

Block Copolymer Assembly through Polymerization-Induced-Phase Separation (PIPS)

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Abstract

Additive manufacturing has reached a critical mass and is demanding break out performance with UV curable technology. While most of the technology to date has been driven by the rigors of the coatings and graphic arts industries, particular focus on the demands of 3D printing highlights a gap in material robustness. To overcome challenges with impact resistance and extend 3D printing materials from prototyping to industrial applications, block copolymers provide a promising avenue to increase the durability of UV cured thermosets. Block copolymers have demonstrated an ability to introduce microstructure, and that microstructure can alter the mechanical behavior of polymer networks. Block copolymers have demonstrated success in traditional epoxy thermosetting resins, however those advances have not been easily applied to photocurable and acrylic chemistry. The use of photopolymerization induced phase separation (PIPS) will be explored as a mechanism to drive block copolymer assembly in acrylic based resins.

Keywords: Additive manufacturing, 3D printing materials, impact resistance, toughness, block copolymers, PIPS, polymerization induced phase separation

Introduction

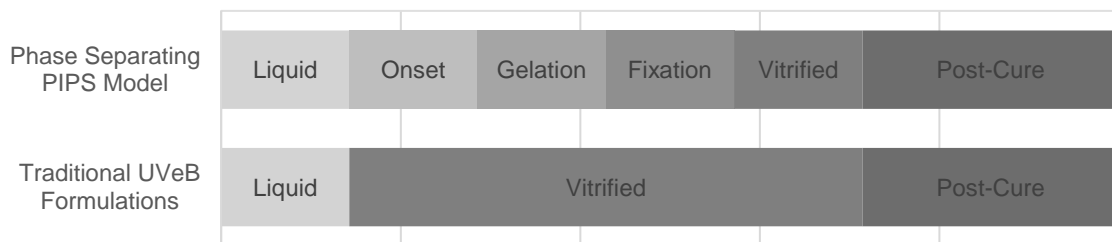
Material advances in 3D printing have been pushing mechanical properties to transition from prototype into functional part requirements. Many of the photopolymer used in the industry have been limited to high throughput modeling or temporary applications. Consumer goods are typically manufactured with traditional thermoplastics, and the challenge lies in delivering materials that mimic these thermoplastics as liquid thermosetting resins. Unfortunately this presents a serious material science challenge. Every textbook written on material science begins with examples of thermosets and thermoplastics and their independent behavior, nonetheless, delivering tougher photocurable thermosets remains our goal. There exists an extensive amount of research for toughening traditional thermosets to consider, however there has been little advances in toughening of photocurable resins.

Toughened thermosetting resins have found commercial success in many high demand applications using a wide array of synthetic, and formulation techniques [6]. One path of toughening targets incorporation of microstructure, more specifically, formation of a polymer matrix with rigid and soft domains [6,13]. Production of a material with distinct phases, delivers a mechanism of energy dissipation producing an overall tougher material than the pure components or miscible blends [3]. Optimal energy dissipation has been shown to exist for phases that have distinct differences in moduli, one soft as an energy absorbing region while the other rigid, providing the structure of the network [7,11]. Successful practice for domain formation has been established for epoxy thermosets through particle dispersion or polymerization induced phase separation techniques [13].

To improve the durability of photocurable systems with microstructure, we consider a mechanism found in adjacent technologies called polymerization induced phase separation (PIPS) to drive rubber portions of a block copolymer into discrete domains. With PIPS, a resin blend begins as a stable solution and during polymerization develops a thermodynamic instability causing phase separation to occur [1]. Existing epoxy based thermosets use PIPS mechanisms, and take advantage of the large change in polarity between the epoxide based resin and ensuing highly polar network that slowly drives instability [1, 11]. This practice is not easily applied to the world of acrylic chemistry due to the relatively small change in X-parameter from monomer to photopolymer during polymerization. Photopolymerization is further challenged with the high speeds of conversion and early vitrification.

Successful deployment of microstructure with PIPS in all acrylic resins, requires an assessment of the variables behind the mechanism. Boots and Kloosterboer outlined a model that identifies four events during curing of PIPS formulations; onset, gelation, fixation and vitrification [4]. Maintaining this pattern of events with the mixture we design will be difficult, given the compressed state of events during photopolymerization cure times. Despite rapid cure rates, differences in cure speed for acrylate > (meth)acrylate > vinyl are well understood and could trend with increases in domain size [12]. Full optimization of this portion of the model will have direct implications on the choice of monomers in regards to their cure speed and functionality [10]. We'll avoid highly functionalized acrylates that would compress the events of the PIPS mechanism, "fixing" the block copolymer into the network instead of allowing them to move, associate and separate.

Figure 1 Stages of Curing in PIPS vs Traditional Formulations



As our network is polymerizing through the events outlined in the model, the mixture must be designed to provide a driving force for the block copolymer to assemble at each of those events. With our block copolymer designed with a nonpolar rubber block and a polar exterior block, our monomers should be selected to maximize affinity to the polar portion. Aligning to this thought the polar portion of the block copolymer should remain miscible in the matrix while the rubber portion experiences an aversion to the growing network. As monomer solvent is consumed in the free radicle mechanism, its ability to keep the nonpolar rubber block miscible diminishes, and our onset point is reached. As the network continues to consume monomer, the rubber block continues to grow until our crosslinker gels and subsequently fixes the network.

Figure 2 Desired states of formulation for PIPS alignment
(m) monomer (c) crosslinker (bcp) block copolymer

| | | | | | | |
|---------------------------------------|---------|-------------|----------|-------------|---------------|-----------|
| fully crosslinked network | | | | | m-m-m-c-c-m-c | |
| monomer chains bridge by crosslinkers | | | | m-m-m-c-bcp | | |
| short chains form of monomers | | m-m-m-c,bcp | | | | |
| components in solution | m,c,bcp | | | | | |
| Phase Separating PIPS Model | Liquid | Onset | Gelation | Fixation | Vitrification | Post-Cure |

With a model outlined for PIPS driven assembly of our block copolymers, design of the photopolymer matrix can be outlined for this study with a scope around 3D printable resin targets. Kinetic considerations constrain the design for acrylate monomers to have a single reactive site, while crosslinking oligomers are limited to methacrylate, vinyl or allylic reactivity and exclude acrylate functionality. Polymers in the formulation should be selected based on its ability to provide low modulus domains and target a specific solubility range with each component [3]. Optimal toughness has been observed when there exists overlapping or knitting patterns between phases, promoting excellent interfacial adhesion between domains [7]. For this reason our polymer selection will focus on the use of block copolymers featuring miscible exterior blocks. This effectively reduces the photocurable formulation to a monofunctional monomer, crosslinking methacrylate oligomer and a block copolymer.

Experimental Outline

Formulation design

In this study we will examine resin components that promote a PIPS mechanism to drive out the hydrophobic rubber portions of a block copolymer into discrete domains to improve impact resistance. Given the limitations of the model our starting point formulation (SPF) in figure 3 will consist of a single monofunctional monomer, cross-linker and block copolymer. We will study the effect of each of these components using and their ability to affect the model, referring to the label designation.

| Label | Description | Range | Formulation Contribution |
|-------|------------------------|----------|---|
| BCP | Block Copolymer | 10-40 | design will affect domain size |
| C | Cross-linker | 20-50 | affects time to lock in matrix |
| M | Reactive Monomer | 50-70 | must drive solubility transition |
| | BAPO | +0.5 phr | |
| | <i>Cure Conditions</i> | | <i>600W/in² V-Lamp 100 fpm</i> |

Figure 3 General starting point formulation for systems

Test methods

Dynamic Mechanical Analysis

Analysis of temperature and modulus allows us to evaluate our materials ability to absorb energy and can provide insight into our materials microstructure. Using a ThermoScientific Q800 (DMA) we observe changes in modulus as the material goes through temperature driven transitions from -150C to 250C @ 5C/min. Resulting storage (G'), loss (G'') and $\tan(\delta)$ curves will be plotted and analyzed for presence of rubber inclusions dispersed in the matrix. Specific review of multiple relaxation peaks in our G'' will provide confidence in our PIPS mechanism [5].

Atomic Force Microscopy

Domain size and morphology will be studied with Atomic Force Microscopy (AFM) utilizing a modulus contrast of the material and a topological profile. The AFMs contrast mode will plot modulus across our sample window providing a hardness map. Topographical results will confirm sample preparation and homogenous surface preparation. Overall analysis of the AFM results will describe domain sizes resulting from phase separation.

ASTM D256 – Notched Izod Impact Resistance

Impact resistance via ASTM D256 is carried out with an impact testing apparatus. Samples are notched to provide a direct start to crack propagation and to minimize variability. Samples are placed in an apparatus that allows a hammer to contacts the sample after swinging along a set path from a set angle. As the hammer comes down into the sample, the angular momentum is transferred into the sample which most breaks in two. The angular difference between the hammer in a free swing versus contact the sample is analyzed in a direct energy balance, of which the difference is referred to as impact resistance in units of energy [9].

Results and Discussion

Visual assessment of cross-linker effect

Inside of the PIPS model, time is required for the rubber block to phase separate. If phase separation occurs, given the size of the rubber component in the BCP, visual acuity could be affected. Materials that have domain sizes greater than 400 nm may appear hazy or blue. Knowing that monomer functionality, and group reactivity will affect the gelation time of the mixture, several monomers have been identified for evaluation in figure 4.

| SPF | | varied crosslinker | description |
|------|------|--------------------|-------------------------------------|
| BCP | 10 | DPGDMA | Dipropylenglycol dimethacrylate |
| C | 60 | (EO)BPADMA | 2(EO) bisphenol A dimethacrylate |
| M | 20 | BPADMA | Bisphenol A diemthacrylate |
| BAPO | +0.5 | UDMA | Urethane dimethacrylate |
| | | TMPTA | Trimethylopropane triacrylate |
| | | TMPETA | Trimethylopropane epoxy triacrylate |
| | | DPHA | Dipentaerythritol hexaacrylate |

Figure 4 Formulation outline for cross linkers evaluated for visual acuity

Each of these formulations were cured in bulk at 1/4" thickness using a Fusion V-Lamp at 600W/in² and 100 fpm. When each of these formulations were cured, three visual states of the material resulted. As

shown in figure 5 the observation ranged from clear, hazy and opaque. All of the acrylate functional cross-linkers when used in the SPF cured into a clear state. Only the methacrylate functional cross-linkers resulted in formulations that showed haze or opacity suggesting favorable kinetics for phase separation.

| | Product Code | Description | Viscosity cP @ 25 °C | Molecular Weight | Degradation (°C) | Tg (°C) | |
|----------------|--------------|---|----------------------|------------------|------------------|----------------|-------|
| Monofunctional | SR256 | 2(2-ethoxy)ethyl acrylate (EEOEA) | 4 | 188 | 140 | -55 | Proce |
| | SR324 | C16-C18 alkyl methacrylate | | | | 5 | Proce |
| Difunctional | SR256 | ethylene glycol dimethacrylate | | | | 90 | Fast |
| | SR257 | butylene glycol dimethacrylate | | | | | Tear |
| | SR258 | hexanediol dimethacrylate | | | | | Good |
| | SR259 | HOOMA | | | | | Prox |
| | CV07 | Hydrophobic acrylate est | | | | / | Hyt |
| | SR350AA | triethylolpropane trimethacrylate (TEPTrMA) | | | | $\alpha = 100$ | Fast |

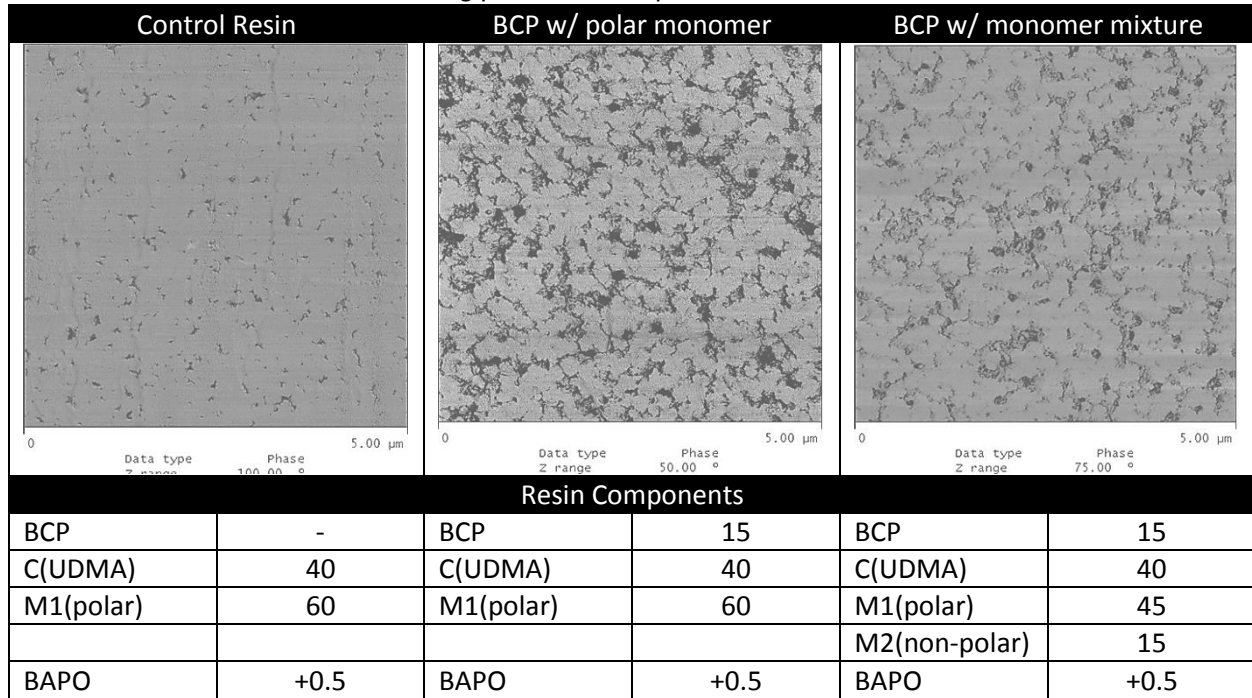
Figure 5 Clarity depiction used for visual assessment of phase separation

Domain integrity with polar and non-polar monomers

As our matrix is progressing through its liquid, onset and gelation stages of polymerization, selection of our monomer solvent needs to drive thermodynamics in a favorable fashion. Considering that solvation and solubility are our major considerations for thermodynamic states of the mixture, we selected a favorable methacrylate cross-linker from previous analysis and studied the replacement of the monomer portion for the mixture. Total replacement of the M portion with non-polar monomers resulted in a clear product, thus we partially replaced portions of the polar monomer with non-polar monomer. These resulting materials exhibited phase separation which we could probe with atomic force microscopy to gauge microstructural differences.

The resulting microstructure appears much more heavily concentrated in rubber domains with the monofunctional monomer chosen exhibits a high degree of polarity. In the AFM image where a mixture of non-polar and polar monomers are used, the thermodynamic drive for the phase separation is reduced. As a result of the reduced driving force, a reduction in domains is observed and the domains are less clearly defined. As our theory of increased mechanical performance is driven by the microstructure allotted through this PIPS mechanism, use of polar monofunctional monomers will be preferred.

Figure 6 AFM results in tapping mode describing difference's in microstructure using polar and non-polar monomers



Block copolymer concentration effects

With the PIPS degrees of freedom constraining the monomer polarity and methacrylate reactivity of the cross-linker, the concentration of block copolymer remains free to vary. Increasing BCP concentration should align with expectations of increased impact performance, however its high molecular weight design will contribute negatively to viscosity. For this portion of the study the block copolymer loading was added to our SPF at levels indicated by figure 7. As expected viscosity increase's with increased block copolymer loading, presenting a useful limitation of the BCP in the 5-20% range.

| SPF | | Concentration of BCP | Viscosity | Tg |
|-----------------|--------|----------------------|------------|------|
| BCP | varied | 0% | 440 cps | 110C |
| C(methacrylate) | 50 | 10% | 2,330 cps | 116C |
| M(polar) | 50 | 20% | 7,200 cps | 101C |
| BAPO | +0.5 | 30% | 55,600 cps | 103C |

Figure 7 Concentration study evaluating BCP levels on viscosity and mechanical performance

While we are limited to the loading of the block copolymer, impact modification has been successful in adjacent technologies at similar levels. To get a gauge on the mechanical performance of the blends in figure 8 we reviewed the storage(G') modulus and tan(delta) using the DMA. The resulting glass transition points shown in figure 7 suggests that the matrix Tg is relatively unchanged. Had the block copolymer remained miscible in the matrix during polymerization we would have expected a mixture effect on Tg and an overall reduction.

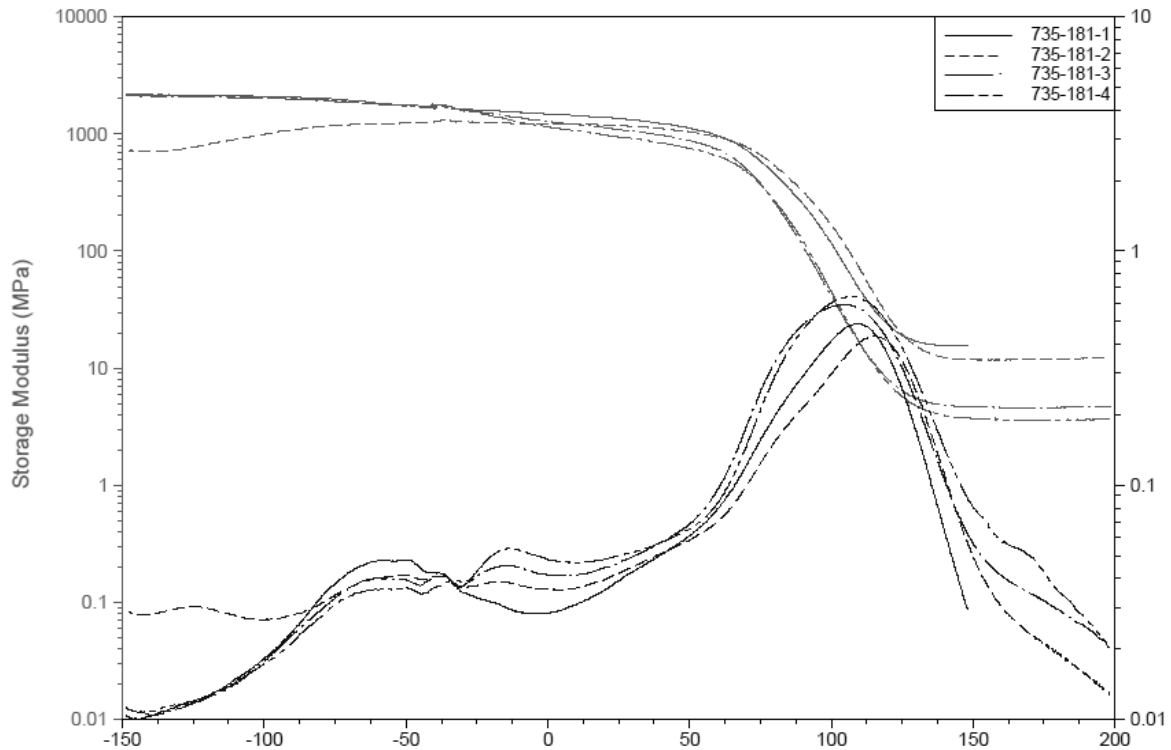


Figure 8 Storage and $\tan(\delta)$ of from -150C to 200C with an increasing block copolymer concentration

Transitioning our analysis to the DMA overlays, we can see our $\tan(\delta)$ depicts three peaks each relating to some relaxation event in the matrix. Typically this very low transition is due to some crankshaft motions in polymers relatively unrelated in this review. The high temperature peak relates to the glass transition of our major network, and is sometimes used to describe the T_g . The presence of a third peak around (-10C) is of particular interest to us. This (-10C) beta-peak suggests another relaxation event, which trends with our BCP concentration. As the rubber portion of our block copolymer has a T_g around a similar temperature, and increasing this concentration increases that peaks response we're confident in that assignment.

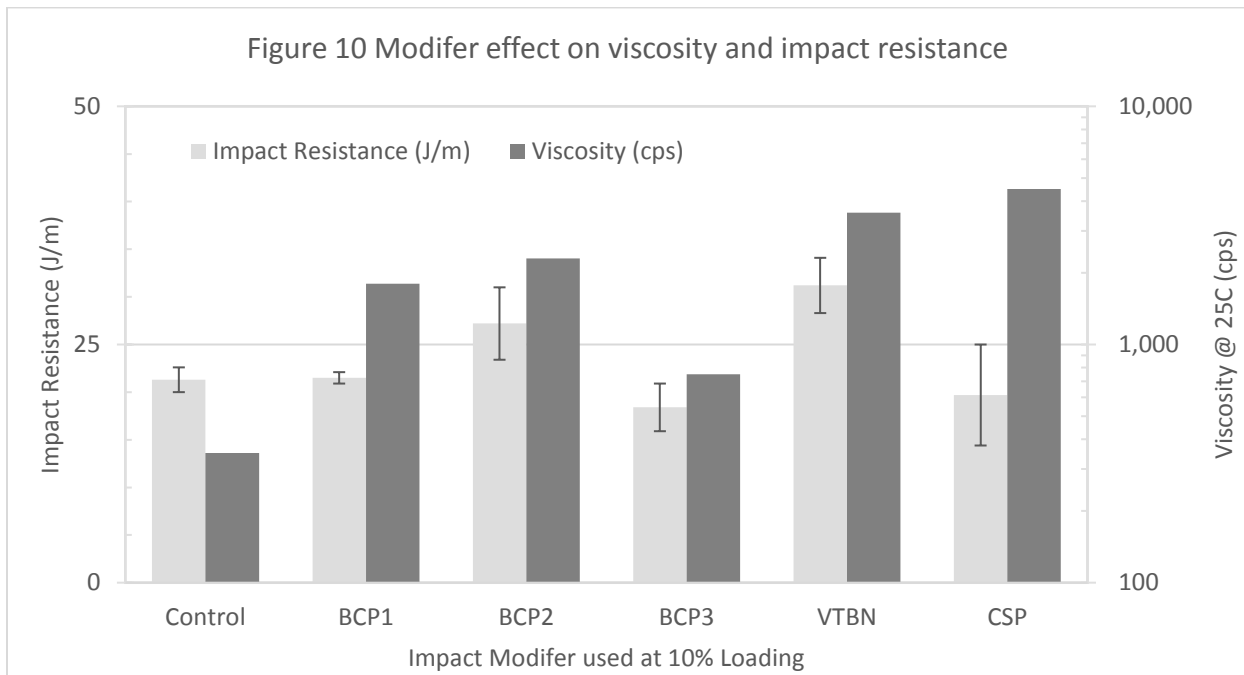
Notched Impact Resistance of impact modifiers

With the formulations components in full alignment with the PIPS model and block copolymer concentration fixed to a suitable range, we can now assess impact resistance. We will contrast a few impact modifiers (IM) to the block copolymers in a series of properties including notched Izod impact resistance. Samples were cured in a bulk fashion using a ¼" x 3" PDMS mold using a 600W/in² Fusion V-Lamp at 100fpm and notched according to the ASTM. Our model formulation has been laid out in figure 9 with descriptions of the impact modifiers used.

| SPF | | IM | Description | Approx. MW |
|------|------|------|--------------------------------|-------------|
| IM | 10 | BCP1 | 75:25 - polar:non-polar | 50,000 g/m |
| C | 45 | BCP2 | 50:50 - polar:non-polar | 50,000 g/m |
| M | 45 | BCP3 | 25:75 - polar:non-polar | 100,000 g/m |
| BAPO | +0.5 | VTBN | <i>Methacrylated Butadiene</i> | 40,000 g/m |
| | | CSP | <i>Coreshell particle</i> | |

Figure 9 Varying types of impact modifier in the SPF outlined

Preparing UVEB formulation for particular applications is rarely a single value optimization effort. Most technologies offer a tradeoff in performance, and in the series of impact modifiers evaluated above we have similar trade-offs. Figure 10 depicts the performance of our materials in notched IZOD impact performance in the left hand axis and the viscosity of the mixture on the right handed axis. As shown in the figure incremental advances can be made with particular impact modifiers at the typical expense of viscosity. In all the cases where block copolymer was just to modulus the impact performance, increases in viscosity were realized. Some of the other technologies that are showcased, depict similar tradeoffs.



Conclusions

Use of polymerization induced phase separation to drive block copolymer assembly has been described in this work. Model variables of kinetic and thermodynamic drivers to cause phase separation of the rubber block of block copolymers have been assigned to particular structures of acrylic monomers and crosslinkers. Use of those constraints promotes phase separation of the block copolymer into discrete domains of submicron levels, and was validated using AFM and DMA analysis. Taking the resin design into the practical world of impact resistance demonstrated 20-30% increases in impact resistance. Increases in impact resistance led to the unfortunate trade in viscosity however suitable levels of block copolymer could still provide incremental advances to the world of toughened photocurable.

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