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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 photo-curing 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-



Test Method



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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 highviscosity 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 middlepressure 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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Shrinkage testing parameters.

Variation	Basic test type	Photoinitiator content (phr)	UV intensity (% @ 10 mW/cm ²)
Monomer	Monofunctional	3	100
Photoinitiator	Multifunctional	0.5, 1, 3, 5	100
UV Intensity	Multifunctional	3	10, 25, 50, 100

3. Results and discussion

3.1. Basic shrinkage testing

Shrinkage of a material is affected by various molecular factors. A typical shrinkage process can be described by the following simple formula:

Shrinkage (%) =
$$\frac{FN \times CR}{Mn}$$
 (1)

where FN is the monomer functionality, CR is the conversion ratio of a curing system, and Mn is the monomer molecular weight. Fig. 2 describes various phases of the shrinkage process: the beginning of the UV exposure, shrinkage initiation, shrinkage increase due to curing, and the final reaction. During the final reaction phase, the ultimate shrinkage of the tested material is determined.

The monomer conversion ratio depends on the internal factors of molecular structure and external factors such as reaction rate and UV irradiation intensity. Fig. 3 show the results obtained for the real-time shrinkage testing of CA and NPA species, respectively, which contain monoacrylate functional groups. The corresponding ultimate average shrinkage values for these two materials were 3.35% and 2.6%. Thus, the relative shrinkage calculated from these data can be described by the ratio of 1:0.77. The molecular weights of CA and NPA are 344 and 450, respectively; therefore, the relative shrinkage per unit mass (mole equivalent) can be expressed as 1:1.009, indicating that the shrinkage values calculated for these materials with respect to their molecular weights do not differ significantly. According to the obtained results, the slope of the graph depicting shrinkage as a function of time represents the



Fig. 2. Different phases of the shrinkage process: 1) beginning of the UV exposure, 2) shrinkage initiation, 3) shrinkage increase due to curing, and 4) final reaction.



Fig. 3. Real-time shrinkage of CA and NPA.

shrinkage rate (it is interpreted as the material curing rate, and thus can be used to predict the degree of curing).

Fig. 4 show the plots obtained by dividing the data extracted from Fig. 3 by the change in time (delta time, Δt). As a result, the mean shrinkage rate (%/s) was calculated for each reaction point. During the initial reaction, the shrinkage rate was negative, owing to the specific features of the measuring method. In particular, shrinkage was detected after the UV curing process moved from the sample surface to its bottom part (along the thickness direction). The initial reaction caused instantaneous thermal expansion, which resulted in a negative value of the shrinkage rate (although both materials belong to the class of monoacrylates, they significantly differ in terms of their reaction rates).

The shrinkage duration for the two studied materials can be obtained from the calculated shrinkage rates, and the corresponding reaction rates – from the maximum peak times. The comprehensive results of the shrinkage testing of CA and NPA are listed in Table 2.

The obtained shrinkage magnitudes for the two materials are equal to 52.1% (CA) and 60.4% (NPA) of the corresponding theoretical values. The theoretical shrinkage rates were calculated based on the assumption that the molecular structure was uniform, and the conversion ratio reached 100%. However, during polymer formation, the presence of bulky groups inhibits the next polymerization step. Therefore, the molecular weight of a polymer cannot increase indefinitely. In addition, the conformation of the acrylate side chain does not allow reaching the theoretical shrinkage rate.

The difference between the theoretical and experimental shrinkages of the two materials can be explained by the bulk properties of the NPA side chain. Because the side chain of CA can move freely, it may form more diverse structures (as compared to the movement of the entire monomer or polymerization unit). As a result, a larger difference in the shrinkage rate is observed.

Fig. 5 describes the measurements of the real-time heat output performed by photo-DSC. When the UV lamp is activated, the measured heat output dramatically increases. After a certain period (about 60 s), its magnitude stabilizes. The observed peak represents the heat flow measured immediately after UV light activation, and the conversion of functional groups during curing can be estimated via peak integration.

Fig. 6 shows the integral values of the heat flow obtained from Fig. 5. In Table 3, results of photo-DSC testing are listed. Ultimately, the measured values reach a constant level (229.9 J/g for CA and



Fig. 4. Shrinkage rate of CA and NPA as a function of time.

Table 2

Shrinkage test results for the monoacrylate systems.

	CA	NPA
Molecular weight	344	450
Theoretical maximum shrinkage (%)	6.43	4.30
Axial shrinkage (%)	3.35	2.60
Maximum shrinkage rate (%/s)	0.163	0.118
Peak approach time (s)	18.1	15.3
Experimental/theoretical shrinkage ratio	52.1	60.4



Fig. 5. Heat flow measured for the monoacrylate systems as a function of the UV exposure time.

116.8 J/g for NPA). The two studied materials contain different numbers of functional groups per unit mass, which can be calculated through the following formula:



Fig. 6. Exothermic areas for the studied monoacrylate systems as functions of the UV exposure time.

Table 3Photo-DSC test results for the monoacrylate systems.

	CA	NPA
Molecular weight (M _n)	344	450
Maximum heat flow (W/g)	23.50	9.21
Peak approach time (s)	3.97	7.27
Exothermic area (J/g, at 70 s)	229.9	116.8

(Example: $0.8 \approx (201 \text{ J/g})/(331 \text{ J/g} \times 0.76)$).

The acrylic functional site number of unit mass was 1:0.76 (1/344: 1/450); the convergence of an advanced (ratio of exothermic area) graph 1:0.67 can be obtained by calculating the value of the functional site number. Since the calculated relative shrinkage was 1:0.77, we can conclude that the differences between the exothermic areas measured by photo-DSC and the corresponding shrinkage rates are not significant.

Figs. 4–6 describe the correlation between the distance and shrinkage rate and the related heat flow. In particular, the regular shrinkage measurement system analyzes shrinkage as a function of distance, while the photo-DCS system analyzes the correlation between the material heat output and the corresponding polymerization rate. The results obtained for the two systems can be interpreted complementary to each other. The photo-DSC technique can be used, not only for the conversion rate determination (via some advanced prediction model), but also for the indirect prediction of shrinkage values.

While shrinkage is related to the bulk characteristics of a material, photo-DSC is a capable of characterizing the reaction between molecular units. Thus, the differences in results observed for these two methods depend on the material structure.

3.2. Shrinkage dependence on external parameters

3.2.1. Photoinitiator content

Multiple factors have an impact on the material shrinkage rate

(in addition to its exterior shape). The type and content of photoinitiator as well as the source of light and its intensity are known factors that affect the polymer curing rate. Therefore, photoinitiator type and light source must be taken into account when optimizing a particular UV curing system [15–17].

A typical radical-based reaction process can be described as follows:



The general expressions for the rate of polymerization (R_p), kinetic chain length (ν), and instantaneous degree of polymerization (DP_n^{inst}) are:

$$R_{p} = k_{p}[M][P_{tot}] = k_{p}[M] \left(\frac{2fk_{d}[I]}{k_{t}}\right)^{1/2}$$
(3)

$$\nu = \frac{R_p}{R_{term} + R_{tr}} = \frac{k_p[M]}{k_t[P_{tot}] + k_{tr}^{mon}[M] + k_{tr}^{sol}[S]}$$
(4)

$$DP_n^{inst} = \frac{k_p[M]}{(k_t + 0.5k_{tc})[P_{tot}] + k_{tr}^{mon}[M] + k_{tr}^{sol}[S]}$$
(5)

In upper equation, [M] is monomer concentration, K_p is the kinetic constant for propagation $[P_{tot}]$ is the concentration of all polymer radicals in the system 'f 'is Initiator decomposition efficiency K_d is Coefficient of Decomposition [I] is concentration of initiator K_t is the kinetic rate constant for termination. R_{term} is rate of termination R_{tr} is rate of transfer. Both the initiator reaction rate and monomer content determine the rate of the polymerization process. The principal factors contributing to the formation of initiator radicals are the initiator fraction and the amount of energy supplied from the outside. The rate of radical formation is proportional to these two important variables, while the overall reaction rate increases as more initiator species are added or more intense radiation is used [17–20].

The monomer conversion ratio is known to be proportional to the reaction rate [19,20]. Shrinkage rate is directly affected by the conversion ratio, and different reaction rates lead to different shrinkage rates.

In this work, the dependence of the polymer shrinkage rate on the photoinitiator concentration was observed. In addition, the UV light intensity was varied to investigate the shrinkage rate dependence on external parameters (other than material properties).

According to the results obtained for the TMPTA system, the shrinkage rate increases with an increase in the photoinitiator



Fig. 7. TMPTA shrinkage dependence on the photoinitiator content.

content (see Figs. 7 and 8). The polymerization reaction also terminates earlier at faster UV curing rates (which are proportional to the photoinitiator content). However, when the photoinitiator content increases from 3 to 5 phr, the overall shrinkages and shrinkage rates do not exhibit significant differences (although, the shrinkage rate tends to decrease when approaching the peak height; see Fig. 9). This phenomenon can be explained by the curl effect on the TMPTA shrinkage rate.

PETA exhibits distinctive properties (as compared to TMPTA). Its shrinkage rate change with the photoinitiator content was twice as much (1.1%) as that for TMPTA (0.5%), and the observed difference was even larger when compared to the overall shrinkage rate (Figs. 10–12). Since PETA exhibits high viscosity and high cohesion to molecular hydrogen, its hydroxyl groups can function as transfer chains and cross-links between molecules, which boosts the overall reaction rate. However, when multifunctional groups are present, these hydroxyl groups can impede the chain reaction. In particular, the multifunctional groups form 3-dimensional structures in the course of a radical reaction, which cage any remaining unreacted sites [13]. When this cage effect occurs, the transfer chains of the hydroxyl groups would terminate the reaction rather than maintain it.



Fig. 8. TMPTA shrinkage rate dependence on the photoinitiator content.



Fig. 9. Dependence of the TMPTA shrinkage characteristics on the photoinitiator content.



Fig. 10. PETA shrinkage dependence on the photoinitiator concentration.

3.2.2. UV intensity and shrinkage behavior

Since photoinitiators have to be UV-activated to form radicals, the intensity of the UV light plays a critical role in controlling the magnitude of activation energy, which significantly affects the process of radical initiation. Although the values of activation energy are different for endothermic and exothermic reactions, it is common to exceed the activation energy barrier via the reaction with incident light. Thus, the rate of polymerization R_p can be expressed as

$$R_{p} = \frac{k_{p}}{k_{t}^{1/2}} [M] (\varnothing \varepsilon I_{0}[A]b)^{\frac{1}{2}}$$
(6)

Here, k_p is the propagation kinetic constant, k_t is the termination kinetic constant, [M] is the molar concentration of a monomer, \emptyset is the initiator efficiency, I_o is the incident light intensity (in light quanta per unit area and second), \in is the initiator absorption



Fig. 11. PETA shrinkage rate dependence on the photoinitiator concentration.

coefficient, [A] is the initiator molar concentration and b is the thickness of the resulting specimen [21].

In addition, the overall activation energy of a reaction (E_a) can be calculated by assuming that the reaction rate follows Arrheniustype behavior. The combination of the Arrhenius equations containing the propagation and termination kinetic constants results in the expression, which describes the effect of temperature on the material polymerization rate:

$$\ln R_p = \ln[A] + \ln\left[R_i^{1/2}[M]\right] - \left(\frac{E_a}{RT}\right)$$
(7)

where T is the absolute temperature, A is the proportionality constant, R is the gas constant, R_i is the rate of initiation and [M] is the monomer concentration [21].

TMPTA was used to investigate the shrinkage dependence on the light intensity. The photoinitiator concentration was varied between 3 phr and 5 phr, which corresponded to the highest shrinkage rate. The light intensity was initially set to 100%



Fig. 12. Dependence of the PETA shrinkage characteristics on the photoinitiator content.

(corresponding to 10 $\rm mW/cm^2$ with an accuracy of 10%) and then lowered to 50%, 25%, and 10%.

Fig. 13 and Table 4 shows the TMPTA shrinkage as a function of the UV exposure. The observed trend is different from that obtained for the shrinkage dependence on the photoinitiator content. The change in the magnitude of shrinkage is characterized by the deviation of more than 3% (between 6.8% and 9.8%) because the UV irradiation directly affects the material activation energy.

The vertical region of the graph depicted in Fig. 13 (corresponding to the initial shrinkage) shifts to the right with a reduction in the UV exposure. For example, the times of initial shrinkages observed at light intensities of 100% and 10% were 7.3 s and 46.2 s, respectively, and their difference was 38.9 s. When the actual exposure to UV light begins, the polymer is not cured immediately since the specified process is delayed by 38.9 s.

The observed delays have a significant effect on the polymer shrinkage properties, which can be explained from the two points of view. The first reason is that a typical coating is characterized by



Fig. 13. TMPTA shrinkage dependence on the UV exposure (the photoinitiator concentration was 3 phr).

a relatively high thickness. In this case, UV light is absorbed only by the upper specimen layer and then transmitted to the lower area. Since the photoinitiator is activated via the absorption of UV light, its intensity gradually decreases from the top along the vertical direction. The cure depth C_d can be determined from the following equation:

$$C_d = D_p \ln\left(\frac{E_{max}}{E_C}\right) \tag{8}$$

Here E_{max} is the energy dosage per unit area, E_c represents the "critical" energy dosage, and D_p is the "depth of penetration" of a laser beam into the monomer, which is inversely proportional to the molar extinction coefficient and photoinitiator concentration. By analyzing the cure depth plotted versus laser writing speed, the magnitudes of D_p and the empirical constant E_c can be determined [22]. Both parameters exhibit a logarithmic dependence on E_{max} , while D_p is inversely proportional to \in and the photoinitiator concentration [PI]:

$$D_p \Leftrightarrow \frac{2}{2.303\varepsilon[PI]} \tag{9}$$

The coating thickness, which is capable of transmitting light, obeys the relationship described by Eq. (9) and is inversely proportional to the photoinitiator content. Lowering light intensity decreases the probability that the UV irradiation will reach the coating bottom part. Since the cure depth C_d is proportional to the logarithm of the maximum light intensity, it can be calculated by using the following equations:

$$\begin{array}{ll} C_{d10} &= Dpln(Emax_{10}/E_c) \\ &= Dpln(Emax_{10} \times 0.1/E_c) \\ &= Dp[ln(Emax_{10}/E_c) + ln(0.1)] \\ &= Dp(C_{d10} - 2.303) \end{array} \tag{10}$$

Consequently, the theoretical value of the cure depth is reduced dramatically when the light intensity decreases; as a result, the total amount of energy reaches a constant value. Thus, the cure depth significantly depends on the total amount of the supplied irradiation energy at a constant value of the photoinitiator content [22].

Therefore, the observed delay in reaction time for the coating

 Table 4

 TMPTA shrinkage characteristics measured at various UV intensities.

UV Intensity (%)	Shrinkage (%)	Maximum shrinkage rate (%/s)	Peak approach time (s)
10	6.8	0.111	70.3
25	8	0.212	32.2
50	9.5	0.299	21.2
100 (10 mW/cm ²)	9.9	0.391	13.2

lower area is due to the lower intensity of UV irradiation. As a result, the material shrinkage is delayed as well. Generally, shrinkage is a very powerful technique for depth profiling because photo-DSC can measure the energy release by molecular units; however, shrinkage represents the bulk properties of the entire class of shrinkable materials. Fig. 14 shows the scheme describing the process of curing transfer from the coating top to the bottom when the specified cure depth problems occur.

The second reason for the observed shrinkage delay is that internal stress is not generated properly due to the slow curing speed caused by the low light intensity. Because the light intensity is weak, the photoinitiator activation process is inhibited at some point, and the overall curing speed is decreased. The amount of the activated photoinitiator is reduced due to radical termination. Consequently, the polymer curing process reaches the point, at which the hardened part exhibits low curing density. During the early curing stages, the stainless steel plate did not move, and the related internal shrinkage stress decreased. As a result, the internal stress is either completely eliminated or induces curing in the side specimen's parts. Fig. 15 depicts the diagram describing the polymer curing process at different photoinitiator concentrations/UV intensities. Depending on the irradiation time, the UV light reaches the sample bottom, and thus generates the difference in polymer curing density, which leads to a shrinkage decrease.

The results of the calculated TMPTA shrinkage rate plotted as a function of the UV irradiation intensity are shown in Fig. 16. Both the shrinkage rate and peak approach time dramatically increase with UV exposure (the peak time is correlated with the delay due to the polymer bulk properties described above).

It is possible to use shrinkage rate (after comparison with the results of photo-DSC) as the index that describes the rate of reaction. The maximum rate of polymerization is proportional to the incident light intensity:

$$R_p \propto (I_0)^{\alpha} \tag{11}$$

When α is 0.5, the classic rate equation suggests that bimolecular termination occurs. In this experiment, the obtained values of α vary in the region of 0.5–0.6. Fig. 17 shows the results normalized by the light intensity raised to the power of 0.6. This resulting value of α indicates that a combination of bimolecular and unimolecular

termination is observed during polymerization. In general, the magnitude of α in multifunctional acrylate systems ranges between 0.5 and 1.0 [23]; thus, shrinkage evaluation allows estimating the value of this initiator power factor. Even increased content of photo-initiator, tend of corresponding to the UV is the same. As the UV intensity increases, the corresponding shrinkage rate increases as well.

The magnitude of D_p is inversely proportional to the amount of photoinitiator; therefore, the observed delay becomes greater for a system with a larger photoinitiator content. Fig. 18 show that when the photoinitiator content is increased to 5 phr, the delay effect obtained at a UV light intensity of 10% is further increased. Hence, the photoinitiator content has a more significant effect on the UV absorbance, and the observed delay becomes larger at low UV exposures.

However, it is possible to verify that the shrink initial time is pulled rather comes to UV intensity increases (Fig. 19). This result reflects the ability of the utilized test method to evaluate material bulk characteristics. As shown in Fig. 15, at low photoinitiator contents, the light transmittance increases, while the related and curing rate partially decreases. Therefore, not only fast curing rates, but also low curing densities cause polymer shrinkage.

The magnitude of E_c can be calculated at a light exposure of 10%. The value of C_d remains the same since the specimen thickness is constant. The magnitude of ε also does not change because the same base material is used. Therefore,

• $E_{max10(3p)} = UV intensity \times time = 1 (mW) \times 46.2(s)$
$D_{p10(3p)} = 2/2.303 \times \epsilon \times [3]$
$C_{d10(3p)} = D_{p10(3p)} \ln(Emax/Ec)$
$= (2/2.303 \times \epsilon \times [3]) \ln(46.2I/Ec)$
• $E_{max10(5p)} = UV$ intensity \times time = 1 (mW) \times 58.8(s)
$D_{p10(5p)} = 2/2.303 \times \epsilon \times [5]$
$C_{d10(5p)} = D_{p10(3p)} \ln(Emax/Ec)$
$= (2/2.303 \times \epsilon \times [5]) \ln(58.8J/Ec)$
$C_{d10(3p)} = C_{d10(5p)}$
$(2/2.303 \times \epsilon \times [3])\ln(46.2J/Ec) = (2/2.303 \times \epsilon \times [5])\ln(58.8J/Ec)$
$[3]\ln(46.2J/Ec) = [5]\ln(58.8J/Ec)$
$(46.2]/Ec) = (58.8]/Ec)^{5/3}$
$\dot{E}_{c} = 32.1 J$
(12)
(12)

Using these formulas for the described system, it is possible to estimate the "critical" energy dosage (Ec), which can be utilized as a variable.

A correlation between the curing rate and the light intensity can be obtained through normalizing the values of the shrinkage rate previously measured for the system with a photoinitiator concentration of 3 phr (an identical trend was obtained for the 5 phr system). Fig. 20 depicts the maximum shrinkage rates for each system normalized by $I_0^{0.6}$.

Both the shrinkage rate and shrinkage parameters were larger at



Fig. 14. A scheme describing the shrinkage delay effect.



Fig. 15. Depth profile dependence on the photoinitiator concentration/UV intensity. (a) Low concentration or high intensity: light penetrates deeply, low curing density. (b) High concentration or low intensity: low penetration, high curing density on the surface.



Fig. 16. TMPTA shrinkage rate dependence on the UV intensity (the photoinitiator concentration was 3 phr).



Fig. 17. Time dependence of the normalized TMPTA shrinkage rate (the photoinitiator concentration was 3 phr).

a photoinitiator content of 3 phr. This can be explained by taking into account non-regular shrinkage phenomena such as curling and maintaining the space between molecules due to internal factors in



Fig. 18. TMPTA shrinkage dependence on the UV light intensity (the photoinitiator concentration was 5 phr).



Fig. 19. Initial shrinkage time dependence on the photoinitiator content and UV intensity.

terms of the decrease free-volume. Thus, although the values of shrinkage and shrinkage rate are lower for the 5 phr system, the shrinkage process itself occurs more rapidly.



Fig. 20. TMPTA normalized shrinkage rate as a function of the UV intensity and photoinitiator content.

4. Conclusions

The comparison of the obtained photo-DSC data with the results of shrinkage evaluation reveals that the latter represents a technique that is capable of evaluating both the UV curing and bulk properties of a UV curable resin. The material structural characteristics were found to significantly affect the UV curing properties. Shrinkage of a polymer depends on various external factors; in particular, varying the UV exposure produced a greater effect than changing the photoinitiator content (although both these parameters have a significant impact on the UV curing process). The described shrinkage evaluation procedure generates data which reflects the dependence of the material bulk characteristic on these external factors [24,25].

Various parameters (such as photoinitiator content, UV light intensity and environmental temperature) may serve as experimental variables. However, in order to compare the corresponding material shrinkage properties, these variables must be controlled.

UV exposure intensity can act as a major factor affecting the curing depth profile, which also depends on the photoinitiator content. At the same time, controlling the energy dosage per unit area is also important for accurate shrinkage evaluation. Therefore, in order to ensure that polymer shrinkage occurs, longer times are required at low light intensities.

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