Altering Network Structure of Radical/Cationic Systems via Photopolymerization-Induced Phase Separation for Thermomechanical Property Control

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Abstract

Photopolymerization of radical and cationic systems is used extensively to create polymer thin films for a number of applications. Typically, these polymers demonstrate a relatively small range of thermomechanical and physical properties. One approach to expand the applications of both radical and cationic polymers is to photo-cure both simultaneously. This work investigates the polymer structure and thermomechanical properties of various radical/cationic hybrid systems with respect to irradiation intensity. We show that different single- and multi-phase polymers are created depending on monomer composition and irradiation intensity. The thermomechanical properties of the multi-phase (phase-separated) polymers are readily controlled by the irradiation intensity, while single-phase systems do not significantly depend on the irradiation intensity. Thus, incorporating both monomers can lead to the formation of phase-separated polymer networks with a wider range of material properties.

Introduction

Photopolymerization offers many advantages including rapid reaction rates at room temperature, temporal and spatial control of initiation, as well as low to no emissions of volatile organic compounds.[1] Photopolymerization can initiate the photochemical reactions of free-radical and/or cationic monomers both of which have advantages and disadvantages.[2] For example, free-radical polymerization of (meth)acrylates are not affected by moisture and cure quickly, but are also inhibited by oxygen and undergo significant volume shrinkage. On the other hand, cationically polymerizable monomers (e.g. epoxides and oxetanes) exhibit good rheological properties, low toxicity, and are not inhibited by oxygen.[3] The latter polymerizations are typically slow and need thermal post-cure to achieve high conversions.[4] Thus, hybrid formulations consisting of both free-radically and cationically polymerizable monomers have been suggested as an alternative means to combine the advantages and to manipulate the polymer structures of these two classes of photopolymerization.[3,5] To date, almost all reports regarding hybrid photopolymerizations have used radical and cationic photoinitiators, and occasionally thermal initiators in order to alter polymerization kinetics, resulting in interpenetrating polymer networks (IPNs) and/or phase separation.[6] This approach has led to controllable mechanical and physical properties such as toughness, abrasion resistance, and clarity.[3]

In an early work, Dean and Cook used dual thermal/photo initiators to investigate the reaction kinetics and polymer structure of hybrid dimethacrylate and epoxide systems.[7] By the appropriate selection of thermal/photo initiators, the polymerization kinetics were controlled to polymerize either the dimethacrylate or epoxide monomer first, which led to single- or multi-phase IPNs depending on the curing conditions. Additionally, another study used thermal-UV dual-process to investigate the polymer structure of a diacrylate/dioxetane mixture and hybrid acrylate-oxetane monomer.[8] Initially, both systems were subjected to thermal free-radical polymerization, which initiated the acrylate double bond conversion. Then, UV irradiation was applied to initiate the ring-opening polymerization of oxetane monomer. As indicated by dynamic mechanical analysis, the hybrid monomer exhibited single-phase structure, but the acrylate/oxetane mixture showed phase separation with two glass transition temperatures (T_g). The latter system showed potential as a damping material that can absorb energy due to the two very broad T_g's.[9]

In this work, we investigated the effect of irradiation intensity and monomer composition on the morphology, optical, and thermomechanical properties of hybrid radical/cationic systems. The polymer structure of different monomer compositions was monitored using a UV/Vis spectrometer, dynamic mechanical analysis (DMA), and scanning electron microscopy. It was found that both monomer concentration and irradiation intensity significantly affected the polymer morphology which greatly influences the thermomechanical and physical properties of polymers.

Experimental

Materials

Monomers and initiators used in this work include: butyl acrylate (BA; Sigma Aldrich), 3-ethyl-3[[(3-ethyloxetane-3-yl)methoxy]methyl]oxetane (DOX, Synasia), 2,2-dimethoxy-1,2-diphenylethan-1-one (DMPA, Ciba Specialty Chemicals) to initiate the radical polymerization, and mixed triarylsulfonium hexafluoroantimonate salts (TSA; Sigma Aldrich) to initiate the cationic polymerization. TSA is diluted in propylene carbonate (50 wt%). All chemicals were used as received.

Methods

Fourier Transform Infrared Spectroscopy (FTIR)

The photopolymerization kinetics of hybrid DOX:BA systems were examined by using a Nexus 670 FTIR. The final conversion of these systems was measured after both UV- and thermal post-cure at 90°C. The formulations were deposited between two salt (NaCl) plates separated by 15 μm spacers. Irradiation was provided by a medium pressure mercury lamp (250-450 nm) at 10, 100, and 1500 mW cm^{-2}. Conversion was obtained by following the decrease of the acrylate C=C stretching band at 1637 cm^{-1} and the oxetane C-O-C stretching band at 980 cm^{-1} (Equation 1).[10,11]

$$Conversion\ (\%) = \frac{A_o - A_f}{A_o} 100 \qquad (1)$$

where A_o is the initial height of each peak before cure and A_f is the peak height at the end of cure.

Scanning Electron Microscopy (SEM)

Images of polymer morphology were obtained using a high vacuum scanning electron microscope (Hitachi S-4800). All the formulations were sandwiched between two glass slides (film thickness ≈ 200 μm) and prepared through photopolymerization at 10 and 100 mW cm^{-2} for 10 minutes using a medium pressure mercury lamp, and at 1500 mW cm^{-2} for one minute using a high-speed belt curing system.

Optical Density

To measure optical properties of polymers a UV/Vis portable spectrometer (Ocean Optics, USB2000) was used. A visible light source that emits a wavelength range of 400-800 nm was used to transmit visible light through the sample. The intensity of 500 nm light transmitted was monitored.

Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (DMA; Q800 DMA TA Instruments) was used to characterize the thermomechanical properties of polymers. To create samples with dimensions of approximately 8 x 6 x 0.2 mm (length x width x thickness), small amounts of liquid mixture were placed between two glass plates with predetermined thickness (two adhesives tapes were attached to create a 0.2 mm thickness). The samples were initially exposed to a UV lamp (250-450 nm) for 10 minutes at 10, and 100 mW cm^{-2}, and for one minute on a belt system at 1500 mW cm^{-2}. Then all samples were thermally post-cured at 90^{o}C for four hours to ensure that no further cure would occur during the thermal scan. A temperature range of -60 to 150^{o}C was applied to examine the tan(δ) profiles. DMA tensile mode was utilized under constant strain at a frequency of 1 Hz and heating rate of 3^{o}C/minute. Also, stress and strain were evaluated at room temperature in tensile mode with a force rate of 0.5 N/minute.

Three systems with monomer ratios of 1:1, 7:3, and 9:1 DOX:BA were prepared by mixing BA and DOX at various weight percentages. The concentration of the radical and cationic photoinitiator was 0.25 and 0.75 wt%, respectively.

Results and Discussion

Post UV-Thermal Cure Conversion

Both monomer composition and irradiation intensity impact the reaction rate and final conversion, which determine the morphology and subsequently the physical properties of polymers.[5,12] Herein, photopolymerization at different irradiation intensities is followed by a thermal post-cure at 90^{o}C for four hours to obtain the maximum conversion of each monomer (Table 1 and 2). In all cases, DOX conversion appears to be around 60-70% depending on the monomer ratio, while the final conversion of BA reaches approximately 100%. It is reasonable to believe that the thermal post-cure conversion of both monomers occurs in place due to the high UV-induced BA conversion and DOX crosslinking. With the maximum conversion for each monomer a better understanding of the relationship between polymer structure and thermomechanical properties can be attained.

Table 1. Post UV-Thermal cure conversion of oxetane functional groups. Experiments were conducted three times to determine reproducibility with the values in parenthesis representing the standard deviation.

Monomer Ratio	**DOX:BA 1:1**			**DOX:BA 7:3**			**DOX:BA 9:1**		
Irradiation Intensity (mW cm^{-2})	**10**	**100**	**1500**	**10**	**100**	**1500**	**10**	**100**	**1500**
Conversion (%)	62 **(+/- 9)**	66 **(+/- 4)**	70 **(+/- 5)**	63 **(+/- 7)**	68 **(+/- 1)**	70 **(+/- 9)**	66 **(+/- 8)**	73 **(+/- 3)**	69 **(+/- 6)**

Table 2. Post UV-Thermal cure conversion of acrylate functional groups. Experiments were conducted three times to determine reproducibility with the values in parenthesis representing the standard deviation.

Monomer Ratio	**DOX:BA 1:1**			**DOX:BA 7:3**			**DOX:BA 9:1**		
Irradiation Intensity (mW cm^{-2})	**10**	**100**	**1500**	**10**	**100**	**1500**	**10**	**100**	**1500**
Conversion (%)	98 **(+/- 0.1)**	99 **(+/- 0.2)**	99 **(+/- 0.2)**	99 **(+/- 0.1)**	99 **(+/- 0.2)**	99 **(+/- 0.1)**	98 **(+/- 0.5)**	98 **(+/- 0.4)**	99 **(+/- 0.3)**

Phase separation characterization

Characterization of the morphology of polymers is crucial to identify phase-separated domains. Furthermore, the dependence of mechanical properties on phase-separated morphologies may also be determined. The polymer structure has a considerable impact on many properties including the optical characteristics of polymer network systems. For example, a first indication of a multi-phase network is reduced transparency (cloudiness) in visible light. The cloudiness is explained by the fact that the created nano-/micro-domains scatter visible light.[13] Figure 1 shows the final transmittance of UV- and thermal post-cured polymers. For DOX:BA ratios of 1:1 and 7:3, a reduced light transmittance of up to 30% is observed. The different transmittance values among the three irradiation intensities are likely related to the various domain size and shape of polymers which scatter visible light differently. For the system with DOX:BA 9:1 ratio, however, the irradiation intensity has a negligible effect on the transmittance, indicating that the polymer structure does not contain domains on the nanometer scale that scatter light. Figure 1b shows photos of the visible scatter of representative polymeric films.

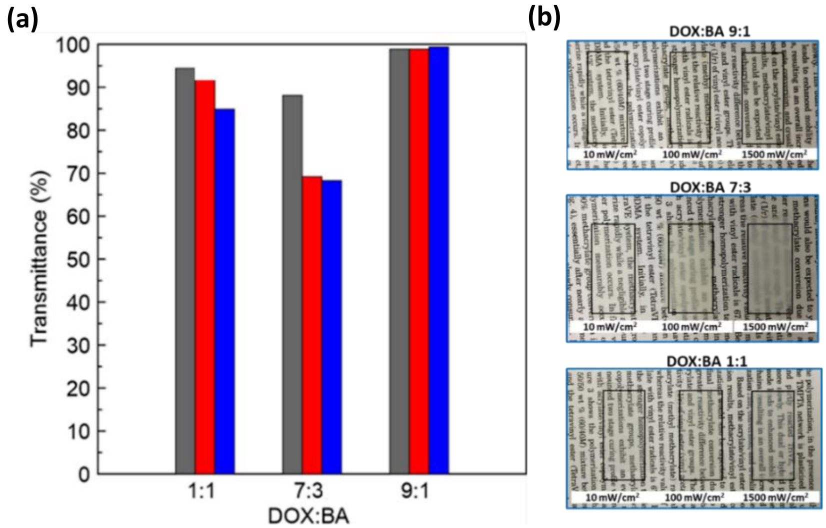

Figure 1. a) Final transmittance of polymers with varying DOX:BA ratio, and b) images of polymer films after curing. All formulations were photocured at 10 (gray), 100 (red), and 1500 (blue) mW cm^{-2} and thermally post-cured at 90^{o}C.

SEM is utilized to further characterize the phase morphology of polymers. The surface morphology of polymers with low BA concentration (DOX:BA 9:1) is shown in Figures 2a-c. Images show that morphology is independent of the irradiation intensity. For these systems, the morphology looks very uniform without any distinct structure because of the large DOX concentration that creates a highly-crosslinked polymer network. These results agree with those of UV/Vis which show that the photocuring intensity does not change the material opacity for this specific monomer ratio (Fig. 1). On the other hand, SEM images for hybrid systems with intermediate BA concentration (DOX:BA 1:1 and 7:3) are shown in Figure 3. Both systems clearly exhibit high degrees of phase separation at each irradiation intensity except for DOX:BA 1:1 system photocured at 10 mW cm^{-2}. The domains of the phase-separated polymers are on the size scale of 200-500 nm depending on the irradiation intensity and monomer composition.

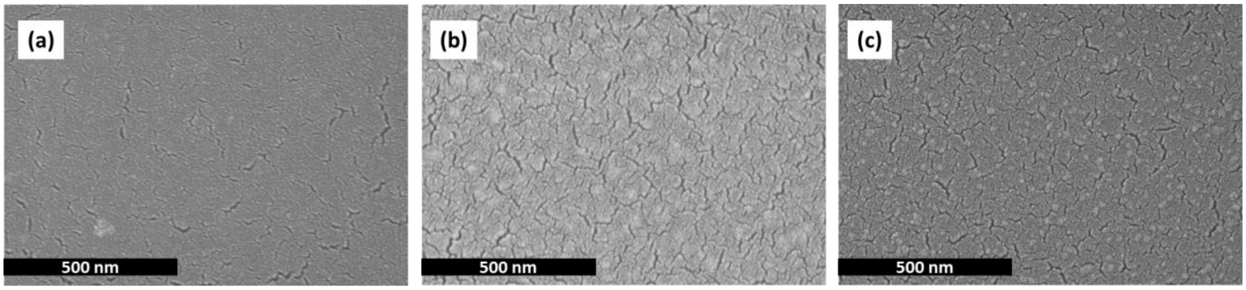

Figure 2. SEM images of 9:1 DOX:BA systems photopolymerized at a) 10, b) 100, and c) 1500 mW cm^{-2} and thermally post-cured at 90°C for four hours.

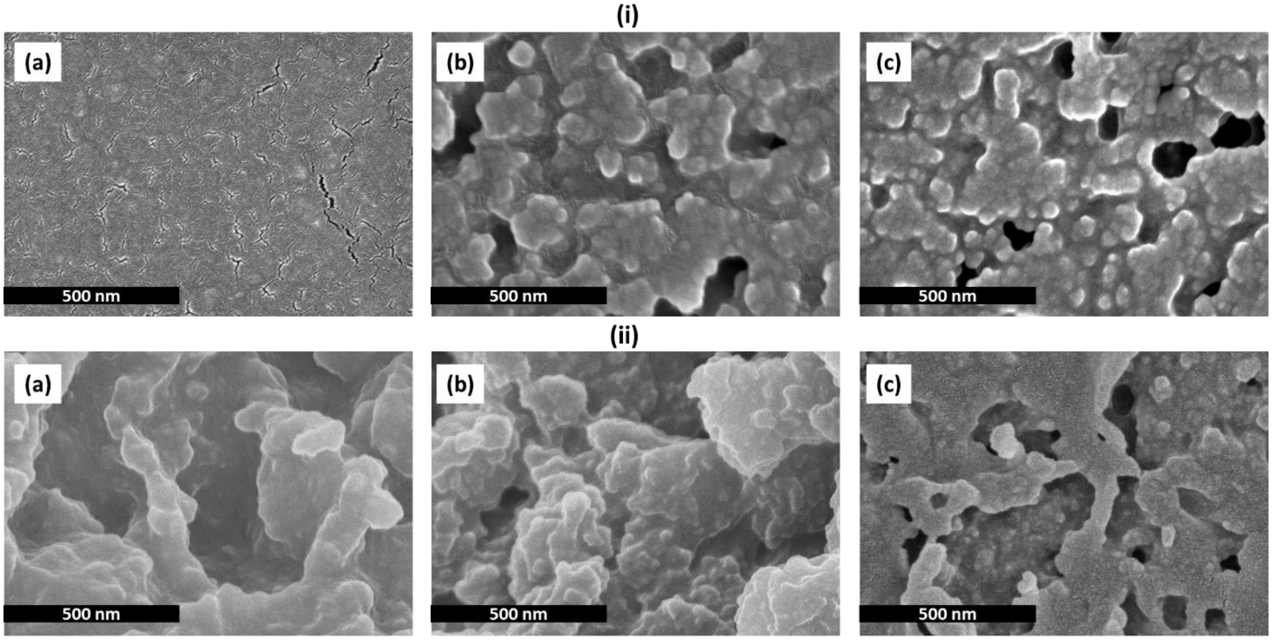

Figure 3. SEM images of i) 1:1 and ii) 7:3 DOX:BA systems photopolymerized at a) 10, b) 100, and c) 1500 mW cm^{-2} and thermally post-cured at 90°C for four hours.

Impact of Irradiation Intensity on T_g

To obtain further information regarding the structure of polymers, tan(δ) experiments are conducted utilizing DMA. Multiple tan(δ) peaks are associated with the formation of phase-separated polymers. The effect of irradiation intensity on tan(δ) profiles of different monomer ratios is shown in Figure 4. For systems with DOX:BA 1:1 and 7:3, two tan(δ) peaks are observed at any irradiation intensity, confirming phase separation. One tan(δ) peak at -30°C is associated with the glass transition temperature of the softer BA phase, and another tan(δ) peak at ~60°C is associated with the harder DOX domain. As the irradiation intensity increases the two T_g's become more distinguished, indicating that significant changes in the polymer structure occur at higher intensities. As for systems with 9:1 DOX:BA ratio, very broad tan(δ) peaks with low height are observed at any irradiation intensity (Fig. 4). In this case, all the tanδ profiles are almost identical, having a peak around 45°C, confirming the formation of single-phase crosslinked polymers.

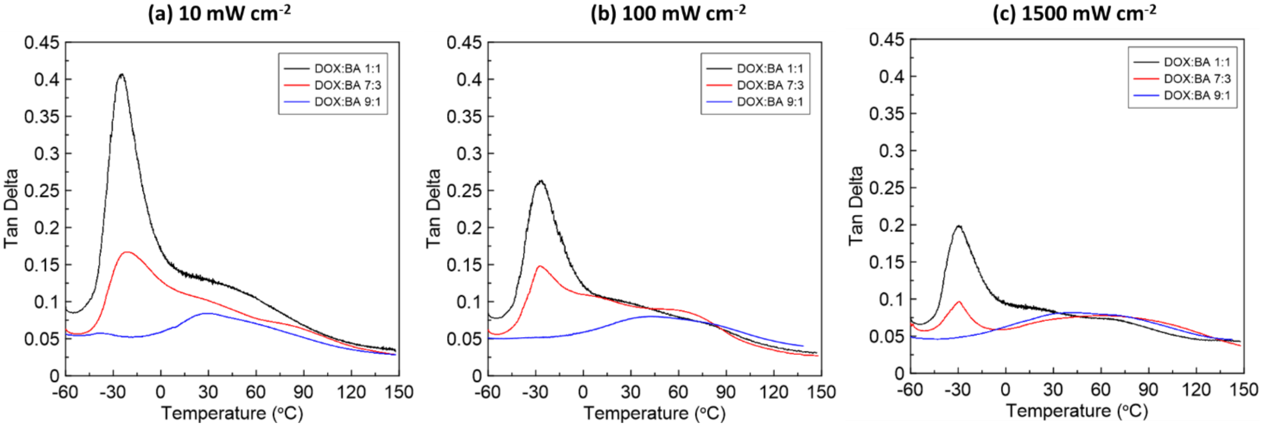

Figure 4. Tan(δ) profiles of varying monomer ratio photopolymerized at a) 10, b) 100, and c) 1500 mW cm^{-2} and thermally post-cured at 90°C.

Polymer Response to Force

The mechanical properties of polymers are directly dependent on structure. Figure 5 shows the effect of irradiation intensity on stress-strain of varying monomer composition. Generally, the modulus of each polymer, as indicated by the initial slope, is increased by increasing DOX concentration. This behavior is related to the higher degree of crosslinking as the DOX concentration increases. The modulus and elongation at break of systems with 1:1 and 7:3 DOX:BA ratio changes more dramatically with increasing the irradiation intensity (Fig. 5). At 10 mW cm^{-2}, all systems show slightly different elongation at break. By increasing the intensity to 100 mW cm^{-2}, the elongation at break increases by 140% and 600% for the systems with DOX:BA 1:1 and 7:3 ratios (phase-separated), respectively, while only a 25% increase is observed for the system that does not phase separate (DOX:BA 9:1). At the highest irradiation intensity (1500 mW cm^{-2}), both phase-separated systems show an increased elongation at break by approximately

100% and 50%, respectively, when compared to those at 100 mW cm^{-2}. On the other hand, elongation at break is increased only around 16% for the single-phase systems. Consequently, it is apparent that different extent of phase separation significantly enhances the mechanical properties of systems with 1:1 and 7:3 DOX:BA ratios because both monomers contribute to these properties synergistically. On the other hand, the single-phase materials behave like thermosets with very high modulus and small elongation at break.

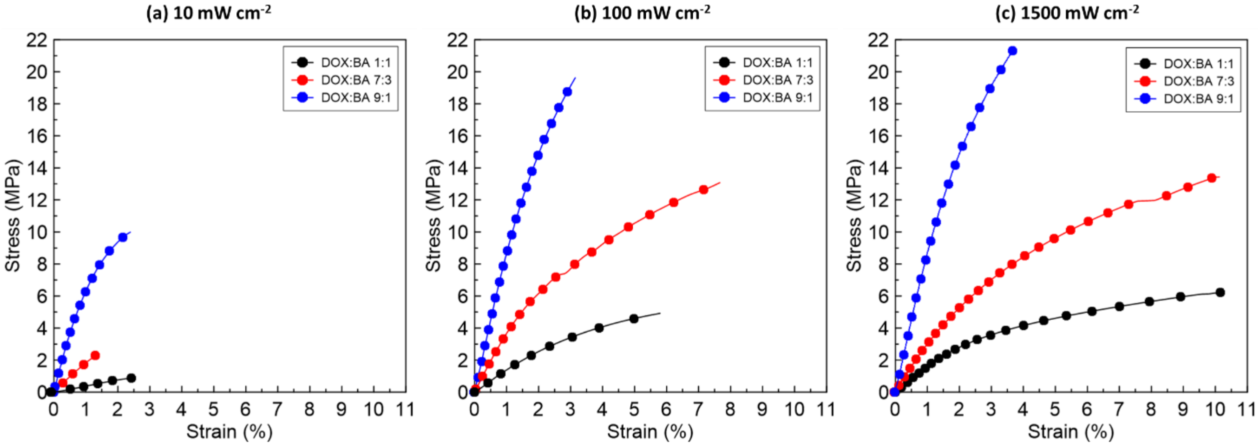

Figure 5. Stress as a function of percent strain at room temperature of system with varying monomer ratio photopolymerized at a) 10, b) 100, and c) 1500 mW cm^{-2} and thermally post-cured at 90°C.

Further, we evaluated the effect of the irradiation intensity and monomer composition on the mechanical properties using design of experiments. For the screening experiment, two-factor three-response data simulations were performed. Figure 6 shows polymer strain, stress, and overall toughness. Based on the response surface, it appears that formulations with lower DOX concentration create polymers with high strain at break when photopolymerized at high irradiation intensities (>900 mW cm^{-2}). As for maximum stress values, high DOX concentrations on their own can achieve high stress values at break with an irradiation intensity as low as 10 mW cm^{-2}.

Additionally, high toughness can be achieved by photocuring under the highest irradiation intensity while using a range of DOX concentration between 40 to 60 wt%. These results highlight the significance of using a predictive model to understand the relationship among various variables in photopolymerization-induced phase separation and how these variables can be used to achieve desired mechanical properties.

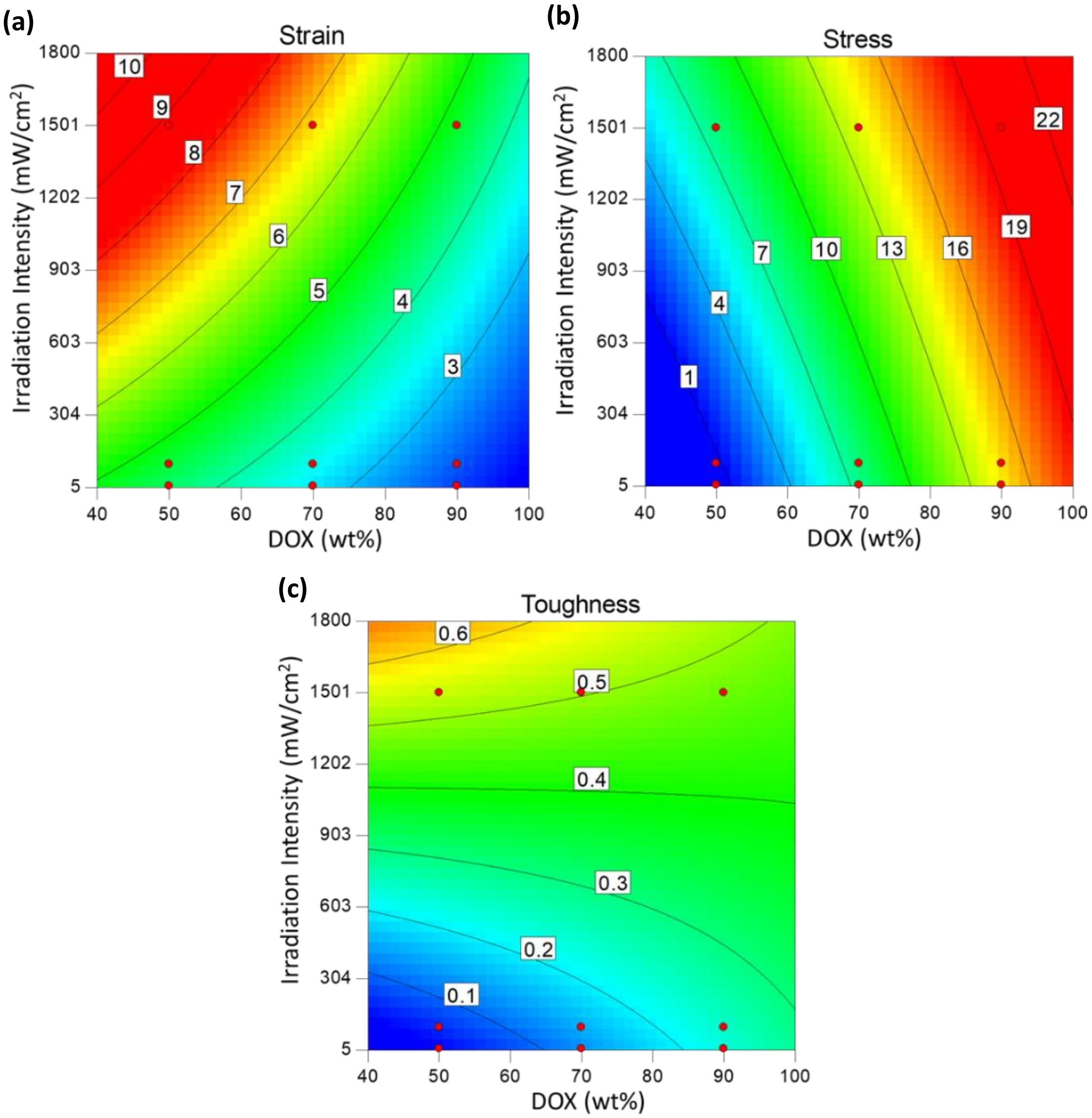

Figure 6. Prediction of a) strain, b) stress, and c) toughness values as a function of the irradiation intensity and DOX concentration with the corresponding BA concentration. Blue indicates lower values, while red indicates higher values.

Conclusions

This research shows that phase separation can be induced by photopolymerization when utilizing the orthogonal chemistries of butyl acrylate and di-functional oxetane. Both the irradiation intensity and monomer composition enable the formation of distinct polymer structures to enhance physical and thermomechanical properties. Specifically, SEM images indicate that formulations with DOX:BA ratios of 1:1 and 7:3 can generate different phase-separated morphologies depending on the irradiation intensity. Phase separation is also confirmed by multiple tan(δ) peaks from DMA analysis. Additionally, the maximum stress and elongation at break are significantly increased due to synergistic properties of the photo-induced phase-separated polymers. On the other hand, SEM images show uniform morphologies for systems with low BA concentration (DOX:BA 9:1). Also, the broad T_g's observed at all curing intensities suggest the formation of single-phase polymers for these systems. Further, the single-phase polymers show only a small increase in elongation at break when increasing the irradiation intensity. We also report a model from design of experiments that predicts the role of irradiation intensity and monomer composition to stress, strain, and overall toughness. In particular, higher maximum stress can be achieved by increasing DOX concentration alone. But to increase the strain at break, both high irradiation intensity and low/intermediate DOX concentrations must be used. This research shows that combining intermediate DOX concentrations and high irradiation intensity result in significant increases in overall material toughness.

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