Shrinkage and Internal Stress in Coatings Cure and UV Curing of Coatings: How Much Do They Shrink

Engin Çörüşlü, EVA Danışmanlık

engin.coruslu@evadanismanlik.com.tr

1

Coatings Cure

- Paints, or organic coatings as a more comprehensive term, are not finished products as they are delivered.

- They can best be called intermediates, because in most cases, they need to be delivered in liquid form to allow application as smooth, uniform layers onto the objects they are intended to cover completely with no discontinuity in the film.

- The liquid film must then undergo further physical and chemical processes. This is necessary for converting the easily perishable wet film into a dry, hard, durable coating which is expected to remain on the surfaces for protecting and decorating them for long periods.

- Discontinuities and many other defects can easily occur not only during application but also during drying. Application, drying, and curing processes require a sound knowledge of surface energies of the coating and the substrate, and a complete command of coating's rheology. An additional difficulty is continuously changing properties during the curing process.

Coatings Cure

- Drying and solidification of paint films involve concomitant and consecutive stages depending on the type of paint and the method adopted for curing the film.

- Paint chemist or engineer is faced with a serious challenge in designing this final stage of the formulation process, because she does not have much command over it since this final stage takes place at customer's facilities, where she can have at best an advisory function.

- Failures in achieving the targeted appearance and surface defects are frequent problems she has to deal with.

- Other significant challenge which perhaps is to be addressed to more at the design stage in the laboratory but still relevant in this final stage is to prevent the defects due to structural changes during the process of drying.

Coatings Cure

Shrinkage During Curing in Solventborne and Waterborne paint films
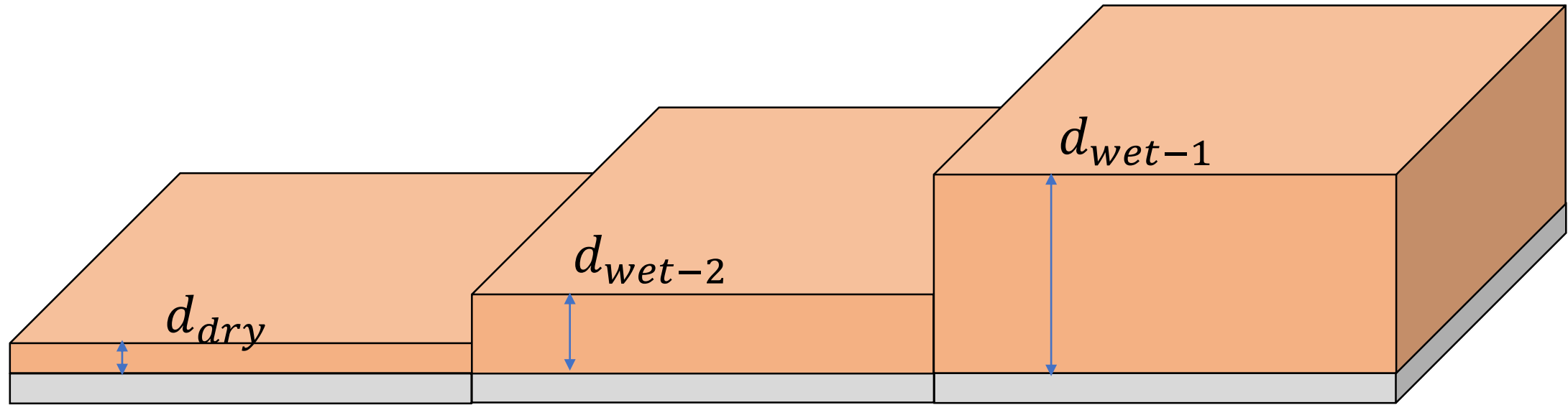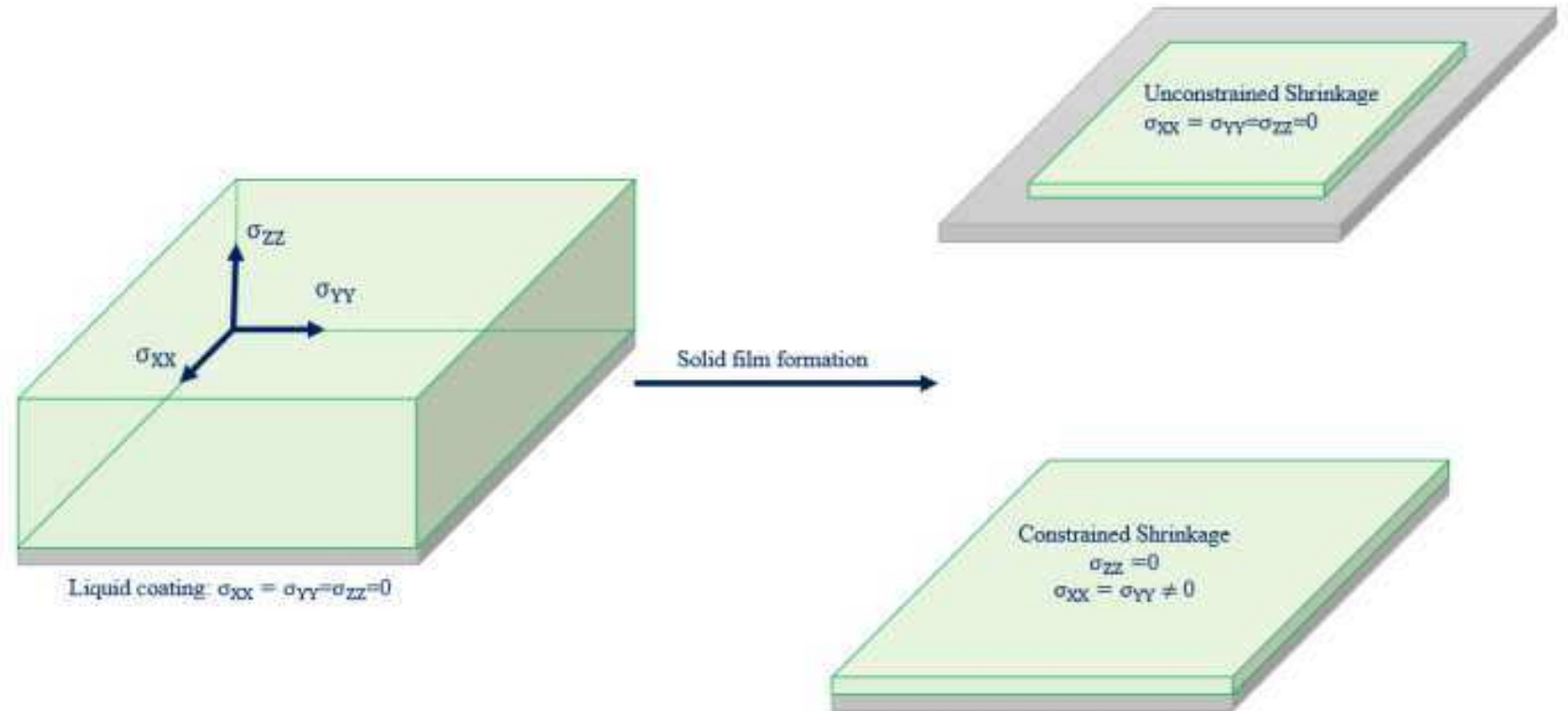

Shrinkage due to loss of volatiles and polymerization. Notice the volume change involves only one dimension.
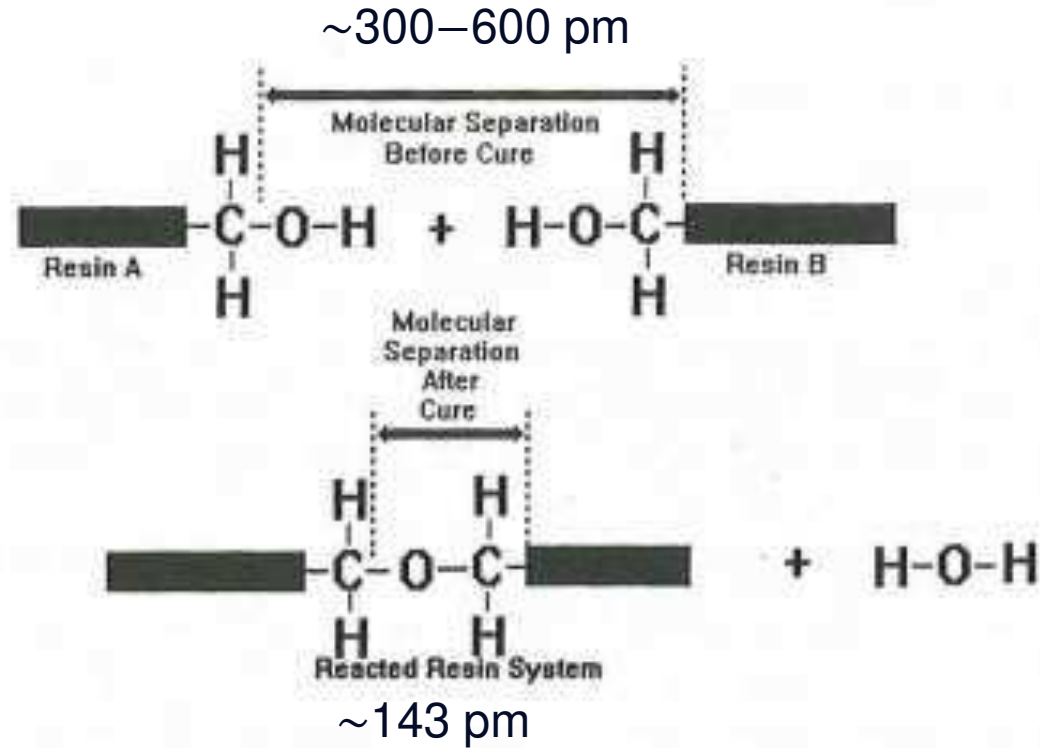
Coatings Cure

Limitation of Relaxation Due to Adhesion to the Substrate

Schematic diagram of curing-induced bi-axial internal stress within coatings. (Li, Q., 2022,. Quantification of internal stress and cracking in ambient temperature curing thermoset coatings. Technical University of Denmark.)

Unconstrained Shrinkage
$\sigma_{XX} = \sigma_{YY} = \sigma_{ZZ} = 0$

σ_{ZZ}

σ_{YY}

σ_{XX}

Solid film formation

Liquid coating: $\sigma_{XX} = \sigma_{YY} = \sigma_{ZZ} = 0$

Constrained Shrinkage
$\sigma_{ZZ} = 0$
$\sigma_{XX} = \sigma_{YY} \neq 0$

Coatings Cure

Shrinkage on polymerization as a source of internal stress (Clive Hare Aircraft Paint Stripping News II Summer, 1997)

Coatings Cure

- In solventborne and waterborne films drying usually starts with the evaporation of solvents or water.

- This process leads to a shrinkage in the film.

- If drying also involves polymerization, i.e. curing, further shrinkage occurs due to this process.

- Both of these processes result in significant changes creating internal stress.

- Internal stress created during curing can weaken adhesion to substrate and cause adhesive failures leading to early failure in the expected coating life. In some cases cohesive failures can also occur due to the same reason.
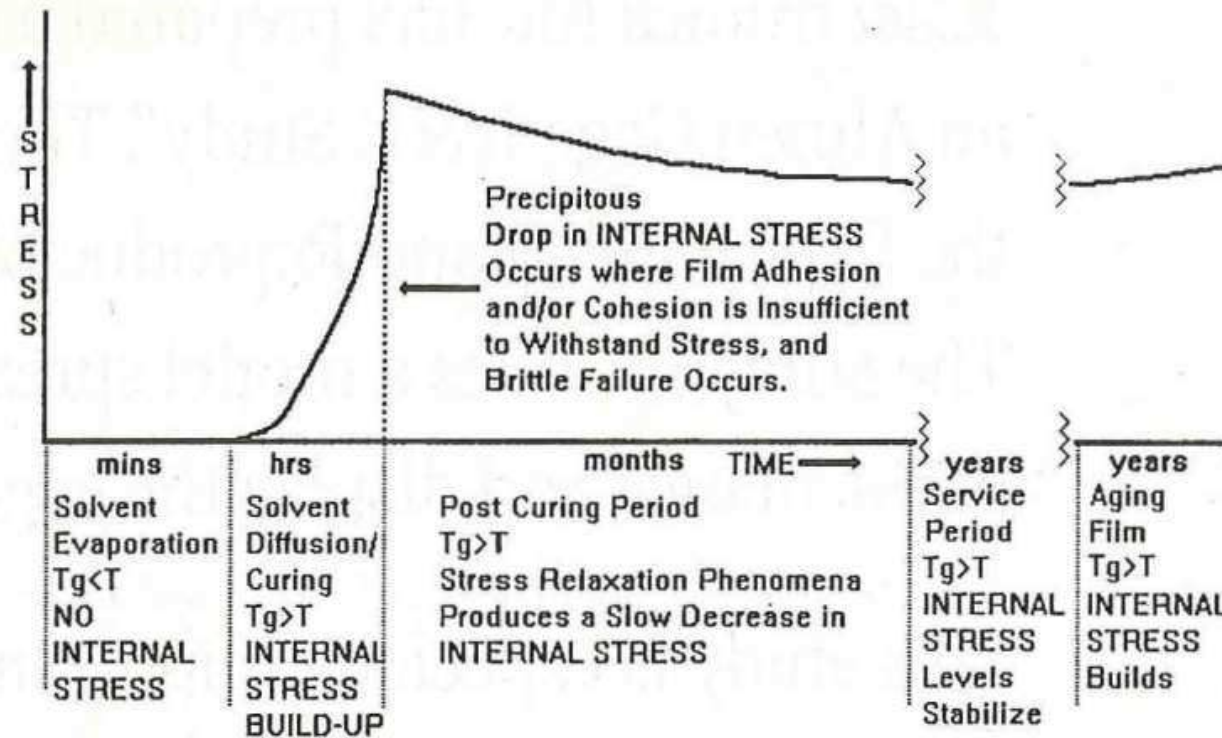
Coatings Cure

Shrinkage due to solvent or water evaporation is less of a problem in case there is no accompanying polymerization, although in some cases it can lead to early failure of thermoplastic paint films.

The only risk here is the fast evaporation of solvent which may reduce polymer mobility enough to prevent them diffusing into the free volumes created by the evaporation of solvent or water.

If however there is polymerization accompanying solvent evaporation, the risk of internal stress formation due to shrinkage is bigger.
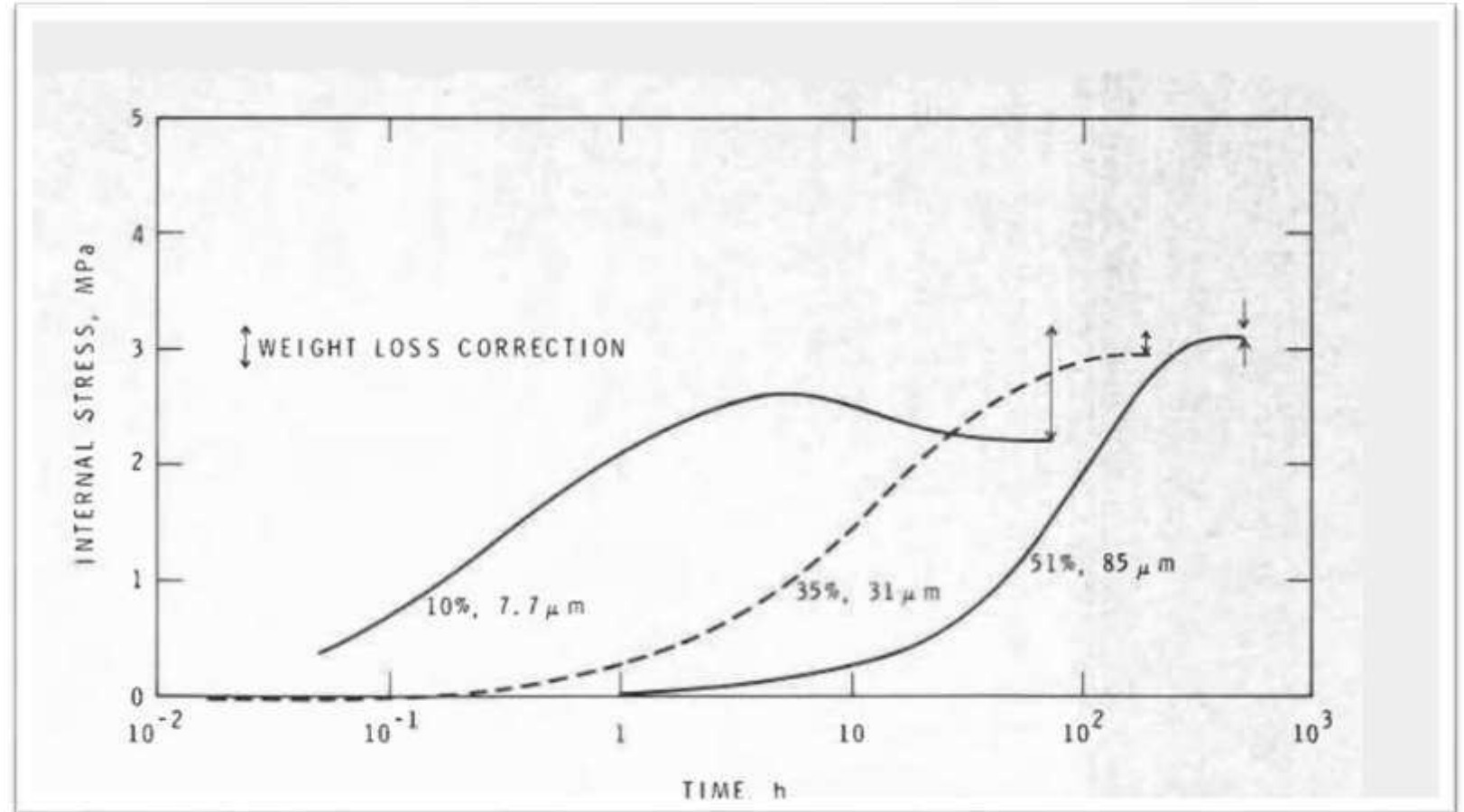
Coatings Cure

Development of internal stress in a solventborne paint with no polymerization (Clive Hare Aircraft Paint Stripping News II Summer, 1997)

Coatings Cure

Internal stress developed in a solvent-cast thermoplastic coating was measured by using the substrate as a cantilever. 1MPa $\cong 9.9\ atm$

Residual internal stress was found to be large and independent of dried coating thickness and initial solution concentration. Polymer was polyisobutylmethacrylate (PIBM), ElvaciteB 2045, which was dissolved in reagent grade toluene.

Development of internal stress, showing initial solution concentration (% WIW) and dried coating thickness (pm) (Croll, S. G. Journal of Coatings Technology, Vol. 50, No. 638, March 1978, 33-38)
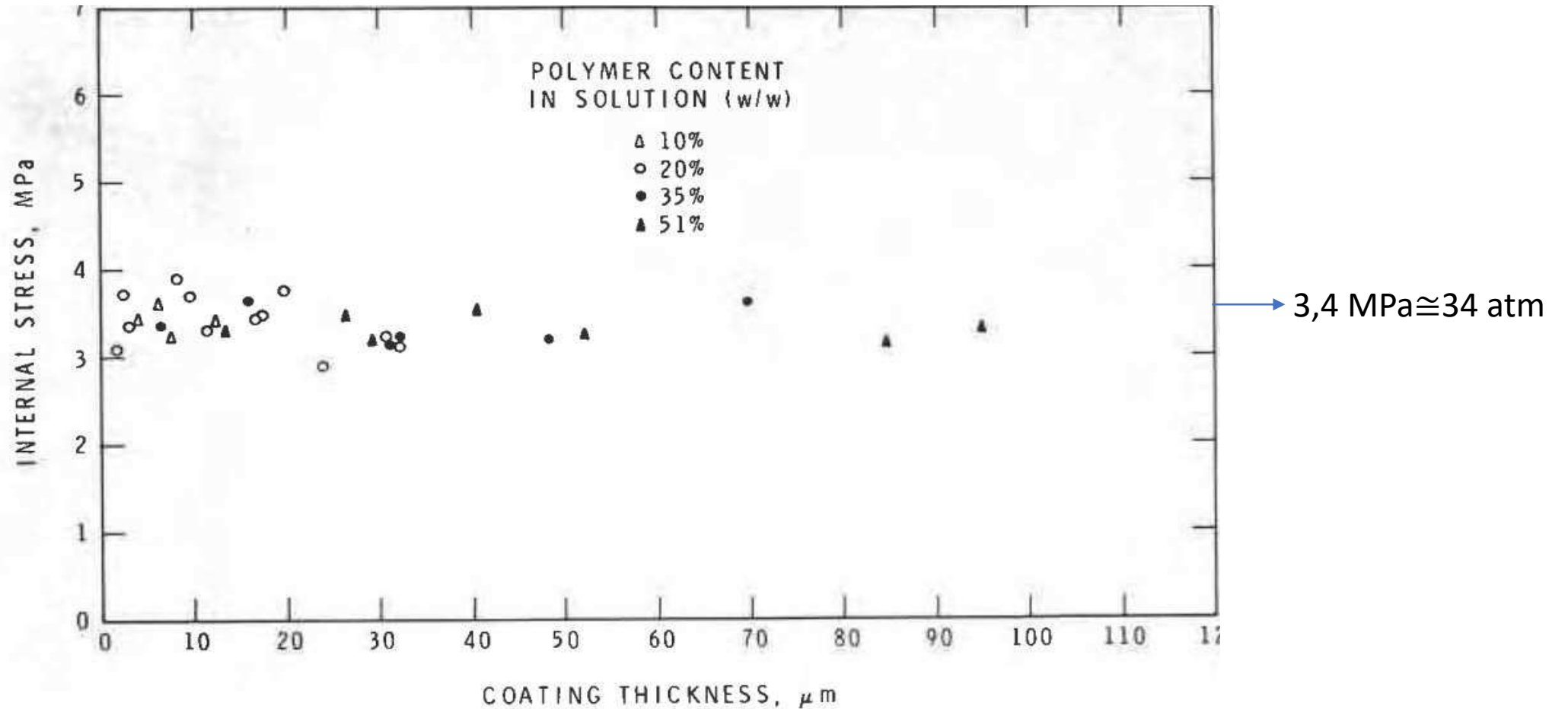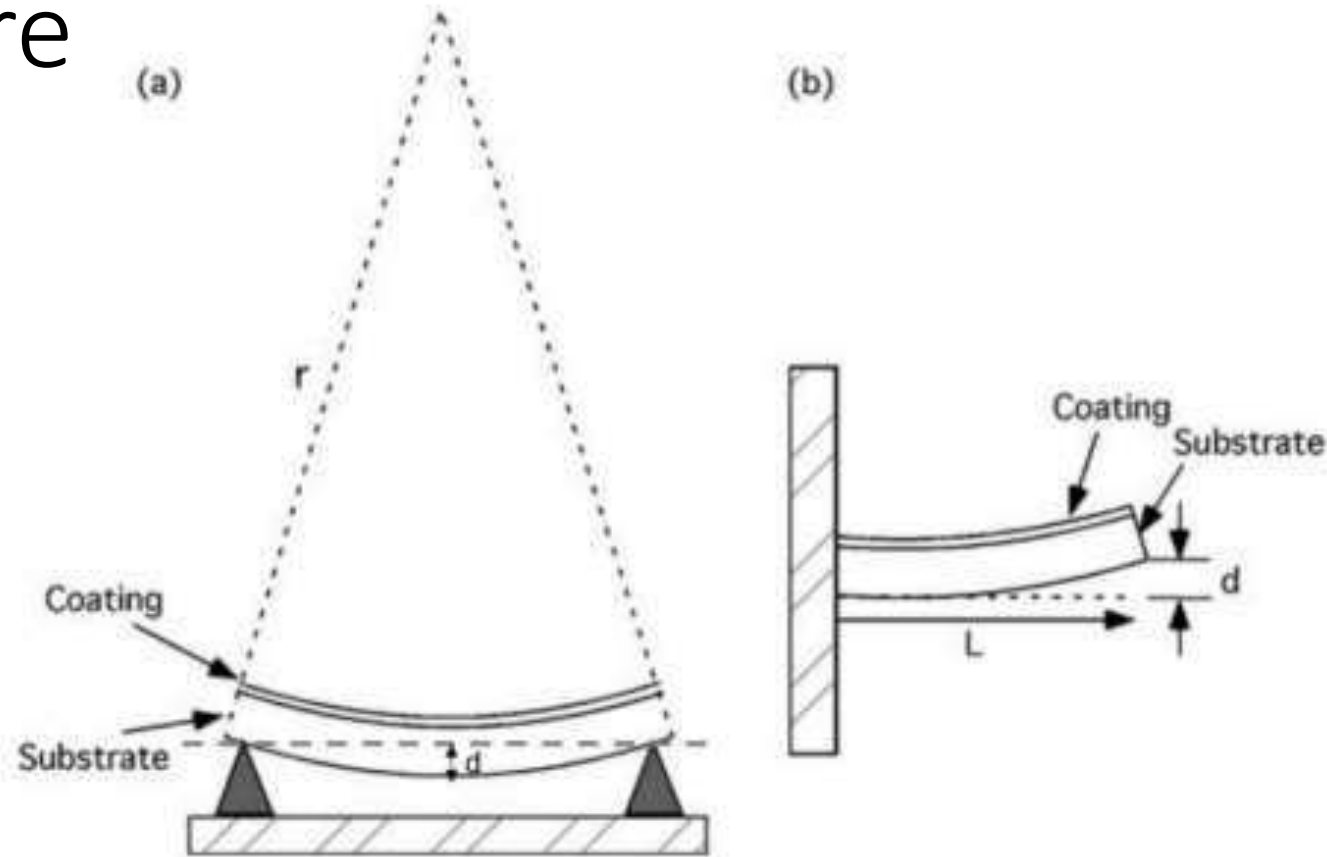
Coatings Cure

Development of internal stress, showing initial solution concentration (% WIW) and dried coating thickness (pm) (Croll, S. G. Journal of Coatings Technology, Vol. 50, No. 638, March 1978, 33-38)

Coatings Cure

Schematic diagram of set-up for curvature (a) and cantilever deflection (b) method to monitor internal stress in coatings . (Li, Q., 2022, Quantification of internal stress and cracking in ambient temperature curing thermoset coatings. Technical University of Denmark.)

Coatings Cure

Internal stress occurs because, as the solvent evaporates from the coating, the volume decreases; the thickness can decrease but the area cannot because the film adheres to the substrate. Thus internal stress arises in the plane of the film. There can be no stress, however, until the viscosity of the drying thermoplastic has increased sufficiently to prohibit polymer flow and prevent the filling of the spaces left by the solvent's evaporating.

(Croll, S. G. Journal of Coatings Technology, Vol. 50, No. 638, March 1978, 33-38)

Coatings Cure

The cause of internal stress during cure, is the hindrance of relaxation of polymer molecules.

- Relaxation is hindered because paint is applied on a more or less rigid substrate which is fixed on a plane, assuming that the paint adheres well.

- Drying or crosslinking of the polymeric constituents in the film is faster than molecular motion and does not allow polymer chains sufficient time for filling free volumes.

Coatings Cure

Coating Strength vs Internal Stress
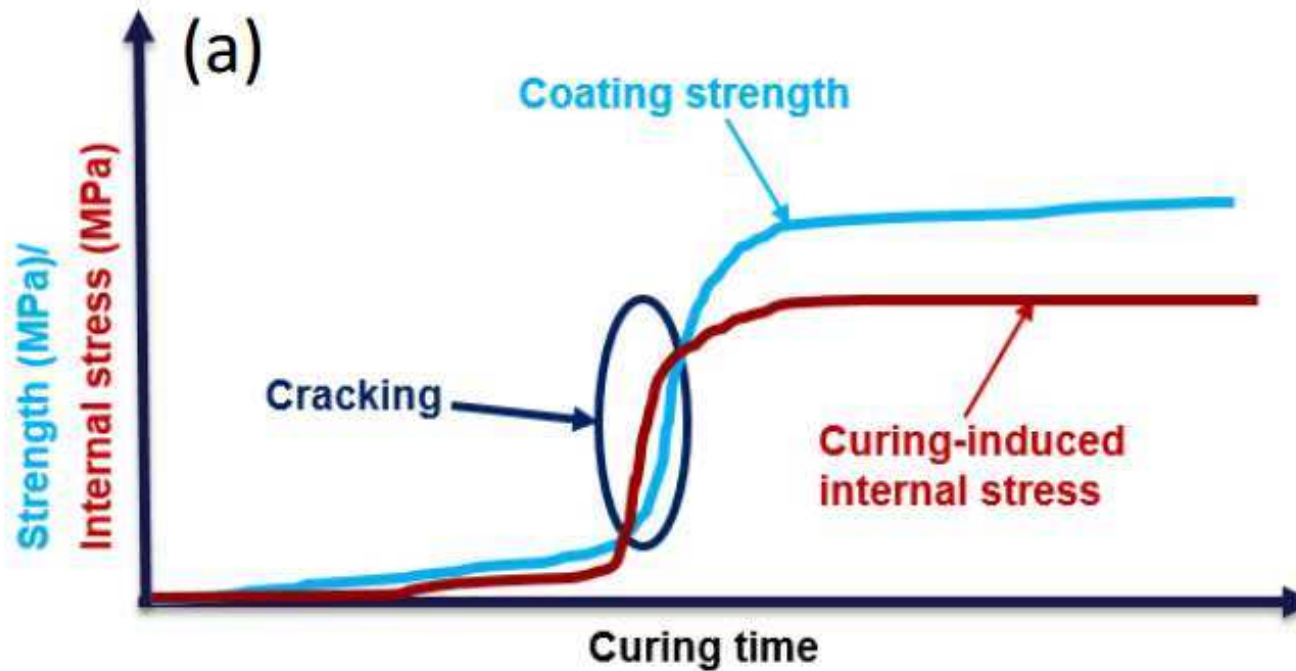
Schematic illustration of the coating strength and the internal stress development during curing. (*Li, Q., 2022, Quantification of internal stress and cracking in ambient temperature curing thermoset coatings. Technical University of Denmark.*)

Coatings Cure

Coating Strength vs Internal Stress
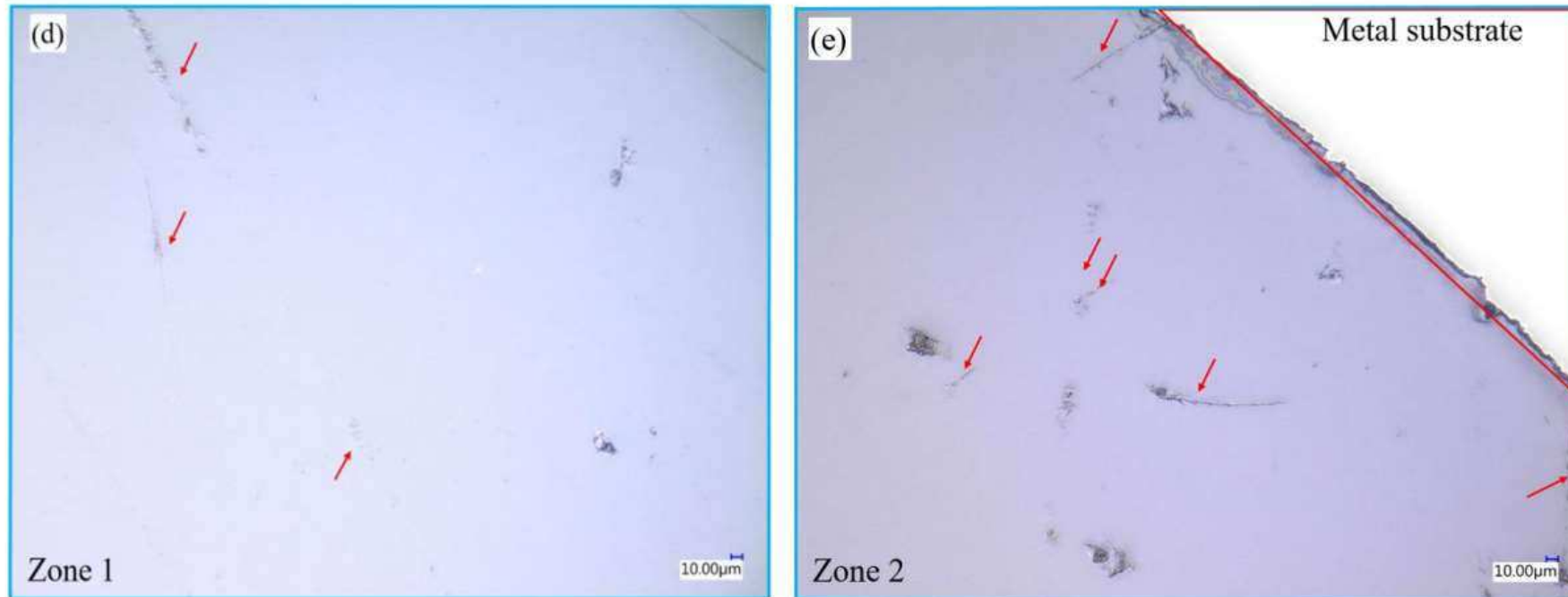
.Morphology of defects and cracks observed with digital microscopy

(Li, Q., 2022, Quantification of internal stress and cracking in ambient temperature curing thermoset coatings. Technical University of Denmark.)

Coatings Cure

Quotation from Qiong Li, Preface of the PhD thesis

This thesis is the outcome of my three-year PhD project carried out in The Hempel Foundation of Coatings Science and Technology (CoaST) Research Centre under the Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU) from February 2019 to February 2022. Financial support from The Hempel Foundation to CoaST is gratefully acknowledged.

Li, Q., 2022, Quantification of internal stress and cracking in ambient temperature curing thermoset coatings. Technical University of Denmark.

UV Cure

- Drying of coatings through photopolymerization offers significant advantages.
- It is radically different from other more conventional methods of curing.
- Coating to be cured is irradiated with UV light and cured within seconds.
- Curing occurs basically through conversion of C=C double bonds to C-C single bonds through free radical polymerization, induced by UV light.
- There is much confusion in coatings industry as to how much shrinkage occurs during UV curing, or whether any shrinkage occurs at all.

UV Curing

Table 4: 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
M4	TPGDA	2	12	17
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	12	20.1
M10	di-TMPTA	4	15	21.7

Shrinkage of UV Oligomers and Monomers by Andreas Moeck, RadLab AG, 8956 Killwangen, Switzerland; Roberto Bianchi, RadLab G, 8956 Killwangen, Switzerland; Volker Petry, RadLab AG, 8956 Killwangen, Switzerland; David Helsby, RadLab AG, 8956 Killwangen, Switzerland; inside Conference Book RadTech International UV & EB Technology, Expo and Conference, Rosemont, Illinois, USA, 12-14 May 2014.

Monomers-Previous Table

IBOA-İzobornil akrilat
HDDA- 1,6-Hekzandiol diacrylate
NPG(PO)2DA-Neopentyl glycol propoxylate diacrylate
TPGDA-Tripropylene glycol diacrylate
DPGDA-Dipropylene Glycol Diacrylate
TMPTA-Trimethylolpropane triacrylate
TMP(EO)3TA-Trimethylolpropane ethoxy triacrylate
GPTA-propoxylated glycerin triacrylate
PPTTA-ethoxylated (5.0) pentaerythritol tetra-acrylate
di-MPTA-Di -Trimethylol propane tetraacrylate

Shrinkage of UV Oligomers and Monomers by Andreas Moeck, RadLab AG, 8956 Killwangen, Switzerland; Roberto Bianchi, RadLab G, 8956 Killwangen, Switzerland; Volker Petry, RadLab AG, 8956 Killwangen, Switzerland; David Helsby, RadLab AG, 8956 Killwangen, Switzerland; inside Conference Book RadTech International UV & EB Technology, Expo and Conference, Rosemont, Illinois, USA, 12-14 May 2014.

UV Curing

- The table on the previous page indicates that there is not enough shrinkage to accommodate all of the possible conversions based on the number of reactive groups.

- If the conversion of bonds is not reflected in shrinkage as indicated in the previous work, it comes to mind whether the covalent bonds formed after curing have the same length as they would have if they would be in a relaxed configuration.

- It is conceivable that the covalent bonds formed during the milliseconds of irradiation are not able to achieve their relaxed bond length but are frozen at a somewhat longer length.

- There is much reference to internal stresses due to shrinkage but it is not certain if this is due to shrinkage or the lack of it.

UV Curing

- Van der Waals bond lengths are ~300-600 pm, whereas C-C bond length is 154 pm, which is basically the type of new bond created in UV curing.

- On the other hand recent work in organic chemistry reveal that C-C bond length can be as long as 290 pm or as short as 120 pm, as opposed to the generally assumed value of 154 pm.

- Depending on the length of the resulting C-C bonds, we would expect somewhat less shrinkage since C=C bonds of 134 pm are replaced by C-C bonds, generally of >154 pm length.
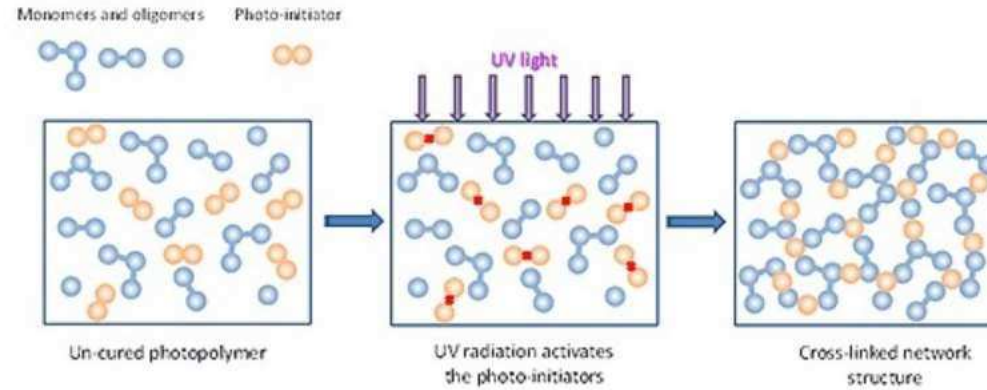
UV Curing

- There are conflicting statements regarding shrinkage of coatings during cure.

- A typical statement in favor of shrinkage goes like this:

- "It is very difficult to achieve low gloss in UV curing coatings due to <mark>lack of shrinkage</mark>"

- One statement is a juxtaposition of conflicting opinions. The author refers to high shrinkage and the difficulty of obtaining low glow films, in two consequent sentences:

- "……UV coatings can have <mark>high shrinkage</mark>, which adversely affects adhesion to non-porous substrates. Lack of solvent coupled with <mark>fast cure reduces the</mark> <mark>formulator's ability to meet low gloss,</mark> low film build requirements……"

- A diametrically opposed view is depicted in the following scheme in explaining why matt coatings are not possible in UV curing coatings. I have included a similar representation on next page.
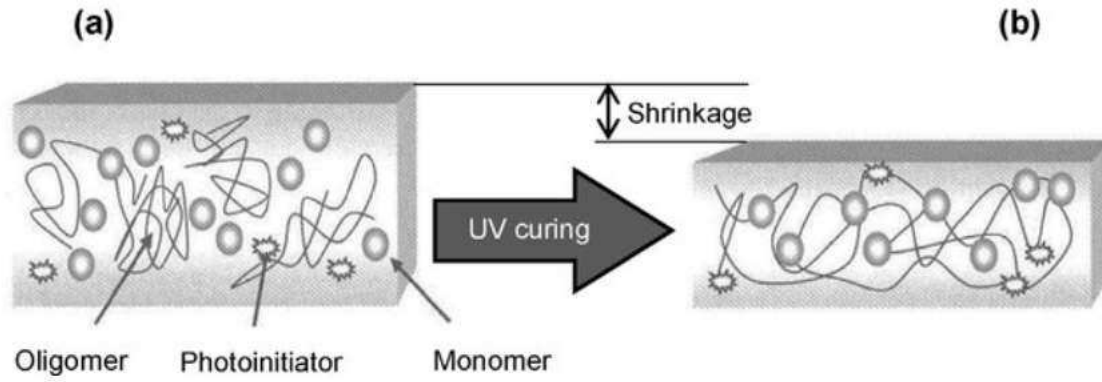
UV Curing
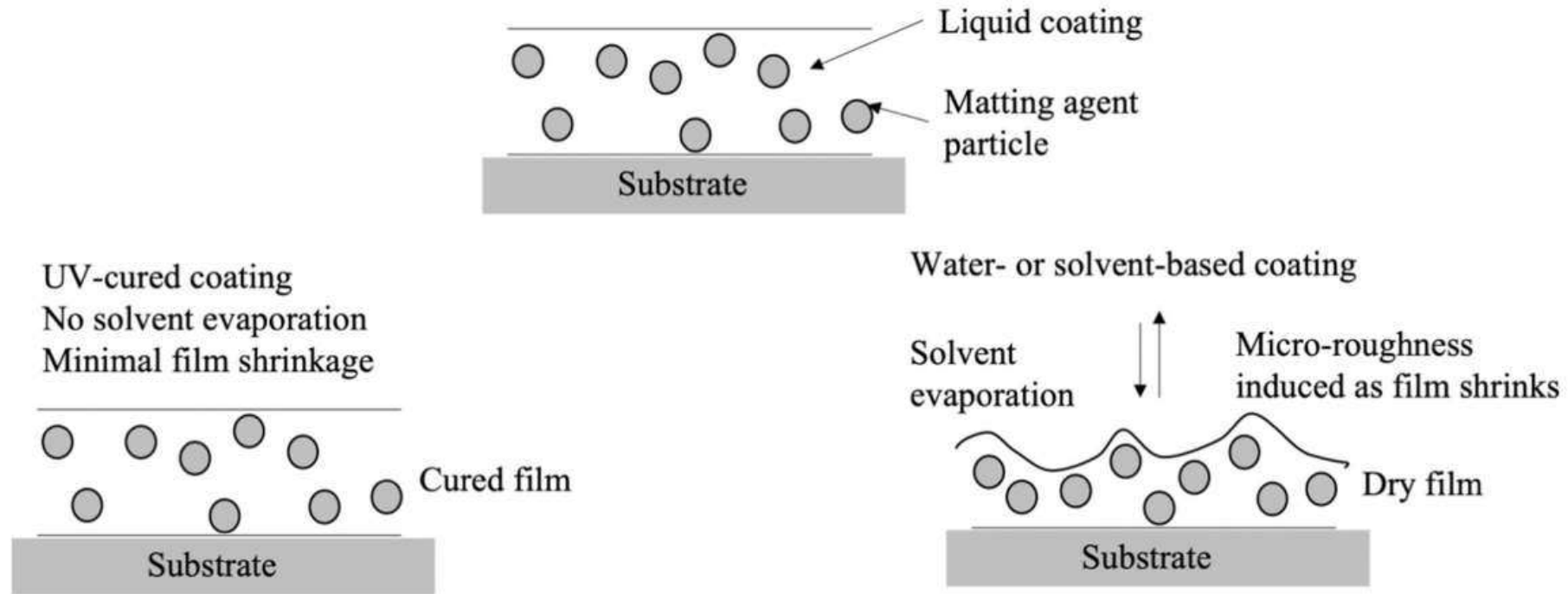
Fig.2. Matting mechanisms. Typically a liquid precursor system with matting agent is initially applied to a substrate (top). In a conventional water-or solvent-based system, evaporation of this liquid leads to surface roughness and segregations of matting agents near the coating surface (bottom, right). In a UV-curable coating, segregation of matting agents is more difficult as there is not a significant change in the volume of the film during curing (bottom, left).

UV Curing

Monomers and oligomers Photo-initiator

UV light

Un-cured photopolymer

UV radiation activates
the photo-initiators

Cross-linked network
structure

➢Immediate Property Development
➢High Cross Link Density
➢Retains Shape

(a)

(b)

Shrinkage

UV curing

Oligomer Photoinitiator Monomer

Does not retain shape

CONCLUSIONS

- Shrinkage of organic coatings during drying and curing can have significant consequences, sometimes leading up to adhesive or cohesive failures.

- Cohesive failures can occur during curing leading to microcracks in the dry film, reducing the service life of paint significantly.

- Adhesive weaknesses reduce film strength very much.

- Stress relaxation is necessary to eliminate or at least minimize the internal stresses resulting from shrinkage.

- However, relaxation of long chains of polymers take longer time and may not be able to compete with the high reaction rates, e.g., as in the case of UV curing and

CONCLUSIONS

- Use of UV—visible spectroscopy in determining free volume distributions during multifunctional monomer polymerizations studies prove that in some cases in even early stages of curing a significant percentage of free volumes may not be accessible.

- Relaxation of internal stress is frequently hindered by inaccessibility of free volumes either because they are trapped within microgels or because T_g of the crosslinked polymer network has increased beyond ambient or curing temperature in a very short time exceeding vitrification temperature, consequently, polymer network has already lost mobility, and cannot relax even if there are available free volumes.

CONCLUSIONS

- Stress relaxation during and after curing is a critical process in maintaining coating integrity.

- Overall, the bond lengths in free radical polymerization are important at various stages of the process, from initiation to propagation and termination, and they play a key role in determining the structure and properties of the resulting polymer.

- In relaxation back to equilibrium, the polymer assumes a new conformation. At first, the response is glassy. This modulus decreases with time as the polymer begins to relax and continues along the whole length of the chain.

CONCLUSIONS

Relaxation can be more difficult in radiation curing of organic coatings, as they reach vitrification very fast, not allowing sufficient time for crosslinked polymers to relax into the available free volumes, even if they are accessible.

Availability of free volumes can be determined during curing which would give a direct indication of the relative rates of two critical processes

- ❏ crosslinking and vitrification
- ❏ relaxation of the crosslinked polymer network

*UV—Visible Spectroscopy To Determine FreeVolume Distributions During Multifunctional Monomer Polymerizations
Kristi S. Anseth, Teri A. Walker, and Christopher N. Bowman Department of Chemical Engineering, University of Colorado,
Boulder, CO 80309-0424, Urban and Provder; Multidimensional Spectroscopy of Polymers ACS Symposium Series; American Chemical Society: Washington, DC, 1995.

CONCLUSIONS

- It is possible to elucidate the degree of shrinkage and relaxation in coatings by two methods, cantilever method, and UV—visible spectroscopy measurements during curing.

- Measurement of shrinkage and relaxation is important particularly in radiation curing coatings as there seems to be a great deal of confusion whether they shrink at all, or if they do, how much they shrink.

- An indirect method would be to determine if fine silica could really be transported by solvents or water migrating to the air-paint interface, as frequently suggested by some paint scientists. This would require modelling the drying process.

- Another method which would give some information about internal stress would be to measure the bond lengths of especially C-C bonds. It is likely that these bonds will be appreciably different in length than they would be if they were relaxed.

Thanks for Listening

Engin Çörüşlü, EVA Consultancy
engin.coruslu@evadanismanlik.com.tr