Preparation of UV curable emulsions using PEG-modified urethane acrylates and their coating properties
III: Effects of epoxy acrylate

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Abstract
Water-dispersible UV-curable urethane acrylate emulsions were prepared with polyethylene glycol (PEG) - modified urethane acrylates (PMUA), containing terminal hydrophilic polyoxyethylene chains. To improve physical properties of PMUA, epoxy acrylate (EA) having high thermal stability and hardness, was mixed with five kinds of PMUA containing different chain lengths of polyoxyethylene (POE). For PMUA/EA mixtures, the composition ratio of EA to PMUA and the chain length of POE greatly influenced the size of droplets of emulsions and the physical properties of their cured films. At higher EA to PMUA ratio, the physical properties decreased, which was due to phase separation between EA and PMUA. Phase separation was confirmed by scanning electron microscopy.

INTRODUCTION
Waterborne coatings have been widely utilized recently in industrial coatings, because this kind of coating make it possible to control pollution, to reduce fire risks, and to improve aspects of occupational health and safety. The use of water soluble or dilutible UV or EB curable formulations may appear contradictory from an energy saving viewpoint, because it is necessary to remove the water before irradiating the formulations. However, the application viscosity of water-based inks and coatings is much reduced by water without the volatile organic compounds (VOC), so these materials find widespread use and are becoming more desirable with ever increasing environmental pressures 1,2.

For the preparation of a water dispersible resin, in order to improve water-dispersibility, a special treatment or structural modification of polymer has been generally done by incorporating pendant hydrophilic groups into the backbone 3-5. However, for ionic water dispersible resins, a neutralizing agent has to be used to neutralize acid groups of polymers, which might release potentially harmful organic amines. In the case where a nonionic pendant hydrophilic group is incorporated, the synthesis of prepolymer having isocyanate end groups and POE pendant groups in the same molecule must be carried out by complicated reactions 6.

In our previous papers 7-9, PMUA was simply synthesized by the reaction of PEG with

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residual isocyanate groups of urethane acrylate. These molecules contained terminal nonionic hydrophilic POE groups, so PMUA could act as a polymeric surfactant and be emulsified without the use of an external surfactant. Emulsions and cured films of PMUAs showed low thermal stability and tensile strength, because the hydrophilicity of POE groups of PMUA decreased at higher temperature and urethane acrylate had inherently low physical properties. When PMUA was mixed with urethane anionomer, the thermal stability of the emulsion was improved, however, the physical properties did not much improve\textsuperscript{10}.

The goal of this study is the preparation of UV curable emulsions using PMUA and EA mixtures to improve the physical property of UV cured PMUA films. Thus, to determine the effect of the EA/PMUA composition on the droplet size of emulsions, viscosity, coating and mechanical properties of cured films will be investigated.

**Experimental**

**Materials**

In the synthesis of PMUA and EA, poly(tetramethylene glycol) (PTMG, Mw=1,000, Hyosung BASF), 2,4-toluene diisocyanate(TDI, Junsei Chemical Co.), 2-hydroxy ethyl methacrylate (2-HEMA, Aldrich Chemical Co.), polyethylene glycol (PEG, Mw = 600, 1000, 2000, and 4000, Junsei Chemical Co.), epoxy resin (Kuk-Do Chemical Co, bis-phenol A type, 11,500-13,500 cps at 25°C) and acrylic acid (Junsei Chemicals Co.) were used. (1-hydroxycyclohexyl) phenylmethanone (Irgacure 184, Ciba-Geigy Chemical Co.) and tert-butyl benzoate (Junsei Chemical Co.) were also used as photoinitiator and thermal initiator, respectively.

**Synthesis of PMUA and EA**

Four types of PMUAs were synthesized by three step processes. The molar ratio of reactants is summarized in Table 1. The reactions were carried out in a 4-necked glass reactor equipped with stirrer, thermometer, reflux condenser and N\textsubscript{2} gas inlet. Detailed procedures was reported in our previous paper\textsuperscript{7}. The average molecular weight of PMUA and confirmation of these reactions by \textsuperscript{1}H NMR and GPC were also reported\textsuperscript{7}. EA was synthesized by the reaction of epoxy resin with acrylic acid\textsuperscript{11}. This resin was blended with PMUA to incorporate suitable characteristics for UV curable formulation. Scheme 1 shows the molecular structures of EA and PMUA

**Preparation of UV curable formulations and UV-curing**

An oil solution (10g) containing additives was placed in a 100ml beaker and heated to 45°C to melt, then cooled to 35°C while vigorously stirring. Distilled deionized (DDI) water was added very slowly until a gel-like phase formed, then remaining water was added gradually to reduce viscosity (Phase inversion emulsification)\textsuperscript{12}. The formulation used in the preparation of UV curable emulsions is summarized in Table 2. In case soap-free emulsions of PMUA/EA mixture were prepared, these resins were mixed prior to emulsification. The UV curing formulation of these mixtures was the same composition as with that of PMUA emulsion.