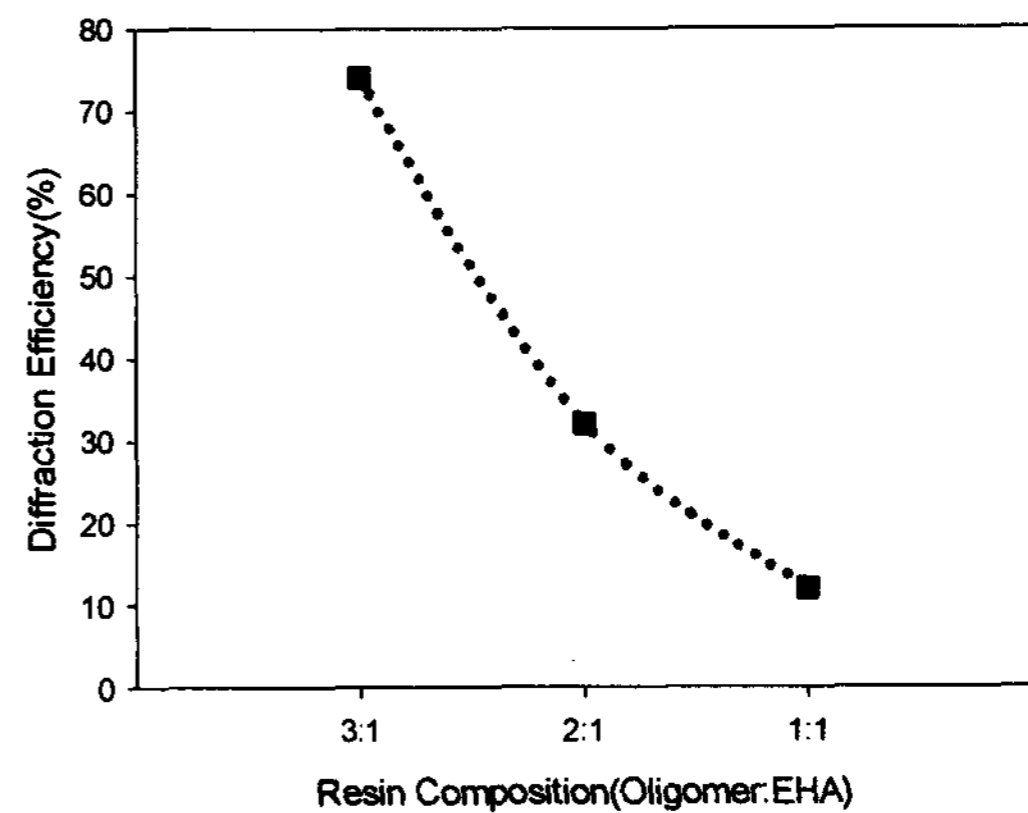


Figure 4. Diffraction efficiency vs. various resin compositions (10wt% aerosil 200, 35wt%LC, 90mW/cm²).

Diffraction efficiencies as a function of the oligomer/reactive diluent composition are shown in Figure 4. The diffraction efficiency decreases as the reactive diluent increases. This is because the functionality and modulus of polymer matrix is increased according to decreasing EHA content. Hence, growth of hopping stress and cure rate lead to increase phase separation and diffraction efficiency.

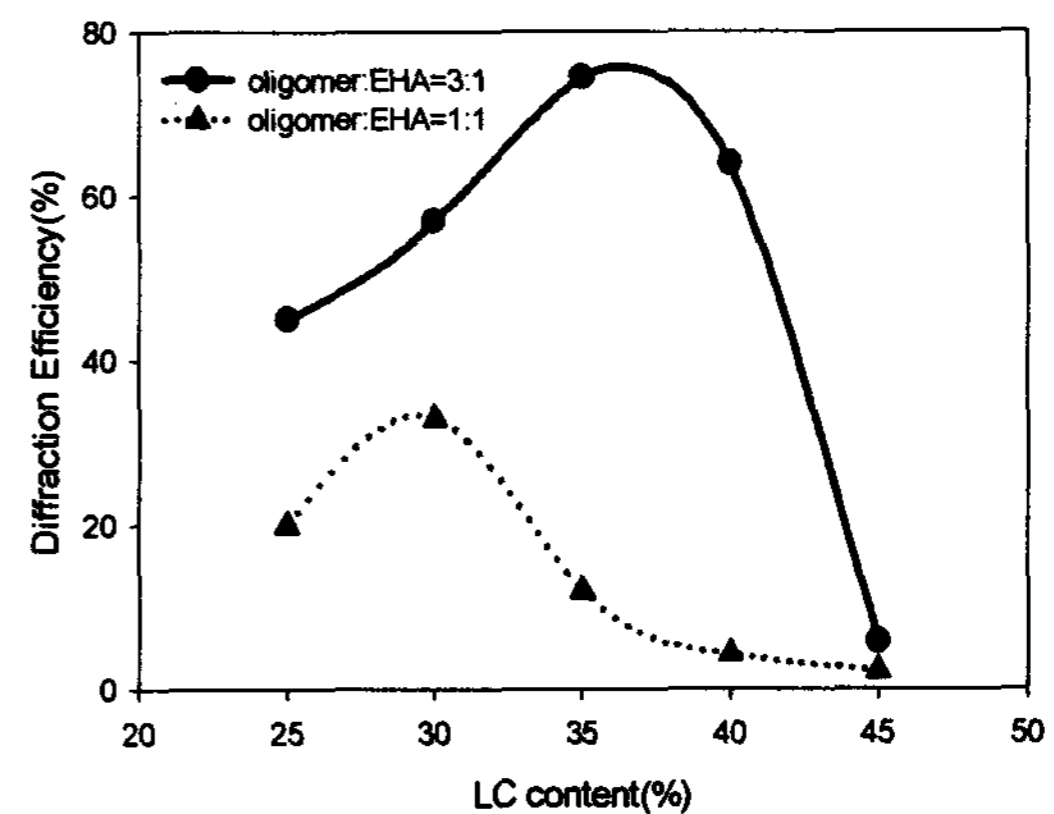


Figure 5. Diffraction efficiency of the HPDLC films vs. LC content(10wt% aerosil 200, 90mW/cm²).

Diffraction efficiencies of HPDLC films as a function of LC content are given in Figure 5. The maximum diffraction efficiency exists for LC 35% at 3/1 system and LC 30% at 1/1 system. It seems that below this maximum the amount of LC is insufficient to form well phase separated gratings as well as insignificant difference in refractive indices between

polymer and LC domains, and above the maximum LC molecules out of the polymer phase allow coalescence leading to large droplets with small droplet density. Large domains decrease diffraction efficiency and cause scatterings.

Typical SEM morphologies of the holographic gratings fabricated at 514nm, 90mW/cm² for 150s exposure time are shown in Figure 6 where dark straits represent LC-rich domains and bright ones polymer-rich domains. Shrinkage ratio is calculated from the following equation⁹:

$$\% \text{ shrinkage} = \frac{d_0 - d}{d_0} \times 100$$

where d_0 is the theoretical grating space, d is the experimental grating space. Shrinkage rate of PUA film without silica is 16.01%, whereas that of PUA film with 10wt% aerosol 200 is 4.1%. It is seen that the grating space(d) is close to theoretical bragg grating space($\lambda=2d\sin\theta$). Namely, the shrinkage of polymer matrix is reduced with addition of silica.

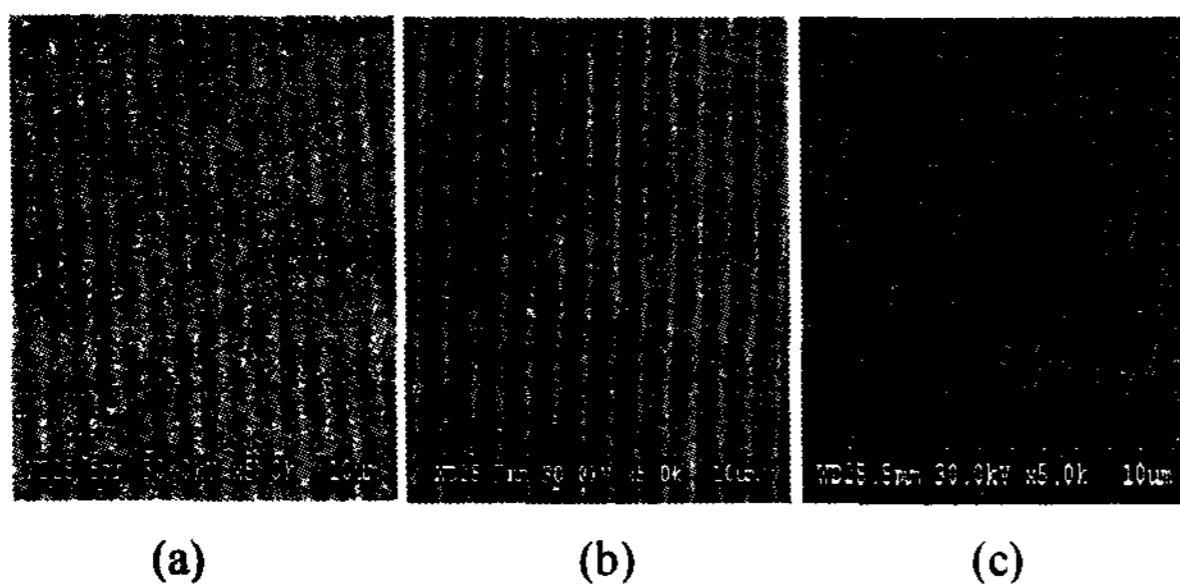


Figure 6. SEM morphologies of bragg gratings (a)w/o silica, $d=834nm$ (b)10wt% aerosil 200, $d=952nm$ (c)10wt% aerosil R812, $d=909nm$ (oligomer:EHA=3:1, 35wt%LC, $2\theta=30^\circ$).

4. Conclusion

The addition of silica did not affect the glass transition temperature(T_g) of the polyurethane acrylate although the storage modulus of the PUA film with silica is increased.

PUA with aerosil 200 gave much higher diffraction efficiency as compared with PUA with aerosil R812.

High diffraction efficiency, good grating formation and low shrinkage have been designed and successfully fabricated based on polyurethane acrylate reinforced with nano-sized silica(aerosil 200).

5. Acknowledgements

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6. References

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