



Residual stress in radiation-cured acrylate coatings

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ABSTRACT

Radiation-cured acrylate-based materials are used in a wealth of applications. For coatings in particular, adhesion is a key property and remains challenging for some substrates such as plastics and metals. Stress build-up during and after resin polymerization is a handicapping issue that may lead to defect formation or debonding which results in bad coating performances. Using the substrate deflection method, stress development has been investigated in ultraviolet(UV)-cured acrylate coatings based on an epoxy acrylate combined with mono-, di- and triacrylate diluents. The coatings were prepared in conditions relevant to industrial practice using high UV intensity and short processing times. Stress measurements were conducted according to the prescriptions of a recent ASTM standard. A new set of data is provided which shows that photo-cured epoxy acrylates develop low stress as compared to other dilution acrylates (monomers). When formulated with most of the reactive diluents, the stress does not exceed 4 MPa as long as the dilution factor stays below 50%. This is fairly low given the high conversion rates. For vitrified coatings, it appears that in addition to polymerization stress, thermally-induced stress represents a non-negligible contribution to the overall stress. In an industrial UV-curing process however, the latter contribution is estimated to be less than 2–3 MPa. Lastly, an estimate of the interfacial fracture toughness between trimethylolpropane triacrylate and carbon steel is inferred from the stress data.

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1. Introduction

The application of a coating on a substrate invariably leads to the development of residual (internal) stress. For instance, the physical or chemical hardening of an organic coating will develop tensile in-plane stress when the material is unable to shrink freely to a stress-free state owing to the adhesion on a substrate [1–5]. The formation of strong covalent bonds between monomer molecules drives the volume contraction for polymerizing systems. Polymerization shrinkage is particularly important in acrylate systems characterized by a high ratio of reactive functionalities to monomer volume. Moreover, the volume change per reacting acrylate double bond is considerably higher than the volume change due to e.g. the ring-opening reaction of an epoxide functionality [6]. Stress accumulation due to chemical reactions is often coined as curing, cross-linking, polymerization or simply shrinkage stress in the literature.

For non-isothermal processes, strain differences due to the thermal expansion mismatch between the coating and the substrate may also lead to residual stress at the service temperature. Less well recognized, but equally important, is the change in (free) volume upon physical ageing of a glassy material which can also contribute to stress build-up over time [7,8]. In summary, any

mechanism inducing a volume reduction of a coating will cause stress build-up in constrained conditions. As predicted by linear elastic fracture analysis, the strain energy release rate of a coating increases proportionally to the square of the residual stress [9,10]. This explains why excessive residual stress in coatings leads to defects such as debonding, cracking or curling which undermines the overall technical performances.

Curing stress is often blamed for impairing the applicability of radiation-cured acrylate coatings on substrates with critical adhesion. However, this commonly accepted picture is still poorly documented. Stress studies of ultraviolet-cured coatings are scarcely reported in the literature and were mostly limited to multifunctional low viscosity diluents which, in practice, are part of more complex coating formulations. The coatings were usually cured with low to moderate light intensities over rather long exposure times which also contrast with the short and powerful irradiation conditions used in an industrial context.

Payne et al. studied the effect of a number of process variables such as photoinitiator concentration and light intensity ($<1 \text{ mW cm}^{-2}$) on the stress buildup during photo-induced free-radical polymerization at room temperature [4]. They reported that the stress grew more rapidly and to higher magnitudes with more photoinitiator or stronger light, i.e., when the polymerization rate is accelerated. A comparison between TMPTA (trimethylolpropane triacrylate) and PETA (pentaerythritol tetraacrylate) also revealed that increasing the functionality results in higher stresses

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at a lower final conversion. This work clearly demonstrates that the final stress level can vary over one order of magnitude depending on the choice of curing conditions.

Stolov et al. were able to provide stress-conversion data obtained simultaneously from beam deflection measurements in conjunction with reflection-absorption infrared spectroscopy for three acrylate monomers, i.e. TPGDA (tripropylene glycol triacrylate), TMPTA and PETA [11]. The UV-radiation intensity was typically $\approx 0.2\text{--}0.3\text{ mW cm}^{-2}$ and the ultimate stress levels were $\approx 2, 4.5$ and 5 MPa for TPGDA, TMPTA and PETA respectively. In a related paper, the effect of coating thickness, light intensity and photoinitiator concentration on the average stress was nicely shown for TMPTA [12]. Ultimate stress values ranging from ≈ 9 to 15 MPa were obtained after 30 min of curing with a light intensity of 0.26 mW cm^{-2} and photoinitiator contents ranging from 0.4 to 4 mol%. Noteworthy, they reported an exponential increase of the stress with decreasing film thickness.

Wen et al. systematically investigated stress build-up relative to double bond conversion for various multifunctional (meth)acrylate coatings [13]. In addition to the effect of light intensity, (i) the effect of functionality was studied by comparing DEGDA (diethylene glycol diacrylate), TMPTA and PETA, (ii) the effect of monomer chain length was verified from a comparison between different polyethylglycoldiacrylates (di-EGDA, tri-EGDA, tetra-EGDA, poly-EG(400)DA), (iii) the effect of a plasticizer (PEG) was examined and (iv) the UV-curing of a multifunctional methacrylate and an acrylate was compared (TMPTA versus TMPTMA). So far this is the most complete published report of stress data for acrylate coatings. Consistent with Payne's data, they found that with increasing monomer functionality polymerization slows down. However, the rate and magnitude of stress development rise with the monomer functionality, even though the final conversion is lower. Increasing the chain length with a flexible segment or addition of a plasticizer leads to a significant drop of the stress, but with a higher final conversion. The behaviour of stress development during the polymerization of the different systems clearly shows that vitrification is the point where significant stress starts to buildup, typically when the glass transition temperature becomes equal to the curing temperature. The conversion then exceeds largely the typical conversion magnitude at the gel point. In the gel state, the coating modulus is too low to sustain any significant stress buildup and the relaxation times are still short enough to relief stress rapidly. After vitrification, the stress increases roughly proportional to the excess conversion, consistent with Croll's assumption that stress development scales with volume contraction after solidification [2]. However, it is noticed that beyond the apparent end conversion level stress still grows significantly, albeit at a much slower rate. This is also observed after irradiation in the so-called dark period. Little attention has been paid to the stress build-up in the post-exposure period. Interestingly, Vaessen et al. reported the effect of UV-lamp cycling on the stress development and showed how the competition between network formation, polymer chain relaxation and lamp cycling determines the stress buildup [5]. A TMPTA coating was cured with a UV-lamp that was cycled on and off while keeping the total radiation dose equal. The alternation of exposure and dark periods was of the order of minutes. Whereas the conversion profile was essentially insensitive to the cycling period, the stress development reduced substantially for the shortest cycling times due to effective stress relaxation in the dark periods at early polymerization stages. Later in the polymerization, at slow conversion and stress relaxation, stress growth was still significant even in the dark periods. The latter was rationalized by assuming a significant Young's modulus increase for few reacting double bonds.

Francis et al. issued a review covering the various aspects of development and measurement of stress in polymer coatings [3]. The approaches for the prediction of stress were also surveyed to

some extent. In this respect, an interesting account is due to Lange and coworkers where the residual stress is estimated from thickness and shear modulus changes of thermally cured epoxy and acrylate resins during polymerization and cooling [6]. From this work, it is worthwhile to note that stress levels of the order of 2 MPa were determined after *thermal* curing of TPGDA above the ultimate glass transition temperature of the system (in the rubbery state, $T_{\text{cure}} = 115\text{ }^{\circ}\text{C}$). Subsequent cooling to room temperature raised the stress by another 4 MPa .

Modelling of stress development during the whole curing process requires a constitutive equation including modulus relaxation and chemical kinetics. Among others, comprehensive models have been proposed by Adolf and Martin, and, Simon and McKenna [7,14,15]. Material parameters describing the cure kinetics and the cure-dependent thermophysical properties are usually incorporated on a phenomenological base. The models were generally applied in thermosetting materials, typically epoxy-amine resins, but never on photoreacting systems to our knowledge.

The following points are addressed in the present work. First, based on the guidelines described in ASTM D6991 for the cantilever deflection method, we try to establish optimum conditions (i) for the application and curing of radiation-curable resins on a metal strip, (ii) for the deflection measurement and (iii) for the calculation of the residual stress. Next, measurements are systematically conducted on several reactive diluents including mono- and multiacrylates, alone or in blend with an epoxyacrylate resin in order to compare a range of acrylate compositions in industrially relevant coating conditions for UV-curing. This extends the body of stress data in radiation-cured coatings and is discussed in perspective with existing data. The coatings are further characterized in terms of conversion, glass transition temperature and volume contraction. Alongside, the effect of coating thickness is also highlighted. The limitations of the experimental methodology are established from a variability analysis of the data. Lastly, from the collected data an estimate of the fracture toughness for a triacrylate coating on carbon steel is provided.

2. Materials and methods

2.1. Resin formulations

Many radiation-curable resins and formulations are used in applications where hard and resistant coatings are required. For these coatings, residual stress is a potential problem and hence, a reference coating system based on an epoxy acrylate (Ebecryl[®] 600) along with "high- T_g " (after polymerization) reactive diluents were chosen in this study. One exception to the rule is PEG(600)DA which is a "low- T_g " acrylate resin. This resin was included as a low modulus reference system. The compounds were all supplied by Cytec Surface Specialties, Drogenbos, Belgium and are detailed in Table 1. The acrylate double bond content was determined by proton NMR (*vide infra*).

In order to apply the deflection method successfully, it is imperative to achieve good coating adhesion on the metal substrates. To this end, 5 w/w% of an organophosphorus adhesion promoter (Ebecryl[®] 171), was added to the resin composition. Additol CPK (1-hydroxy-cyclohexyl phenylacetone) at a level of 4 w/w% was used as the photoinitiator. Hence, the reactive diluent and the oligomer encompassed 91 w/w% of the overall composition of the formulation. The diluent to oligomer ratio was varied according to 100:0, 70:30, 50:50 and 30:70. Ebecryl[®] 600 is a highly viscous oligomer resin and could not be tested as such. An acceptable viscosity level for coating application could be achieved using IBoA in the ratio 10:90 IBoA:BADGE-DA, which was the closest approximation to the full oligomer system.

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