임시 고경형 UV 경화형 우래탄변성 아크릴 집착제에서 디이소시아네이트의 영향

Effect of Diisocyanates in UV Curable Urethane Modified Acrylic Adhesive for Temporary Bonding **김경만, 이호엄, 장정규

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1. Introduction

Typically, UV-curable acrylates are composed of reactive oligomer or polymer, reactive diluents, and photo-initiator. In the semiconductor industry, UV curable acrylates have been used for their temporary bonding adhesives or films such as back-grinding and dicing progress because of their loss of adhesion properties by UV exposure. UV curable reactive polymers have reactive vinyl functionality in the side chain, which is made from the reaction of hydroxy, epoxy and carboxylic acid functionality in the side chain of the polymer. Urethane modified UV curable acrylates have been prepared by the reaction of hydroxy function in the side main polymer methacryloyloxyethyl isocyanate which is expensive chemical specialty. Therefore, some less expensive and readily accessible chemicals or methods to introduce vinyl group into the polymer side chain are required. Our idea is the use of urethane prepolymer prepared by easily accesible chemicals as a linker to the main polymer and vinyl functionality. Polyurethanes are a unique class of polymers that can be readily modified by the variations of their diisocyanate and polyol components. Also, polyurethane materials possess very attractive bulk mechanical properties due to the presence of phase-separated structures.

In this study, UV-curable polyurethane modified acrylates were prepared from hydroxy functional polyacrylate, 2-hydroxyethyl methacrylate (HEMA) and diisocyanate. Effects of diisocyanate types such as

were studied in terms of thermal and storage stability during the preparative process.

2. Experimental

Extra pure grade 2,4-toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), 1,6-hexanediisocyanate (HMDI), 2-hydroxyethyl methacrylate (HEMA), benzophenone and ethylhexyl acrylate were used without further purification. Ethyl acetate (EA) was used as solvent.

UV-curable polyurethane acrylates were synthesized using a two-step reaction procedure. At the 1st stage, polyacrylate with hydroxyl functionality was prepared with 2-hydroxyethyl methacrylate (HEMA) and ethylhexylacrylate by solution polymerization in the presence of azobisbutyronitrile (AIBN) as radical initiator in EA as solvent in 50wt% of solid contents. At the 2nd stage was the introduction of vinyl group using diisocvanates and HEMA by polyurethane reaction. Finally, photo catalyst was introduced, mixed thoroughly to the UV curable polyurethane modified acrylate and stored in dark condition. To measure the 180 °C peel test, film was prepared approximately 10 µm in thickness, and the film was irradiated UV from both sides with 40 W-UV(365 nm) lamp for 3 min at room temperature.

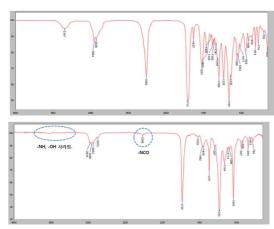


Fig. 1. IR specta of IPDI-HMMA pre-polymer at reaction after 30 minutes (up) and 2hours (below)

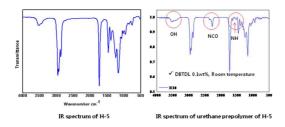


Fig. 2. IR specta of base acrylate and their urethane pre-polymer

3. Results and Disscusion

Morphology of polyurethane pre-polymer was observed and showed differently depending on the diisocyanate such as TDI, IPDI and HMDI. The pre-polymer of HEMA with TDI appear as white solid and those with IPDI and HMDI apperer as liquid. The viscosity of The pre-polymer with IDDI showed the lower than with HMDI. When the introduction of vinyl group into the polyacrylate with hydroxyl functionality by the reaction with NCO-terminated urethane prepolymer were conducted, the effect of the type of diisocyanate on the shpa of polmer showed differently. The reaction with TDI based prepolymer appear easy gelation and HMDI based prepolymer turned gradually gelation by the time. However, the reaction with IPDI prepolymer showed stable at room temperature for more than 1 week enough to proceed the next stage to carry out to test the physical and thermal properties.

The chemical resistance and thermal stability of the film showed enough to use as semiconductor handling supporting material.

4. Conclusion

For the preparation of uv-curable polyurethane modified acrylate, polyurethane prepolymers was prepared and compared with easily accesable diisocyanates such as TDI, IPDI and HMDI. The most usefull diisocynate was found to be IPDI, which showed liquid type pre-polymer with HEMA. Also with this prepolymer gave a stable UV curable polyacrylate. The authors appreciate the financial support from MCP Core Technology for the Next Generation Project of MKE (Ministry of Knowledge Economy) of Republic of Korea.

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