

Test Method

Characteristic shrinkage evaluation of photocurable materials



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ABSTRACT

Photocurable materials have many advantages such as rapid curing, low energy consumption and a broad variety of favorable characteristics; as a result, their application areas are currently expanding. In order to fully utilize the properties of these materials, the related “shrinkage” problem (corresponding to the specific volume reduction due to the reaction between monomer species) must be resolved first. In this study, we investigated the dependence of the linear shrinkage of a monomer in the axial direction on various internal and external factors. In addition, a complementary relationship describing the photocuring behavior of a polymer was studied by photo-differential scanning calorimetry (photo-DSC). The observed shrinkage characteristics depend on the monomer size and structure, UV radiation intensity and photoinitiator concentration. In contrast to the photo-DSC results, the monomer shrinkage parameters are related to the bulk properties of a material. Hence, the dependence of the material depth profile on external factors was evaluated.

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1. Introduction

Ultraviolet (UV) curing technology is a method for forming a polymer structure via the chain reaction between rings or double bonds, which occurs due to the presence of activating radicals and cations of the initiator after its exposure to UV light [1]. In general, it is necessary to distinguish between UV polymerization and UV curing techniques. The UV polymerization technique is similar to the technology utilized for the preparation of linear polymers, and thus can be easily applied to bulk polymerization. UV curing produces three-dimensional polymer structures of multifunctional monomers, such as 1,6-hexandiol diacrylate and dipentaerithritol hexacrylate, through crosslinking caused by UV initiation [2].

Since the Bayer chemical company (Germany) developed a UV curing coating method in 1986, the UV curing technology has been applied to curing film coatings in the field of paints. Recently, it has been utilized as a technique for producing functional polymers (such as adhesives), mobile devices, industrial coatings and nano-imprinted biomimetic products [3,4].

The definition of “shrinkage” corresponds to the amount by which something decreases in size, value, weight or a similar parameter. For casting/molding industries, it represents a slight dimensional reduction, which is related to the reduction in volume of the cast or molded material as it cools and solidifies. When the shrinkage of a specific part leads to fitting problems (such as interchangeability), a slightly bigger casting pattern/mold cavity is fabricated.

The shrinkage phenomenon has been studied in various fields. In particular, it has been investigated to maximize stability and minimize external defects of an industrial product. For example, a study of the change in product appearance has been conducted in the field of extrusion and injection molding of polymeric materials. It was found to be dependent on various external factors such as injection velocity, injection temperature, the difference between the internal and external temperatures, cooling rate and mass production technique utilized [5]. Shrinkage control is the most important part of the practical use of UV curable materials, which rapidly shrink during the curing process, reaching theoretical shrinkage values above 20% [6]. The observed shrinkage behavior can induce material warpage and generate internal stress, thus significantly affecting the quality of a final product.

The volume shrinkage of acrylates and methacrylates occurs during polymerization due to the replacement of weak long-

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distance Van der Waals interactions with strong and short covalent bonds between the carbon atoms of different monomer units. It causes serious problems, including a significant accumulation of internal stress (which results in defect formation) and dimensional changes (which are responsible for the deterioration of the mechanical properties of shrunk UV oligomers and monomers) [7]. Volume shrinkage is one of the main drawbacks of UV cure coatings, which can lead to their premature failure. Therefore, it is important to analyze possible curing mechanisms (depending on various internal and external factors) and their effect on the material shrinkage behavior. For this purpose, a new technique for continuous shrinkage monitoring has been developed. It allows the selection of a test method (characterized by a certain margin of error), an object of measurements and a system of elements. However, this technique does not take into account all possible internal and external shrinkage factors [8–12].

In this study, shrinkage characteristics of polymer materials are examined. The obtained data are compared with the results of photo-differential scanning calorimetry (photo-DSC) in order to analyze the possibility of using the proposed method for evaluating the photocurability properties of UV curable materials.

2. Experimental

2.1. Materials

Since the low viscosity of monoacrylate systems can negatively affect the accuracy of shrinkage testing, the authors selected high-viscosity materials, which are expected to exhibit elastic shrinkage rates. Monoacrylates were used to analyze the UV curing characteristics through shrinkage and photo-DSC measurements. Because no shrinkage problems were detected for the acrylate cage [13], it was selected as a reference point for evaluating polymer shrinkage rates. While monoacrylates were utilized for basic testing, caprolacton acrylate (CA) and exothylated nonyl phenol acrylate (NPA) were used as UV curable materials (Fig. 1). In addition, multifunctional trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA) systems were selected to analyze shrinkage external factors due to their high shrinkage and reaction rates.

2.2. Shrinkage testing

Shrinkage of a material was evaluated by a linometer (Plustek,

Seoul, Republic of Korea). First, the designated amount of material was loaded onto a stainless steel plate and covered with a glass slide, which was in turn placed on a displacement measurement sensor and transducer (the glass slide was fixed on the top). After specimen shrinkage due to UV irradiation, the stainless steel plate was moved up, and its traveled distance was recorded as a function of time. Finally, the measured axial shrinkage in the vertical direction was converted into volumetric data, and the corresponding volume shrinkage was calculated. UV light intensity in the wavelength range of 300–545 nm was 10 mW/cm² was utilized, while the volume of sample placed on the test plate was about 1 mL. All measurements were conducted at 25 °C.

2.3. Photo-DSC testing

Photo-DSC is a technique that measures the difference in energy generated between the specimen and the reference. Its biggest difference from general DSC is that the majority of DSC measurements use a temperature ramp (in other words, almost all photo-DSC runs are conducted at isothermal conditions). Therefore, photo-DSC measures the heat of reaction as a function of external energy at a constant temperature (in contrast to regular DSC, which measures the first and the second transition points).

In this study, photo-DSC experiments were conducted using a DSC Q-200 apparatus (TA Instruments) equipped with a photocalorimetric accessory, which emitted light from a 100 W middle-pressure Hg lamp (its intensity was determined by placing an empty DSC pan into the sample cell). The intensity of the UV irradiation directed at the sample was 10 mW/cm², and the corresponding wavelength range was 300–545 nm. The weight of the sample placed into the open Al DSC pan was about 1 mg. All measurements were performed at 25 °C.

2.4. External shrinkage factors

The photoinitiator content and UV light intensity were used as external factors affecting the curing process. Both parameters were found to have a significant impact on the reaction rate [14]. Hydroxydimethyl acetophenone (HP-8) was used as a photoinitiator. Its content was varied between 0.5, 1, 3, and 5 phr (parts per hundred resin), while the UV light intensity was changed in the range of 1.0–10.0 mW/cm² (with an accuracy of 10%). The parameters of the conducted tests are listed in Table 1.

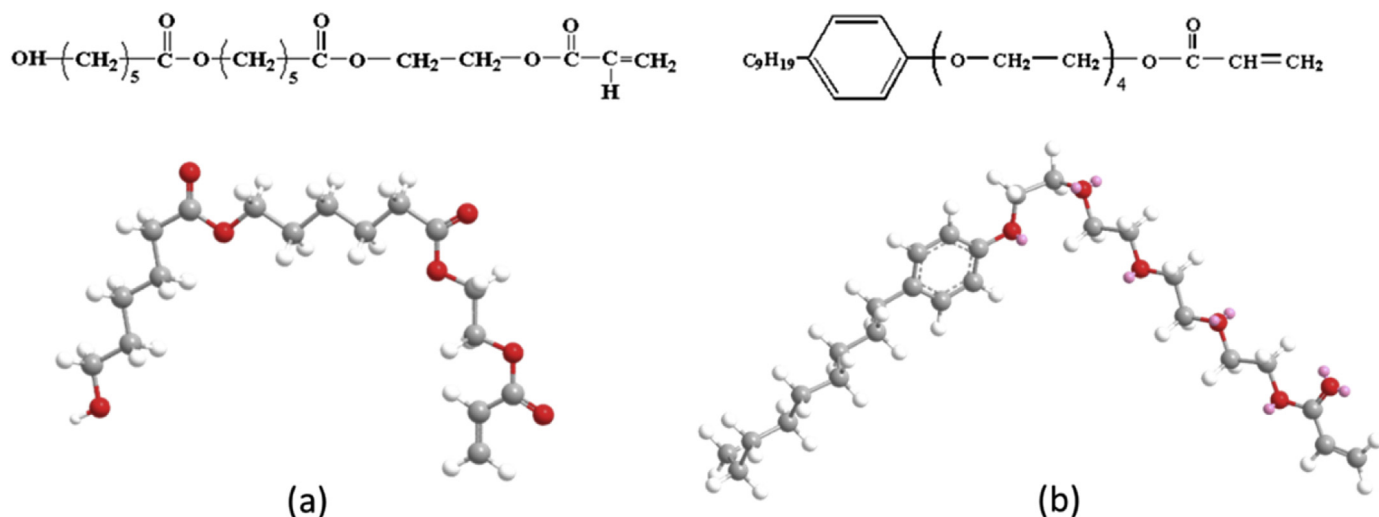


Fig. 1. Selected acrylates utilized for shrinkage evaluation: (a) caprolacton acrylate (CA) and (b) nonylphenol acrylate (NPA).

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