Shrinkage of UV Oligomers and Monomers

Andreas Moeck, RadLab AG, 8956 Killwangen, Switzerland
Roberto Bianchi, RadLab AG, 8956 Killwangen, Switzerland
Volker Petry, RadLab AG, 8956 Killwangen, Switzerland
Reto Weder, Rahn AG, 8050 Zurich, Switzerland
David Helsby, RadLab AG, 8956 Killwangen, Switzerland

Introduction

In the decorative and protective coating industry UV-curing is widely used due to its advantages like fast curing speed, low curing temperatures and the absence of solvents.[1,2] One major drawback of UV-cured systems is the volume shrinkage that can lead to premature coating failures such as cracking, delamination and loss of adherence.

The components of UV-curable systems include reactive oligomers, reactive monomers, photoinitiators, and other additives.[3,4] The main types of UV oligomers are based on Epoxy, Polyester, Polyether or Urethane chemistry. The commonly used reactive monomers for free radical photopolymerizations are acrylates and methacrylates.

The volume shrinkage of acrylates and methacrylates occurs during polymerization and is due to the replacement of long-distance connections via weak Van der Waals force by strong short covalent bonds between the carbon atoms of different monomer units. This 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.

In this work we determined quantitatively the shrinkage behavior of a wide range of UV monomers and oligomers. Comparisons of theoretical calculations versus practical measurements of shrinkage were addressed as well as the influence of parameters like Double Bond Conversion, Glass Transition Temperature (Tg) and UV intensity. This study should help to get a better understanding of why UV-cured systems shrink, and with awareness of how to mitigate that shrinkage, end users are better able to choose raw materials that perform as needed and as expected.

Determination of shrinkage

Shrinkage can be measured during polymerization by techniques like dilatometry[5] or real-time laser reflection.[6] The method we applied is based on density measurements. Shrinkage is related to the density of monomer (low) and polymer (high) through the following formula:

Equation 1: $$Shrinkage\% = 100 \times \frac{dp - dm}{dp}$$

      dp: *density of polymer (after curing)*
      dm: *density of monomer*

Experimental determination of shrinkage

Formulation: 100g oligomer or monomer
                                      1g photoinitiator (GENOCURE* LTM)
Curing Conditions: High pressure Hg-lamp; 240W/cm at 5m/min

Preparation: 3g of formulation in aluminum lid with a diameter of 4cm

                                                        2 to 4(max) passes through UV-lamp for a tack-free surface

Density measurement: Pycnometry at 20°C

Table 1: Shrinkage values of selected UV-oligomers

Acronym	Oligomer	Description	Functionality	Experimental Shrinkage %
Epoxy Acrylates				
EA1	GENOMER* 2235	Aliphatic Epoxy Acrylate	2	7.2
EA2	GENOMER* 2253	Modified Epoxy Acrylate	2	3.0
EA3	GENOMER* 2255	Modified Epoxy Acrylate	2	5.1
EA4	GENOMER* 2259	Modified Epoxy Acrylate	2	4.5
EA5	GENOMER* 2263	Epoxy Acrylate	2	3.4
Polyester Acrylates				
PESTA1	GENOMER* 3485	Polyester Acrylate	4	7.6
PESTA2	GENOMER* 3611	Polyester Acrylate	6	7.4
PESTA3	PESTA 03-849	Polyester Acrylate	3	5.4
Polyether Acrylates				
PETHA1	GENOMER* 3364	Polyether Acrylate	3	8.3
PETHA2	GENOMER* 3414	Polyether Acrylate	4	6.2
PETHA3	GENOMER* 3497	Polyether Acrylate	4	6.7
Urethane Acrylates				
UA1	GENOMER* 4188	Aliphatic Urethane Acrylate	1	<1
UA2	GENOMER* 4215	Aliphatic Urethane Acrylate	2	2.9
UA3	GENOMER* 4217	Aromatic Urethane Acrylate	2	1.8
UA4	GENOMER* 4230	Aliphatic Urethane Acrylate	2	<1
UA5	GENOMER* 4267	Aliphatic Urethane Acrylate	2	2.3
UA6	GENOMER* 4269	Aliphatic Urethane Acrylate	2	<1
UA7	GENOMER* 4312	Aliphatic Urethane Acrylate	3	4.7
UA8	GENOMER* 4316	Aliphatic Urethane Acrylate	3	2.5
UA9	GENOMER* 4425	Aliphatic Urethane Acrylate	4	5.7
UA10	GENOMER* 4622	Aromatic Urethane Acrylate	6	10.3
UA11	GENOMER* 4690	Aliphatic Urethane Acrylate	6	7.7
Methacrylate oligomers				
EMA1	EMA 97-053	Epoxy Methacrylate	2	3.8
UMA1	GENOMER* 4205	Aliphatic Urethane Methacrylate	2	6.7
UMA2	GENOMER* 4256	Aliphatic Urethane Methacrylate	2	<1
UMA3	GENOMER* 4297	Aliphatic Urethane Methacrylate	2	6.8

Theoretical calculation of shrinkage

A method based on group contribution techniques can be used to calculate theoretical shrinkage.[7] The calculated value is the maximum shrinkage corresponding to full (100%) conversion of double bonds. For the most commonly used monomers experimental values of monomer density are available enabling the use of following simplified equation to calculate the maximum shrinkage:

Equation 2:
$$Maximum\ shrinkage\ \% = -1.38 + 2668 \times \frac{Functionality \times Monomer\ density}{Monomer\ Molecular\ weight}$$

Experimental values of shrinkage of UV-monomers have been compared with calculated values of maximum shrinkage. In general, experimental values are lower than calculated values (Table 2).

Table 2: Shrinkage values of selected UV-monomers

Acronym	Monomer	Functionality	Experimental Shrinkage %	Calculated Shrinkage % (100% conversion)
M1	IBOA	1	5.5	11.3
M2	HDDA	2	14	23.8
M3	NPG(PO)2DA	2	9	16.0
M4	TPGDA	2	12	17.0
M5	DPGDA	2	14	21.8
M6	TMPTA	3	12	28.6
M7	TMP(EO)3TA	3	11	19.3
M8	GPTA	3	15	19.3
M9	PPTTA	4	13	20.1
M10	di-TMPTA	4	15	21.7

Figure 1: Comparison of calculated maximum shrinkage versus experimentally measured shrinkage of selected UV-monomers
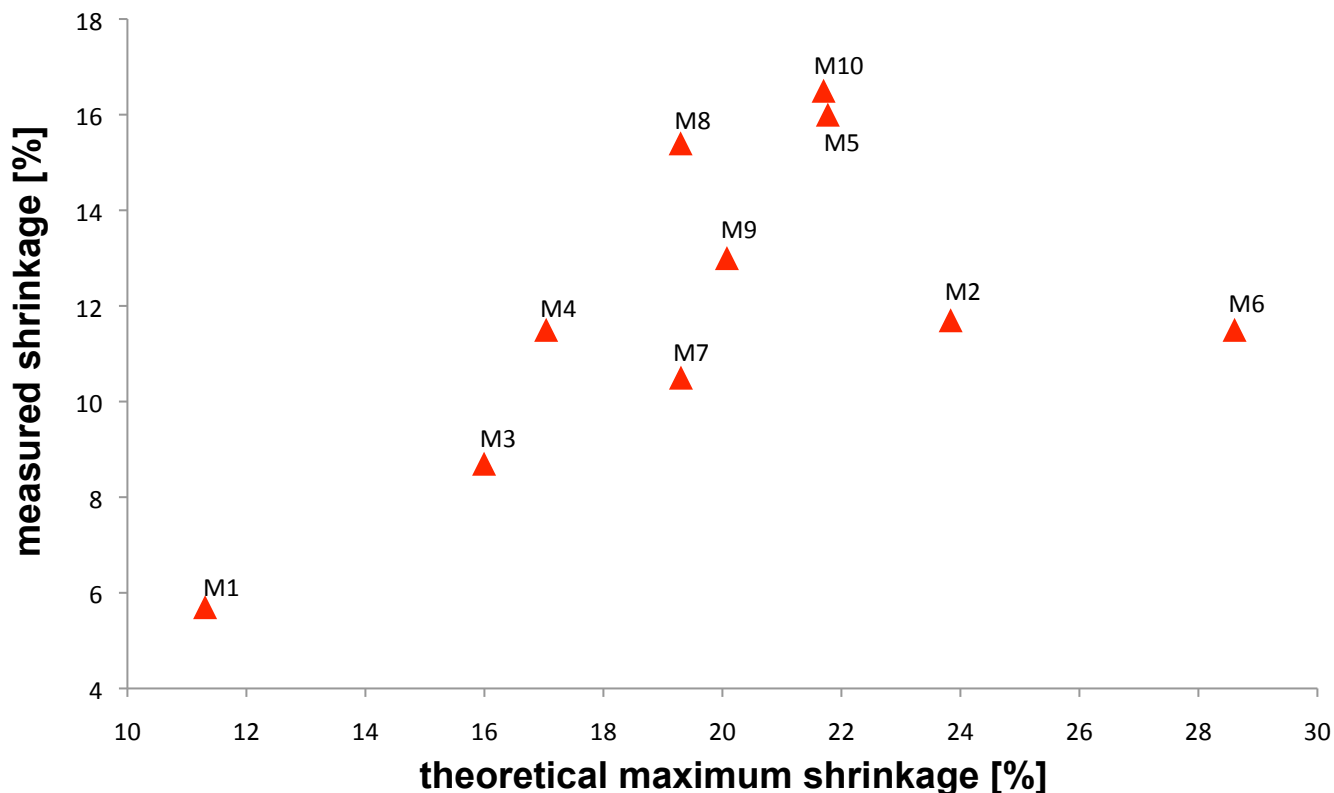
Discussion

Various parameters influence the shrinkage behavior of UV-monomers and can be used to explain why measured shrinkage is lower than calculated shrinkage:

Double Bond Conversion

Instead of calculation for 100% conversion, measured conversion (e.g. by infrared spectroscopy) could be taken into account. Since actual conversion is always below 100%, calculated maximum shrinkage would result in lower values and would be closer to measured values.

Glass Transition Temperature (Tg)

During the crosslinking process, the glass transition temperature Tg of an UV cured film increases with the double bond conversion. If the glass transition temperature Tg of the film reaches a value close to the value of the curing temperature Tc, then reduced mobility of chains and radicals in the UV cured film strongly limits further double bond conversion, and the final degree of conversion may stay relatively low. In this situation the rate of shrinkage is no longer proportional to the rate of polymerization. This phenomenon is described as vitrification.[8] Conversion may continue with time, particularly where the ambient or use temperature exceed Tg. Low shrinkage under these conditions can be explained by the low matrix stress that results from diffusion-controlled addition reactions in this circumstance.

UV Intensity

Curing at either low or high UV intensity can have an impact on shrinkage. Typically, higher shrinkage values were obtained with higher light intensity. This is related to both higher double bond conversion and faster, less discriminating cure (i.e. less diffusion-controlled addition) prior to vitrification.

Formulation

Basically the shrinkage of formulations is additive and can be calculated by following formula:

Equation 3: $Shrinkage\ of\ formulation = X_a \times S_a + X_b \times S_b$

$X_{a,b}$:   *Ratio of Monomer a and b*
$S_{a,b}$:   *Shrinkage of Monomer a and b*

Since formulations show different viscosities, Tg's and double bond conversions compared to single components, shrinkage of formulations can differ from calculated values.

Conclusion

Volume shrinkage of UV-curable systems is caused by double bond polymerization and can be determined experimentally from measurements of the densities of the used monomers/oligomers and the resulting polymers.

Maximum shrinkage can be calculated from functionality and molecular weight of monomers. Differences observed between experimental shrinkage measurements and calculated maximum shrinkage for multifunctional acrylates can be explained by limitations of mobility in network matrices (vitrification phenomena). The shrinkage of formulations can be estimated from a simple additive rule which accounts for vitrification.

It was our purpose within this work to address the key subject of shrinkage in UV-cured formulations. Significant shrinkage, especially when unanticipated, can provoke system failure due to poor adhesion, delamination or cracking. With a better understanding of why acrylates shrink, and with awareness of how to mitigate that shrinkage, end users are better able to choose raw materials that perform as needed and as expected.

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