Volume shrinkage of UV-curable coating formulation investigated by real-time laser reflection method

Yu Jian, Yong He, Tongzhou Jiang, Chunguang Li, Wantai Yang, Jun Nie

Abstract Volume shrinkage is one of the main drawbacks of UV-cured coatings and can lead to premature coating failures. Due to the rapid polymerization during UV-curing, real-time volume shrinkage has been challenging to measure accurately. In this article, the shrinkage process of UV-curable formulations was systematically investigated by a recently developed laser reflection method. The influence of oligomers, monomers, and photoinitiators on shrinkage process has been evaluated. Compared with the oligomers, the monomer was the main contributor to shrinkage due to the high concentration of double bonds. Polymerization shrinkage could be reduced by increasing the oligomer/monomer ratio. Because monomers were the main contributors of shrinkage, the chemical structure of monomers was important for decreasing shrinkage. Methacrylate monomers decreased the final shrinkage but unfortunately reduced the conversion. Monomers with a high degree of ethoxylation lowered the shrinkage and simultaneously increased the conversion. The concentration of photoinitiators had no obvious effect on the normalized shrinkage. Thus, the low shrinkage caused by the low concentration of photoinitiators was only attributed to the significant drop of the conversion.

Introduction

UV-curing is widely used in decorative and protective coatings due to its advantages such as low curing temperature, fast curing rate, and the absence of solvents.[1–3] The components of UV-curable systems include reactive oligomers, reactive monomers, photoinitiators, and other additives.[4–7] For free radical photopolymerization, the commonly used oligomers and monomers are (meth)acrylates. However, (meth)acrylates have obvious and inevitable volume shrinkage due to the replacement of long-distance connection via weak Van der Waals force by strong short covalent bonds between carbon atoms of different monomer units.[8] The volume shrinkage causes serious problems including a large build-up of internal stress, which results in defects formation, and dimensional changes, which are responsible for decreased mechanical properties.[9]

Adjusting the compositions of UV-curable systems is a convenient way to decrease the volume shrinkage. However, studies on decreasing shrinkage of coating formulations were hindered because there were no classical analytical methods that could be followed to analyze the fast photopolymerization. Fortunately, in our previous study, the laser reflection method had been developed, and it proved to be accurate for measuring the shrinkage of UV-curing in real time.[10] In this article, this new real-time method was employed to monitor the volume shrinkage of UV formulations. The effect of components in coating formulas such as oligomers, monomers, and photoinitiators on the shrinkage has been systematically investigated. This work should prove helpful in finding ways to optimize the coating process, i.e., to achieve low shrinkage and shrinkage rate with high conversion of double bonds.

Y. Jian, Y. He (✉), T. Jiang, C. Li, W. Yang, J. Nie
State Key Laboratory of Chemical Resource Engineering and Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
e-mail: heyong@mail.buct.edu.cn

Experimental part

Materials

The radical initiators including ethyl (2,4,6-trimethyl-benzoyl) phenylphosphinate (TPOL), 2-isopropyl-thioxanthone (ITX), and ethyl 4-(N,N-dimethylamino) benzoate (EDAB) were obtained from High-Tech Insight Co., Ltd. (Beijing, China). The trimethylolpropane triacrylate (TMPTA, SR351), ditrimethylolpropane tetraacrylate (DTMPTTA, SR355), trimethylolpropane trimethacrylate (TMPTMA, SR350), 3 mol ethoxylated trimethylolpropane triacrylate (TMPT(EO)3A, SR454), 9 mol ethoxylated trimethylolpropane triacrylate (TMPT(EO)9A, SR502), 15 mol ethoxylated trimethylolpropane triacrylate (TMPT(EO)15A, SR9035) were supplied by Sartomer. Scheme 1 showed the chemical structures of monomers and photoinitiators. The oligomer Desmolux XP 2513 (aliphatic polyurethane acrylate with molecular weight 2000 g/mol and functionality of 3.2) was supplied by the Bayer Material Science.
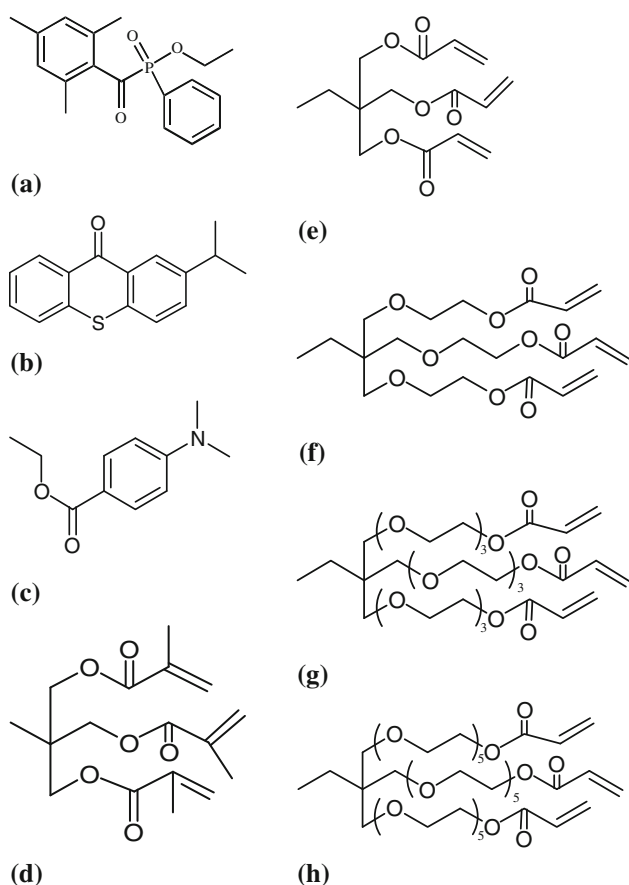
Scheme 1: Chemical structure of photoinitiators (a) TPOL, (b) ITX, (c) EDAB; and UV monomers: (d) TMPTMA, (e) TMPTA, (f) TMPT(EO)3A, (g) TMPT(EO)9A, (h) TMPT(EO)15A
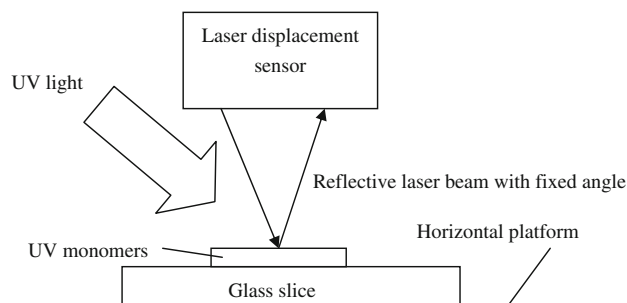
Shrinkage measurements

A laser reflection method based on the laser displacement sensor (LK-G10, Keyence, Japan) was used to directly measure shrinkage of UV-curing systems.[10] As shown in Scheme 2, the laser displacement sensor detected the displacement of the sample surface (thickness change) due to the shrinkage of photopolymerization by recording the motion of a mirror reflecting laser with the fixed reflection angle on charge-coupled device (CCD). When a sample was irradiated with 385 nm UV-LED source (UVEC-4, Lamplic, China), the thickness change of the sample was recorded as the function of time. Percentage shrinkage (St) was defined by the dimensional change according to the following equation:

$$S_t = (H - H_t)/H = (1 - H_t/H) \times 100\% \qquad (1)$$

where H is the initial thickness and H_t is the thickness at time t. The measured shrinkage was actually the linear shrinkage. However, as the planar dimensions were much greater than the thickness and the planar shrinkage was constrained by the substrate, the linear shrinkage appropriately equaled the volumetric shrinkage.[8] The initial thickness of samples measured in this work was around 100 μm to avoid the negative influence of oxygen on the photopolymerization.[11] The sampling interval for shrinkage measurement was 10 ms. The radiometer (Honle UV Technology, Germany) was used to detect the light intensity on the surface of samples, and UV intensity was 5 mW/cm².

Conversion measurements

Fourier transform infrared spectra (FTIR) were recorded by a Nicolet 5700 instrument (Thermo Company, USA). The spectrometer was operated in a rapid mode with an average collection rate of 3 scans s⁻¹. Samples were sandwiched between two KBr crystals and irradiated by UV light. The conversion of double bonds was calculated by the decrease of the area of (meth)acrylate double bond absorption peak around 810 cm⁻¹.[12,13] UV intensity in FTIR

Scheme 2: Experimental set-up for shrinkage measurement (side view)[10]

measurements was adjusted to 5 mW/cm^2 to match the shrinkage measurements.

Results and discussion

The effect of the oligomer content on shrinkage

A clear coating formula based on the monomer (TMPTA) and the oligomer (Desmolux XP 2513) with 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB was used. We varied the weight ratio of oligomer/monomer (100:0, 75:25, 50:50, 25:75, and 0:100) to investigate the effect of oligomer (or monomer) content on photopolymerization shrinkage. As shown in Fig. 1, the commencement of irradiation was at 0 s, at and before which there was no shrinkage. Shrinkage of each coating formula significantly increased after UV irradiation and tended to reach the equilibrium at 280 s ("final" shrinkage). In our previous work, we proved that the polymerization shrinkage depended on the double bonds conversion and the concentration of
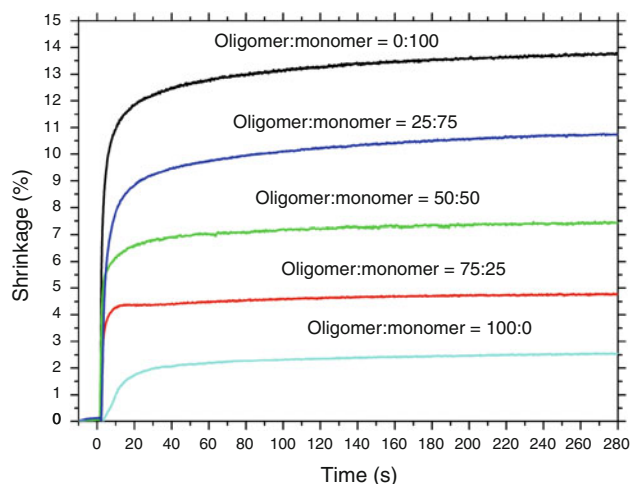

Fig. 1: Shrinkage profiles for formulations with different oligomer/monomer ratios. Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB

Table 1: Calculated and experimental shrinkages for formulations: photoinitiator concentration 2 wt% TPOL, 0.5 wt% ITX, and 0.5 wt% EDAB; monomer was TMPTA and Oligomer was Desmolux XP 2513

Monomer:Oligomer	Calculated shrinkage (%)	Final shrinkage (%)	Final conversion (%)
100:0	–	13.83	41.60
75:25	11.03	10.77	61.48
50:50	8.19	7.42	68.96
25:75	5.37	4.78	72.54
0:100	–	2.54	95.59

double bonds.[10] The concentration of double bonds (C_{db}) was defined as:

$$C_{db} = \text{Functionality} \times \text{Monomer density}/$$
$$\text{Molecular weight} \qquad (2)$$

As shown in Fig. 1 and Table 1, the shrinkage of the monomer (TMPTA) was 13.83% at 280 s, but the shrinkage of the oligomer (Desmolux XP 2513) was 2.54% at 280 s. It was due to the significant difference between oligomer and monomer. Desmolux XP 2513 had a very low concentration of double bonds (1.84×10^{-3} mol/L) compared with that of TMPTA (11.24 mol/L). Generally, the (meth)acrylate monomers had obvious shrinkage (>8%).[10] In contrast, the oligomers had low shrinkage due to the low concentration of double bonds.

By varying the ratio of oligomer/monomer, the shrinkage could be adjusted. The experimental shrinkage values of monomer and oligomer could be used to calculate the shrinkage of the formulation because the final shrinkage was the concerted efforts of monomers and oligomers. Thus, the calculated shrinkage for formulations was defined as:

$$\text{Calculated shrinkage} = \text{Percentage weight A}$$
$$\times (\text{Shrinkage of monomer A})$$
$$+ \text{Percentage weight B}$$
$$\times (\text{Shrinkage of oligomer B}) \quad (3)$$

Results are presented in Table 1, and good correlation was obtained between experimental and calculated data for formulations. It was clear that as oligomer/monomer ratio increased, the shrinkage decreased. Thus, adding the oligomers was remarkable in decreasing the "final" shrinkage for the formula. Figure 2 shows the conversion of the formulations with different oligomer/monomer ratios. Unlike the shrinkage behavior, the "final" conversion increased with increasing oligomer/monomer ratio. These results indicated that the conversion did not play a dominant role in shrinkage of formulations. Another important factor, the concentration of double bonds, was responsible for the shrinkage behavior. Because the monomer was the main contributor to the concentration of double bonds, shrinkage was significantly decreased by increasing the oligomer/monomer ratio. Thus, the formulation could exhibit low shrinkage even at high conversion when the weight content of monomer was low.

The effect of the monomer structure on shrinkage

As we just discussed, compared with oligomers, monomers were the main contributor to shrinkage. Thus, it was important to know which kinds of monomers exhibited low shrinkage. The ethoxylation

monomers and methacrylate monomers were used to explore the chemical structure effect of monomers on the shrinkage behavior. The formulation used was oligomer/monomer with a weight ratio of 50/50.

The shrinkage of methacrylate monomer (TMPTMA) or acrylate monomer (TMPTA) blended with oligomer (Desmolux XP 2513) is shown in Fig. 3. As we anticipated, the formulation containing TMPTMA exhibited much lower shrinkage at any given time than the formulation containing TMPTA. When taking derivatives of the shrinkage curve with time, the shrinkage rate can be obtained as a function of time. The peak value of the shrinkage rate was the maximum shrinkage rate. The maximum shrinkage, related to the polymerization rate
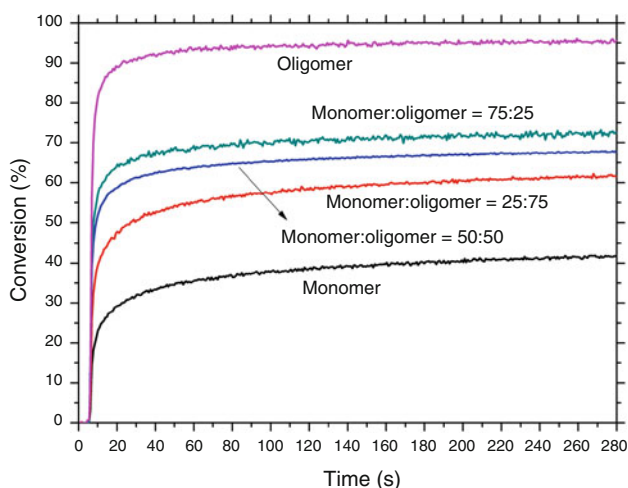

Fig. 2: Conversion for formulations with different oligomer/monomer weight ratios. Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB
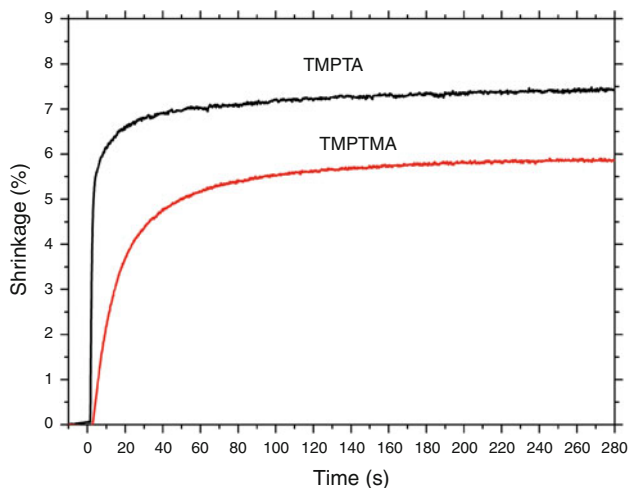

Fig. 3: Shrinkage profiles for the formulations with the oligomer/monomer ratio of 50/50: the oligomer is Desmolux XP 2513, and the monomer is TMPTMA (methacrylate) or TMPTA (acrylate). Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB

and the concentration of double bonds, was an important factor affecting the property of coating. One could envision that the coating subjected to the huge shrinkage rate, was more likely to lose adhesion to the substrate. As shown in Fig. 4 and Table 2, the TMPTA exhibited much lower shrinkage than TMPTMA. Unfortunately, the low shrinkage of the formulation with TMPTMA was due to the significant decrease of conversion (Fig. 5). Thus, using methacrylate monomers was not attractive to solve the shrinkage problem due to the obvious drop of conversion.

Ethoxylation was useful in increasing the monomer chain length and molecular weight. Using ethoxylation monomer to substitute TMPTA may be a promising way to lower the shrinkage. Ethoxylation monomers including TMPT(EO)3A (3-mol ethoxylation), TMPT(EO)9A (9-mol ethoxylation), and TMPT(EO)15A (15-mol ethoxylation) were used with an increasing degree of ethoxylation. As shown in Figs. 6 and 7, the shrinkage and shrinkage rate decreased with the increase of the degree of ethoxylation. This was due to the drop of
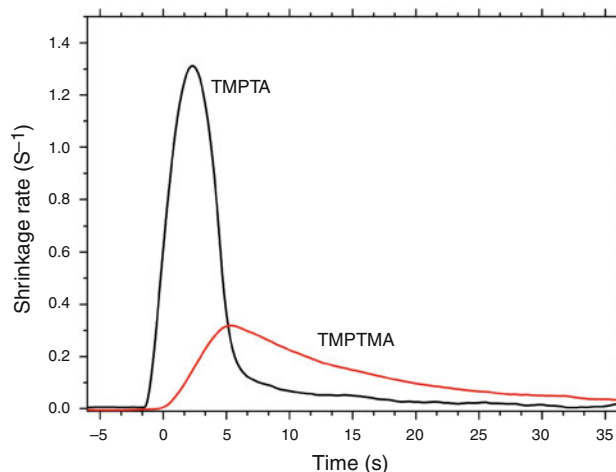

Fig. 4: Shrinkage rate for the formulations with the oligomer/monomer ratio of 50/50: the oligomer is Desmolux XP 2513, and the monomer is TMPTMA (methacrylate) or TMPTA (acrylate). Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB

Table 2: Photopolymerization shrinkage and kinetics: the oligomer (Desmolux XP 2513)/monomer ratio was 50/50 in weight

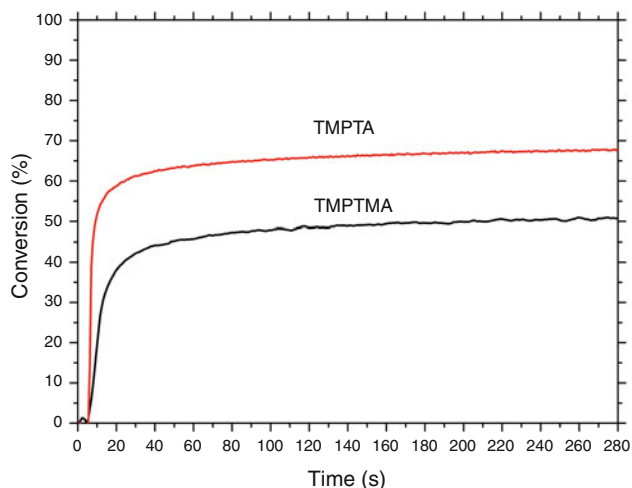| Monomer	Final shrinkage (%)	Final conversion (%)	Maximum shrinkage rate (s^{-1})	C_{db} (mol/L)
TMPTMA	5.87	50.70	0.32	9.42
TMPTA	7.42	67.75	1.31	11.24
TMPT(EA)3A	6.00	87.16	1.13	7.73
TMPT(EA)9A	4.83	96.76	0.89	4.81
TMPT(EA)15A	4.05	98.58	0.71	3.49

Fig. 5: Conversion profiles for the formulations with the oligomer/monomer ratio of 50/50: the oligomer is Desmolux XP 2513, and the monomer is TMPTMA (methacrylate) or TMPTA (acrylate). Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB
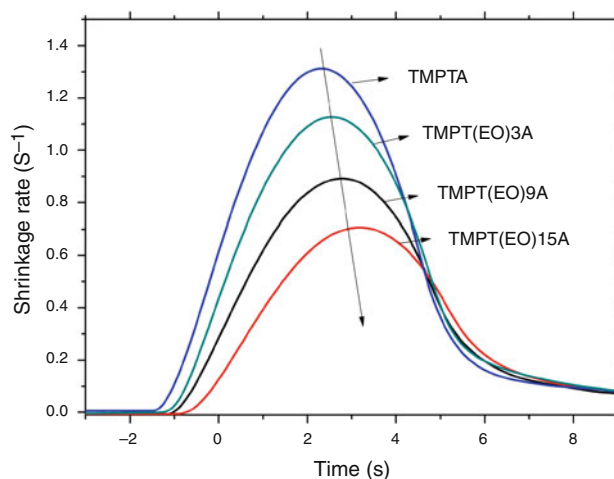

Fig. 7: Shrinkage rate for the formulations with the oligomer/monomer ratio of 50/50: the oligomer is Desmolux XP 2513, and the monomer is TMPTMA (methacrylate) or TMPTA (acrylate). Photoinitiator: 2 wt% TPOL and 0.5 wt% ITX and 0.5 wt% EDAB
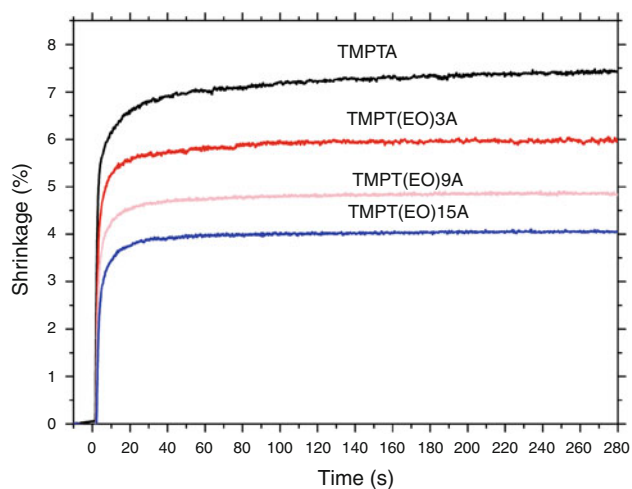

Fig. 6: Shrinkage profiles for formulations with the oligomer/monomer weight ratio of 50/50: the oligomer was Desmolux XP 2513, and the monomers were TMPTA, TMPT(EO)3A, TMPT(EO)9A or TMPT(EO)15A (increasing degree of ethoxylation). Photoinitiator: 2 wt% TPOL, 0.5 wt% ITX and 0.5 wt% EDAB
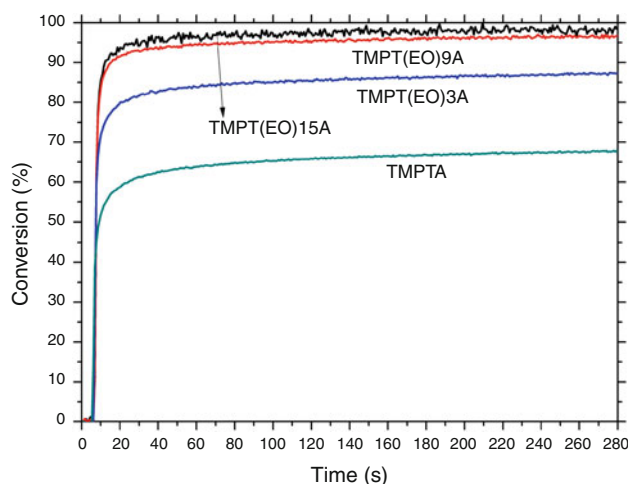

Fig. 8: Conversion profiles for formulations with the oligomer/monomer weight ratio of 50/50: the oligomer was Desmolux XP 2513, and the monomers were TMPTA, TMPT(EO)3A, TMPT(EO)9A or TMPT(EO)15A. Photoinitiator: 2 wt% TPOL, 0.5 wt% ITX and 0.5 wt% EDAB

the concentration of double bonds. Table 2 shows that the concentration of double bonds of monomers decreased with increasing degree of ethoxylation due to the increasing molecular weight. Because the concentration of double bonds in formulation mainly depends on the monomer, shrinkage and shrinkage rate could be significantly decreased by using a monomer with a high degree of ethoxylation. Fortunately, the conversion increased with the rising degree of ethoxylation (Fig. 8). It corresponded with the previous report that as the

degree of ethoxylation was raised, the propagation was less diffusion-limited. Apparently, as the segmental diffusivity of pendent double bonds rises; less highly crosslinked networks formed allow higher mobility of free radicals and monomeric and pendant double bonds.[14] Thus, conversion increased with a rising degree of ethoxylation.

Compared with the methacrylate monomers, using the monomer with a high degree of ethoxylation could significantly lower the shrinkage of formulation without decreasing the double bonds conversion.

The effect of photoinitiator on shrinkage

Photoinitiators played a major role in polymerization in spite of its lowest weight ratio in a coating formulation.[15–19] Here, the type I photoinitiator TPOL
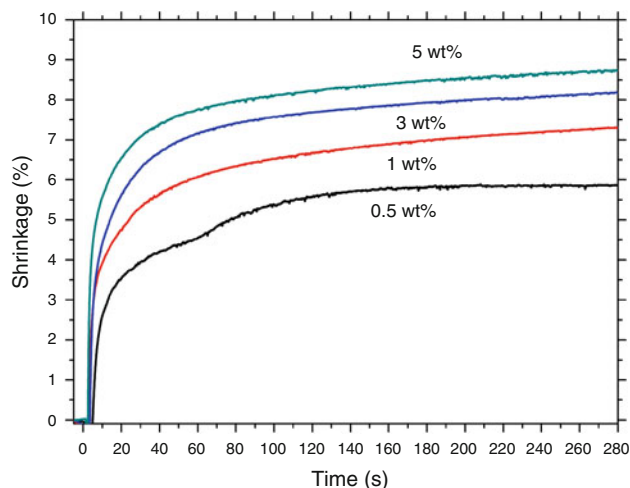

Fig. 9: Effect of photoinitiator (TPOL) concentration on shrinkage for a formulation with the oligomer 2513/TMPTA ratio of 50/50 in weight
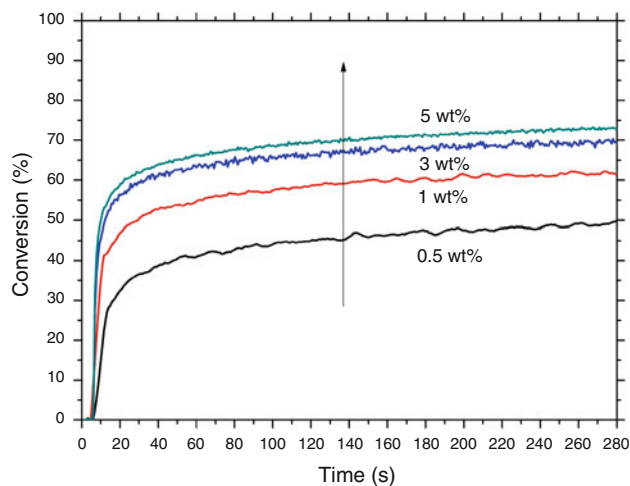

Fig. 10: Effect of photoinitiator (TPOL) concentration on conversion for a formulation with the 2513/TMPTA weight ratio of 50/50

was used to evaluate the concentration effect of initiators on the shrinkage. The clear coating formulation used was Desmolux XP 2513/TMPTA with 50/50 in weight. As shown in Fig. 9, when the concentration of initiator was raised, the shrinkage increased. The conversions could be used to explain the shrinkage behaviors. Figure 10 showed that the conversion increased with the concentration of initiators. It confirmed the classical view that higher concentration of initiator below the maximum or optimum concentration led to higher active species concentration, and consequently faster curing rate and higher degree of conversion.[20,21] Because the shrinkage was a result of double bonds conversion, the decrease of conversion and curing rate led to the low shrinkage and maximum shrinkage rate. To compare the shrinkage values at the same conversion level, the normalized shrinkage (S_n, defined as the shrinkage at 100% conversion) was defined according to equation (4):

$$S_n = S_{280S}/DC_{280S} \qquad (4)$$

where S_{280S} is the equilibrium shrinkage at 280S, and DC_{280s} is the equilibrium conversion at 280S. Unlike the "final" shrinkage, the normalized shrinkage value at each concentration of initiators was much closer (between 11.8 and 12.0 in Table 3). These closer normalized shrinkage values indicated that the concentration of photoinitiators had no obvious influence on the shrinkage at 100% conversion. Thus, the change of shrinkage could be only attributed to the change of the conversion.

Conclusions

The photopolymerization kinetics and shrinkage were measured during UV-curing of (meth)acrylate coatings by real-time FTIR and a recently developed laser reflection method. The polymerization shrinkage depended on double bonds conversion and the concentration of double bonds. The components of the coating formula including oligomers, monomers, and photoinitiators affected the shrinkage behavior. The monomer was the main contributor to shrinkage because of the high concentration of double bonds. Polymerization shrinkage could be reduced by adjusting oligomer/monomer ratio. Substituting methacrylate monomers for acrylate monomers in the coating

Table 3: Effect of different concentrations of photoinitiator (TPOL) on the polymerization shrinkage and kinetics

Concentration of initiator (wt%)	Maximum shrinkage rate (s^{-1})	Shrinkage at 280S (%)	Conversion at 280S (%)	Normalized shrinkage
0.5	1.30	5.86	49.53	11.83
1	3.06	7.32	61.68	11.87
3	4.11	8.18	69.05	11.85
5	5.89	8.74	72.94	11.98

formulation led to low shrinkage and unfortunately low conversion. Monomers with a high degree of ethoxylation decreased shrinkage and fortunately increased the conversion. The low concentration of photoinitiators decreased the shrinkage but exhibited no obvious influence on the normalized shrinkage (shrinkage at 100% conversion). Thus, the low shrinkage caused by the low concentration of photoinitiators was only attributed to the significant drop of the conversion.

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