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Effect of oligomer length on the buckling of long and high aspect ratio microwalls UV embossed from oligomer/monomer mixtures

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Abstract

High aspect ratio microwalls separating long and deep microchannels are important for high sensitivity and high throughput microfluidic devices. Ultraviolet (UV) embossing is a feasible replication method for such microstructures. But buckling easily happens with thin and tall UV embossed microwalls with some formulations due to shrinkage stress. In this paper oligomer/monomer mixtures containing principally (68 wt.%) bisphenol A diacrylate with different degrees of ethoxylation (0, 3, 10 and 30) were used to study microwall buckling; these mixtures were denoted by E0, E3, E10 and E30, respectively. The effect of oligomer length on shrinkage, shrinkage stress, cross-linking kinetics and modulus and their inter-relations was studied. The fugitive multi-acrylated monomers present (trimethylolpropane triacrylate (20%) and dipropylene glycol diacrylate (10%)) caused the four mixtures to exhibit similar ultimate shrinkage stresses; this is contrary to the observation that long oligomers develop low shrinkage stress in neat oligomer systems. However, the E30 mixture network has the smallest modulus. The high shrinkage stress and low modulus of E30 mixture cross-linked network explains the buckling of long and high aspect ratio UV microwalls UV embossed from it.

The in-plane shrinkage stress in the cured thin film was found to be the integrated effect of modulus and shrinkage rate built-up: only at high conversions did the stress developed drastically. Almost 100% conversion could be reached with the more flexible and mobile E10 and E30. E10 and E30 also have higher shrinkage values than E0 and E3.

Keywords: Ultraviolet photopolymerization; Mixture; Oligomer; Monomer; Acrylate; Stress; Shrinkage; Modulus; Kinetics

1. Introduction

In typical liquid ultraviolet (UV) embossing, a photopolymerizable liquid resin is dispensed into a mold and a carrier substrate placed over it. The resin is then UV irradiated to harden it and then demolded. Our group has previously reported UV embossing of various resins [1–4]. UV formulations often contain mixtures of oligomers and monomers to achieve the desired physical and processing characteristics; the oligomers typically impart the desired properties such as hardness (e.g. with polyester-based resins) or chemical resistance (e.g. with bisphenol A-based resins) whilst the monomers are added to decrease viscosity and increase processability. We have observed that when long oligomeric diacrylates are used in UV embossing mixtures, long and high aspect ratio molded microwalls tend to be wavy and these require an additional step of thermal stress relaxation to straighten out. Wavy microwalls result when these were UV embossed from a mixture containing 68% ethoxylated (30) bisphenol A diacrylate, 32% monomers and 0.3% photoinitiator [1]. No such waviness exists for microwalls molded from a similar mixture containing shorter ethoxylated (3) bisphenol A oligomeric diacrylate. According to the buckling theory [5], the wavy microwalls is an effect of accumulated shrinkage stress and modulus during curing.

During acrylate polymerization, the conversion of van der Waals bond to covalent bond causes shrinkage or increased free volume; the modulus also increases. Stress builds up when shrinkage is constrained. The stress build-up is related to the evolution of shrinkage strain, modulus and glass transition temperature of the formulation during the curing process. [6] There are two main transitions during cure: gelation and vitrification [7]. Gelation corresponds to the formation of an infinite network,

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while vitrification occurs when the glass transition temperature (T_g) of the reacting system reaches the cure temperature. When cured above the ultimate glass transition temperature (T_g^∞) of the network, only gelation will occur; when cured below the (T_g^∞), the network will first experience gelation and then vitrification though vitrification commences immediately after gelation with the two events being virtually indistinguishable and lasting until the end of the reaction [7]. Stress is negligible before gelation because the flow of liquid monomers and oligomers rapidly accommodates the shrinkage. At the gelation point, a loading–bearing network forms and the system starts to develop stress if it is constrained. When the system enters the vitrification state, the modulus becomes high and the stress relaxation becomes slow so that stress development becomes significant when the reaction proceeds in the vitrified state.

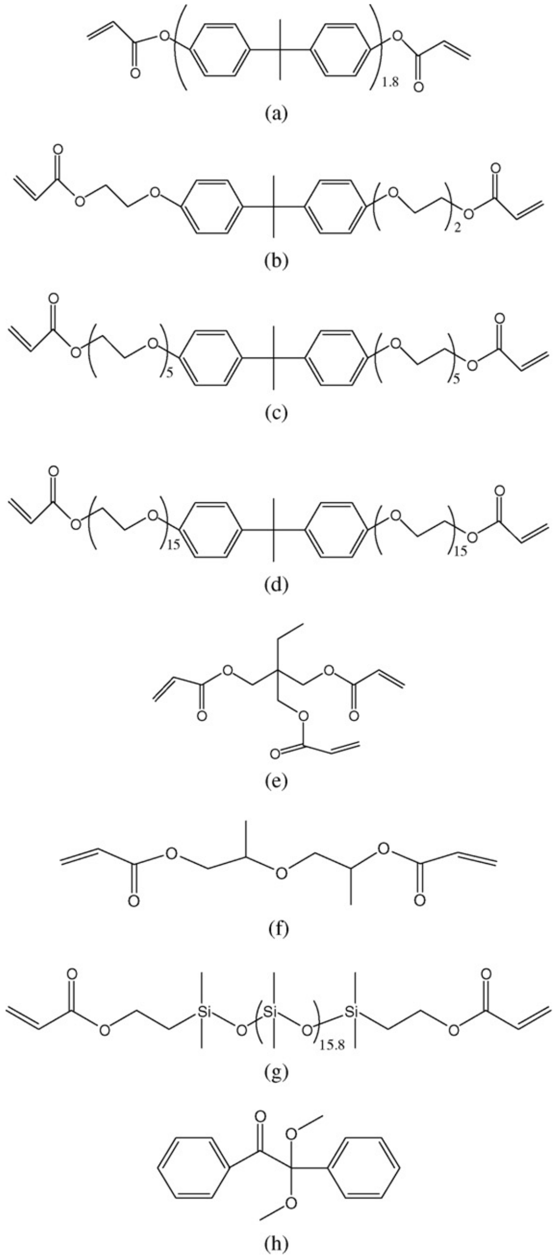
Ultraviolet (UV) photopolymerization of multi-acrylated monomers and oligomers are complicated by diffusional effects causing severe hindrance to the mobility of free radicals or monomers/oligomers resulting in autoacceleration and autodeceleration [8]. The photopolymerization is affected by the oligomer length and flexibility and monomer concentration. It has been observed that for longer neat oligomer [9,10] almost full conversion can be attained but the polymerization rate will be decreased. Short oligomer increases polymerization rate but results in low conversion. Short oligomer length also results in high cross-linked density and improved modulus but excessive stress and defects such as cracking, delamination, and buckling [1,11,12]. Wen et al. reported on the effect of oligomer length on the stress development in neat photocross-linkable oligomers [13]. They found that both the stress growth rate and ultimate stress decrease when the oligomer chain length is lengthened. The presence of fugitive monomers, as well as oligomer length, would potentially affect network evolution and stress developed. However, none of the numerous reports on the influence of multi-(meth)acrylated oligomer length on the ultra violet (UV) photopolymerization focuses on oligomer/monomer mixtures as most studied neat systems (i.e. neat monomers or neat oligomers) [14–17].

In this paper, the effect of oligomer length on the dynamic shrinkage stress, cross-linking kinetics and modulus were measured and also correlated with each other. Four mixtures containing 68 wt.% bisphenol A diacrylates with varying ethoxylation of 0, 3, 10 and 30 mixed with two monomers (trimethylolpropane triacrylate and dipropylene glycol diacrylate), labeled as E0, E3, E10 and E30, respectively, were studied. Two of the mixtures (E0 and E3) produced glassy networks and the other two (E10 and E30) rubbery ones. Useful insights into the effect of oligomer length on the network evolution, shrinkage stress, modulus and buckling were gathered.

2. Experiments

2.1. Materials

Scheme 1 shows the chemical structures of the constituents of the mixtures. The trimethylolpropane triacrylate (TMPTA) was supplied by Aldrich. EB600, which is bisphenol A diacrylate, was supplied by UCB Chemicals. SR349 (ethoxylated (3) bisphenol A diacrylate), SR602 (ethoxylated (10) bisphenol A diacrylate) and CD9038 (ethoxylated (30) bisphenol A diacrylate) were supplied by Sartomer. Dipropylene glycol diacrylate (DPGDA) was supplied as SR508 by Sartomer. EB350, a silicone diacrylate supplied by UCB Chemicals, was used as a release reagent. 2,2-dimethoxy-1,2-diphenylethan-1-one supplied as Irgacure 651 (I651) by Ciba Chemicals, was used as the photoinitiator. The composition of the resin mixture used was 68/20/10/2/0.3 (w/w) of X/SR508/TMPTA/EB350/I651 where X = EB600, SR349, SR602 and CD9038; these mixtures are hereafter denoted by formulation *En* ($n = 0$, 3, 10, and 30 to denote the degree of ethoxylation in the oligomers, respectively).



Scheme 1. Chemical structure of (a) EB600, (b) SR349, (c) SR602, (d) CD9038, (e) TMPTA, (f) DPGDA (SR508), (g) EB350 and (h) Irgacure 651: 2,2-dimethoxy-1,2-diphenylethan-1-one.