

Characterization of Poly(isobornyl acrylate) as a Construction Material for Microfluidic Applications

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ABSTRACT: Isobornyl acrylate (IBA) is a photopolymerizable monomer that is employed in microfluidic devices because of desirable properties, such as inertness, transparency, and resolution. However, some of the mechanical properties of poly(isobornyl acrylate) are greatly affected by subtle changes in the manufacturing techniques. In this study, the parameters of exposure time, UV intensity, and aging are varied to study their effect on the material properties of thin samples of isobornyl acrylate construction material (<0.25 mm). Mechanical testing was used to obtain properties, such as elasticity, maximum strength, and maximum strain. It was observed that when using high levels of both exposure time and intensity, the poly-

mers strength was increased. Lowering one of these two parameters immediately reduced the construction materials strength. It was also noted that aging weakens the material in as little as 1 day. In addition, an anisotropic response that produces curling in samples has been studied. It showed to have a negligible effect on the mechanical properties of the material; however it may have a major effect on device quality and shelf-life. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1894–1902, 2007

Key words: tension; stress; photopolymerization; strain; stiffness

INTRODUCTION

In the last few years, photopolymerizable materials have become attractive for microfluidic devices because of less fabrication time, low cost, and require simple protocols. Examples of these materials are polydimethylsiloxane,^{1–4} 2-hydroxyethyl methacrylate,^{5,6} poly(methyl methacrylate),^{7,8} thiolene-based resists,^{9,10} and poly(isobornyl acrylate).^{5,11–15} The material addressed in this study is IBA.

IBA is a photopolymerizable acrylate monomer that has been employed in microfluidic applications because of its desirable characteristics. This monomer, which is used to make the “construction material” for microfluidic devices has the qualities of low viscosity during injection, optical patterning and good resolution for exposure, transparency for visual observation, and low shrinkage during polymerization. In addition IBA polymer is an advantageous construction material because of its inertness. It does not react with common solvents,

such as methanol, ethanol or isopropanol.¹³ The capability of this polymer is to be photopolymerized from the liquid phase in seconds, and simple fabrication protocols make this a desirable polymer to use as a construction material for devices, such as microchannel networks,^{13,14} anchor posts, and a serpentine chaotic mixer in an immunosorbent assay system,¹⁵ “smart” magnetically driven micropumps,¹¹ and “sealing” gloves for micropump actuators¹² among others.

Although manufacturing devices like these is rapid and simple, researchers have observed variability in their final device properties. Many of the differences in properties are caused by subtle changes in manufacturing techniques. An example of this is low stiffness in the material after lowering the UV exposure time by as little as 1 s. This sensitivity has also been detected through preliminary FTIR tests that show that the rate of conversion changes dramatically within a second of exposure. Such changes in stiffness can lead to unfavorable outcomes such as viscoelastic failure of a micropost because of bending. Another concern is how the polymerized material might change over time, which influences how long a device can be expected to function predictably. Additionally, there exists non-uniformity in the way different researchers craft the “same” construction material, which makes it difficult to determine the reasons why a finished product may not have functioned properly. If these issues

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are resolved, scientists will be able to spend more of their effort on the microfluidic applications than on the actual fabrication of the device.

The knowledge of how the material properties of the construction material are affected by variations in manufacture can be used as an engineering tool for design of microfluidic devices. Some of the parameters that can be varied during fabrication are as follows: UV exposure time during curing, UV intensity, crosslinker concentration, and aging. This study evaluates the mechanical properties of the IBA construction material, such as strength, elasticity, and elongation of the construction material, showing how minor changes in fabrication techniques can affect the final product. The values of the experimental parameters are limited to a finite range by the analytical techniques employed. High and low levels within these ranges allow mapping of the parameter space. Care was taken to utilize sample preparation techniques that are similar to those used to fabricate the microfluidic devices to ensure relevance of the results to microfluidic applications.

MATERIALS AND METHODS

Sample preparation

Polymer composition

Samples are fabricated with the same technique that is used for microfluidic devices made from IBA, *in situ* polymerization.¹³ The prepolymer mixture traditionally used for channel walls and posts in microfluidic systems¹³ consists of the monomer, IBA [Surface Specialties UCB], a crosslinker, tetraethylene glycol dimethacrylate, and a photoinitiator, 2,2'-dimethoxy-2-phenyl-acetophenone. The quantities of each are 92, 5, and 3 wt %, respectively. This prepolymer solution is referred to as "construction material" because of its ability to form walls and other structures.¹³ Data is reported for tetraethylene glycol dimethacrylate crosslinker concentration of 5%, based on standard use reported in the literature.

The IBA was purchased with 82–130 ppm of 4-methoxyphenol, an inhibitor that prevents spontaneous polymerization during storage. This is a low enough amount to avoid having to distill the IBA before polymerizing.

The reactants are weighed, combined in a brown bottle to avoid spontaneous polymerization, and sonicated to speed dissolution process or allowed to dissolve overnight.

Parameters

A number of parameters are expected to have an impact on material behavior under mechanical stress. The results reported here explore exposure time, intensity of ultraviolet light, and aging.

Exposure time. This refers to the amount of time that the prepolymer mixture was exposed under UV light at a given intensity. The highest exposure time used was 13.5 s because longer exposure would produce sample strength that was above the limits of the tensile test machine. The lowest exposure time chosen was 10 s because lower values would produce a gel-like sample that is difficult to handle and test.

Intensity of UV exposure. This refers to the watts per area of UV light that was used to cure the sample. The highest intensity value chosen was ~ 20 mW/cm², and the lowest intensity value chosen was 12 mW/cm², using the same criteria that were followed for exposure time.

Aging. This refers to the amount of time that has passed between curing to actual testing. This parameter varied between a high value of 1 day of aging and a low value of 0 days, in which the samples are taken directly to tensile testing. The high value was chosen as not more than 1 day to avoid excessive curling and brittleness, which would cause handling difficulties.

Crosslinker density was also studied but found to be a statistically insignificant parameter within the range studied. Samples at a low 4 wt % crosslinker had similar results for high 5 wt % crosslinker. (Data not shown.) A wider range was not studied because below 4% the samples were too soft for handling and over 5 wt % the sample had higher strength than the tensile tester was able to achieve.

Specimen fabrication technique

Special considerations must be taken when preparing the test samples to maintain consistency from sample to sample and relevance to standard microfluidics manufacturing techniques. Properties of materials used in microscale applications are sensitive to the preparation techniques employed. For example, specimens that are prepared by injection may exhibit polymer orientation effects. This is especially pronounced in thin samples.¹⁶ The *in situ* polymerization technique chosen for this study is the same technique that is used to make microfluidic devices. In the case of microfluidics, the prepolymer is injected into a cartridge and then photopolymerized through a mask with the device design. For this study, *in situ* polymerization of sample consists of injecting the prepolymer solution into a square mold, covering with a mask of high-resolution film designed with the sample shape needed, and exposure to UV light. The exposed area is photopolymerized into the mask shape, whereas the unexposed areas remain as prepolymer, and are washed away.

Since the microfluidics application generally uses films of 0.25 mm or less, the sample thickness was chosen to be 0.25 mm with a tolerance of ± 0.1 mm. Using this dimension and ASTM 638-02, Type I

specimen, the dimensions of width, length, gauge length, etc., were determined. Type I specimen is used for thin specimens with thicknesses less than 7 mm. These dimensions are summarized in Figure 1 and Table I. The mask, containing five identical samples with these dimensions, was printed on high-resolution transparency film. The image printed on the film is the negative of the desired polymerized product.

The mask is then included in a stack for *in situ* photopolymerization as illustrated in Figure 2. The first glass sheet is placed as a base and then a small piece of a polymeric thin film of Melinex[®] over the glass, to avoid adhesion of the poly(IBA) to the glass. Between the glass and the film, it is recommended to place a drop of water to achieve adhesion through the capillary effect to obtain maximum flatness of the substrate. Over these two layers, the flat stainless steel rectangular frame is located. Within that space, prepolymer solution is injected until a convex meniscus is visible, ensuring the space is entirely occupied. The mask is positioned over this layer; another drop of water is added to achieve the capillary effect between the mask and the next layer, which is the second sheet of glass. This second drop of water and glass sheet is very important because without it, the prepolymer solution will tend to create suction on the mask, pulling the center of the mask down causing the samples to have an uneven thickness distribution.

This arrangement is then submitted to ultraviolet light [Acticure EFOS A4000] filtered to a wavelength

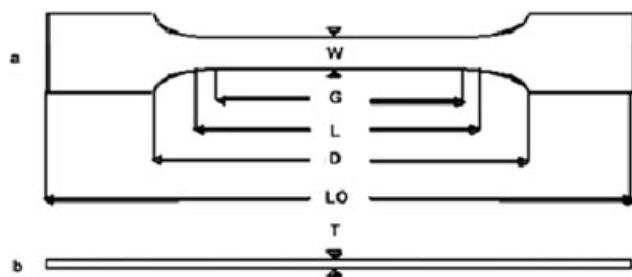


Figure 1 (a) Top view of sample dimensions. (b) Side view of sample dimensions.

TABLE I
Tensile Test Sample Dimensions

Feature	Symbol	Size (mm)
Thickness	<i>T</i>	0.25 ± 0.1
Width	<i>W</i>	2.0 ± 0.1
Length of narrow section	<i>L</i>	8.8 ± 0.1
Width overall	WO	3.0 ± 0.1
Length overall	LO	25.0 ± 0.2
Gage length	<i>G</i>	7.7 ± 0.1
Distance between grips	<i>D</i>	18.0 ± 0.2
Radius of fillet	<i>R</i>	12.0 ± 0.2

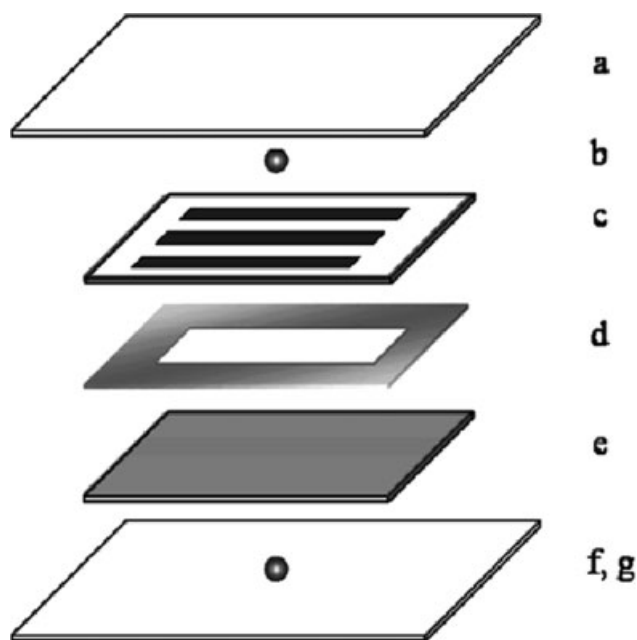


Figure 2 Sample preparation stack. (a) Glass sheet for uniform thickness, (b) drop of water for capillary effect, (c) mask for *in situ* polymerization, (d) stainless-steel frame with rectangular cavity to inject prepolymer mixture, (e) Melinex[®] film, (f) second drop of water for capillary effect, and (g) glass sheet base.

of 365 nm with intensity (*I*) and time (*t*) according to the desired test described in "Parameters" section. The UV light source is located 8 in. from the assembly.

When removing the tensile test samples from the glass and film sandwich, special care was taken to prevent prestressing the material or creating defects. The excess prepolymer was then washed off with deionized water and the samples were detached from the edge of the rectangular frame by use of a razor blade.

Storage conditions between the time when the sample is fabricated and tested is another factor that can affect the results of the mechanical testing. It was observed that a sample that was stored in air from the time of fabrication to the time of testing can undergo severe curling (Fig. 3), damaging the sample. Regardless of the method used for storage it

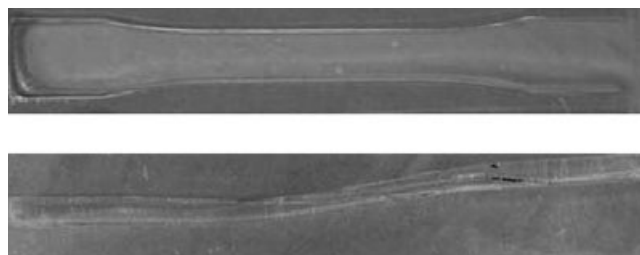


Figure 3 Top: uncurled sample. Bottom: curled sample. Curling in this sample has taken place in air after ~ 1 h.

was found that some curling of the material occurs in the direction opposite to the side closest to the UV light source. To minimize this effect, the samples are kept between two clamped glass slides lined with the same polymeric film used during curing. Additional details on this issue will be addressed in "Material inhomogeneity and curling" section.

Tensile testing

The mechanical properties of the material were studied via tensile tests. An Instron Model 5548 MicroTester with a 10 N load cell was used to carry out this characterization. The tensile test specimen was located in the grips of the instrument, and the initial grip separation noted. The testing was carried out with displacement control at 10 mm/s and data was collected every 0.1 s.

Strains were calculated by dividing elongation by the original grip separation. Stresses were calculated by dividing load by the original cross-sectional area. The cross-sectional areas were obtained by slicing a portion of the sample in the gauge length area after testing was completed. This small segment was located under a Nikon Eclipse microscope with a Diagnostic Instruments camera and measured using MetaMorph software. Given that the cross section varied from sample to sample and to some extent within single samples, three slices were obtained from each sample after testing. The slices were obtained from the two extreme locations in the gauge length and one from the center. The thickness of each slice was measured and the obtained cross sections were averaged. This average cross section was the value used for calculating the stress in each sample.

RESULTS AND DISCUSSION

As was stated before, the parameters of UV intensity, exposure time, and aging have been studied to understand their effect on the construction material and its properties. It may be noted that the parameters were tested within a narrow range of values. UV intensity was tested for 12 and 20 mW/cm²; time at 10 and 13.5 s. Aging was studied for the length of one day. In addition, crosslinker concentration was tested for 4 and 5 wt % and the results were nearly identical, making it an insignificant factor. (Data not shown.) In the case of all of the parameters, the chosen ranges of values were chosen according to what was relevant to the application and what was physically possible to test with the available equipment. As discussed earlier, lower exposure times, UV intensities, and crosslinker densities made soft and/or brittle samples to the extent that it was impossible to handle without prestressing

or causing imperfections. These imperfections would then give rise to cracks during the testing that would not have happened otherwise. The same would happen if aged for more time than one day. Higher exposure time and intensity would make the sample be able to withstand maximum elastic stress values larger than the tensile tester was able to achieve given the sample size and load cell used.

In agreement with ASTM 638-02, at least five specimens were tested for each parameter set. Since many samples needed to be discarded due to slippage, rupture at the grip, and visible defects, 10 samples were always fabricated, but in most cases only four to six samples were actually considered as reliable data sources.

The experimental results obtained are summarized in Figures 4–8 and 10. They are presented as follows: stress–strain plots shown are representative plots for the samples that most closely matched the average values for modulus of elasticity, maximum elastic and fracture stresses, and maximum strain. The maximum elastic stress was obtained from the point in the diagram where elastic deformation ended. Fracture Stress was obtained from the point where the sample ruptured. Modulus of elasticity was obtained by finding the slope in the linear range of the curve. Maximum strains were obtained from the maximum strain at rupture. Other data are presented by means of histograms whose height represents the average value of the samples with error bars that represent the standard deviation of the values.

Statistical analysis for the difference in means was carried out for distributions that needed to be compared and had overlapping error bars. The method utilized to analyze these samples is a *t*-statistic hypothesis test with a level of significance of 0.1, except for the case where the effect of aging is being studied, and a level of significance of 0.2 is used.

There are cases in some sample groups where a data point fell considerably far from all other data points. These points were considered outliers because of "gross errors" and were not believed to show any important aspect of the behavior of the material strictly in the case that was being considered. In situations like this, a statistical *q*-test may be constructed that will indicate if those values may be rejected.¹⁷ All data points that were eliminated can be justified statistically and circumstantially. They all exceeded a critical value at the 99% confidence level. The physical circumstances that validate elimination of these points fall into one of the following categories: high variation in cross-sectional area distribution within single sample; high percent difference in average cross-sectional area of the single sample to average cross-sectional area of sample group; or a defect in the sample that had not been detected prior to testing.

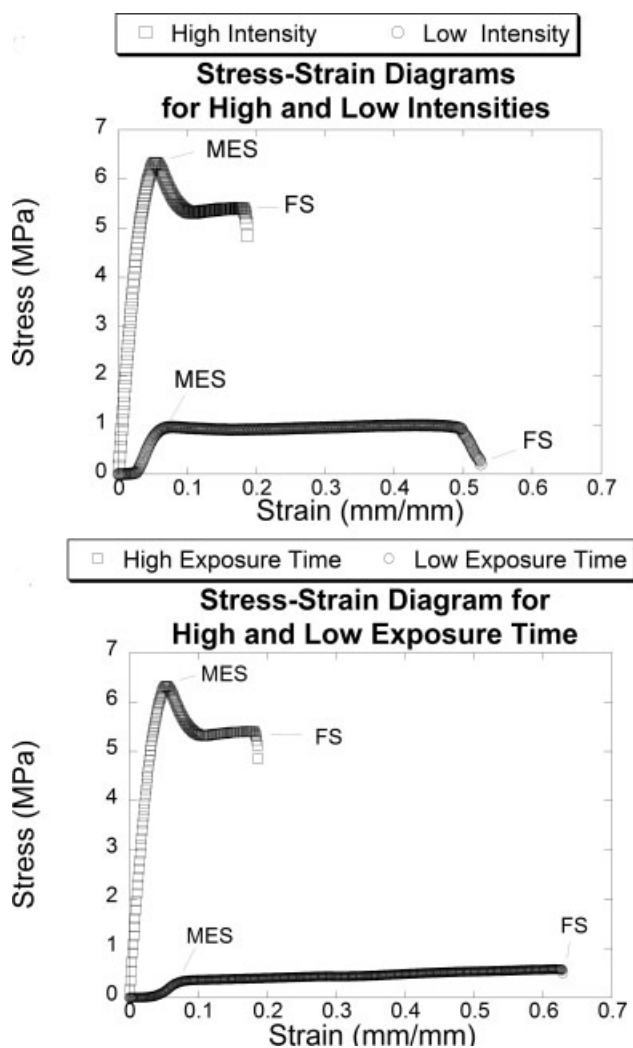


Figure 4 Representative stress–strain diagram showing the effect of UV intensity (top) and UV exposure time (bottom) in mechanical behavior of IBA with 5 wt % crosslinker in the prepolymer mixture. Intensities shown are 12 and 20 mW/cm² and exposure times are 10 and 13.5 s. The maximum elastic stress is labeled MES and the fracture stress is labeled FS.

Influence of time and intensity on the properties of the construction material

Figures 4, 5, and 6 compare the effect of intensity and time on the material properties of IBA. In this group of figures all the samples have been produced with the standard amount of crosslinker, 5 wt %. Figure 4 shows how the behavior of the material changes when high values of intensity (top) and exposure time (bottom) are compared with low values of intensity and exposure time. It is evident from these diagrams and the histograms in Figures 5 and 6 that both intensity and exposure times have similar effect on the properties of the construction material. Lowering intensity or lowering exposure time individually both lower the modulus of elasticity and

increases the maximum strain of the sample. Figure 5 shows that lowering one of these two properties generate a material with lower stiffness. These two charts show how the modulus of elasticity decreases an order of magnitude when a low intensity or low exposure time is used. They also show that when both a high exposure time and a high intensity is used modulus of elasticity increases. This is the type of effect that would be desirable in application such as microposts or other moveable parts in a microfluidic device.

At a first glance, it also seems in Figure 6 that maximum strain decreases with higher exposure time and intensity, which would produce a material with high stiffness. However, the large overlapping error bars on the histogram make it difficult to hold this conclusion with confidence. A statistical *t*-test showed no evidence that that maximum strain is affected by changing the exposure time or the

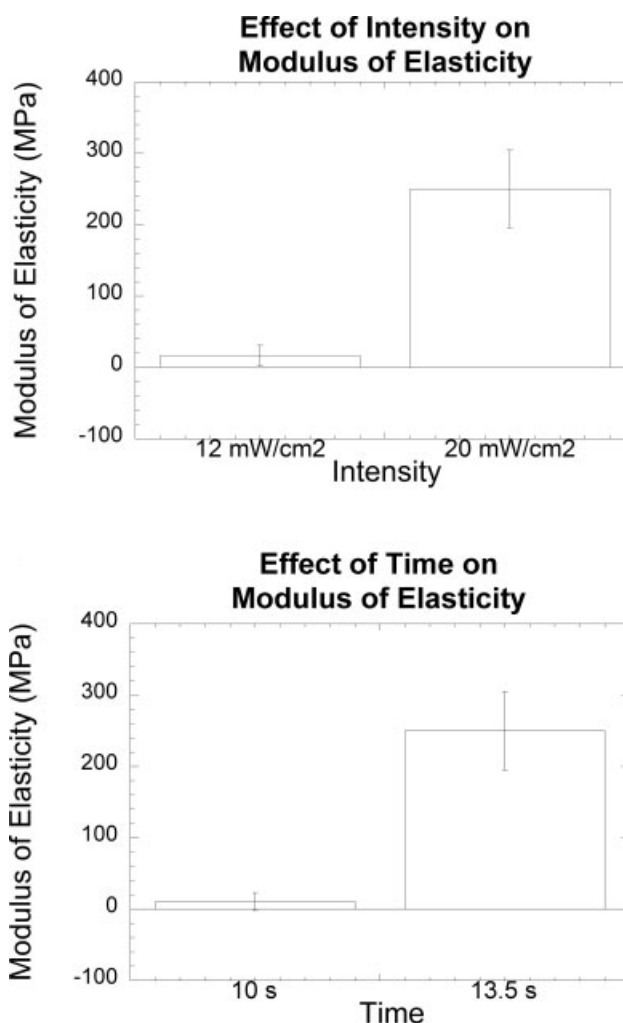


Figure 5 Comparison of the effect of UV intensity (top) with the effect of exposure time (bottom) on the polymers modulus of elasticity. Intensities shown are 12 and 20 mW/cm², and exposure times are 10 and 13.5 s. Construction material has 5 wt % crosslinker.

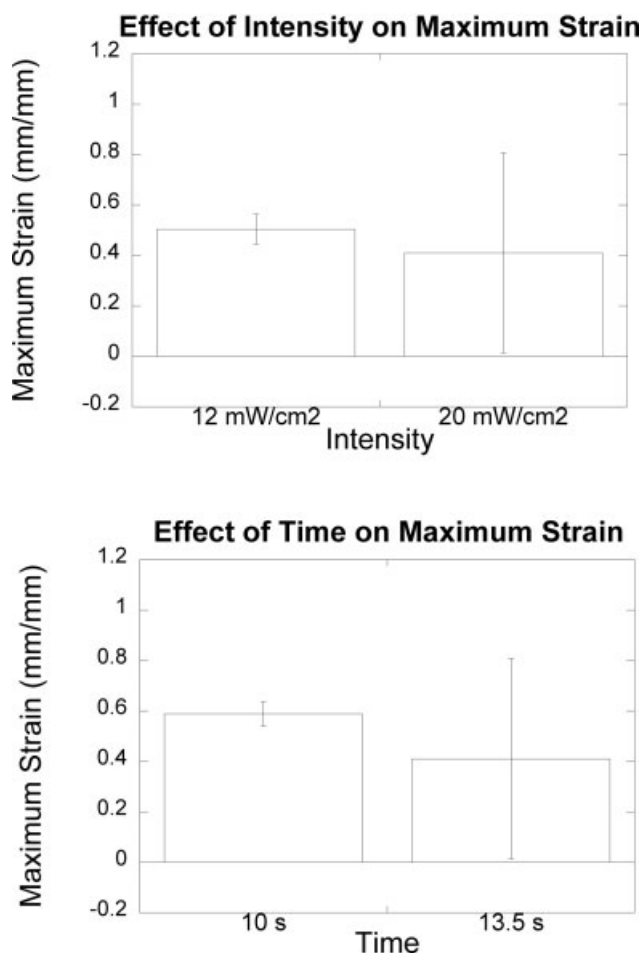


Figure 6 Comparison of the effect of UV intensity (top) with the effect of exposure time (bottom) on the polymers strain. Intensities shown are 12 and 20 mW/cm², and exposure times are 10 and 13.5 s. Construction material has 5 wt % crosslinker.

intensity. Even after eliminating outliers from the low intensity and low time groups, the difference was not provable.

It is important to recognize that high stiffness can only be achieved when both of these parameters are high. In Figure 5 top, the histogram showing results for low intensity has been produced with a high exposure time, while in Figure 5 bottom, the histogram showing results for a low exposure time has been produced with a high intensity. This tells us that the sample is not dependent only of the energy dose of UV light (watts per area times exposure time), but on the individual parameters of both intensity and exposure time. As a result, the parameters of exposure time and intensity are not interchangeable. The importance of this statement is to realize that it is not possible to make up for low intensity by increasing the exposure time because there will be a loss in stiffness and strength, even if your energy dose product is high. The lowering of either one of the parameters will

cancel out the strengthening effect of the other parameter. Always consider that “high” and “low” values are meant to be relative to the application.

Influence of aging on the properties of the construction material

The effect of aging on the construction material was tested and results are shown in Figures 7 and 8. For samples that are 1 day old, there is a decrease in maximum strain and a decrease in modulus of elasticity. The decrease in strain after aging was verified by means of a *t*-test with a significance level of 0.2. With the lessening of these two properties the material becomes less stiff (low modulus) and more brittle (low elongation). An outlier was eliminated in the above data set that was suspected to have an undetected defect, since the sample fractured before undergoing any plastic deformation. Also, the sample had a higher area than all of the other samples of the group. Further justification for eliminating the data point was obtained using a *q*-test at 99% confidence level.

The effect of aging should be acknowledged because it can have a negative impact on the life of a microfluidic device. Researchers have noticed that, in devices that have been fabricated a day before use, cracks may be found in the IBA construction material. Devices often may only be used one time, causing the researcher to have to spend valuable time in fabrication of the apparatus that would rather be spent on applications. This is also important because it shows that microfluidic devices with intricate parts made from this material have low shelf life, which means that they must be made and

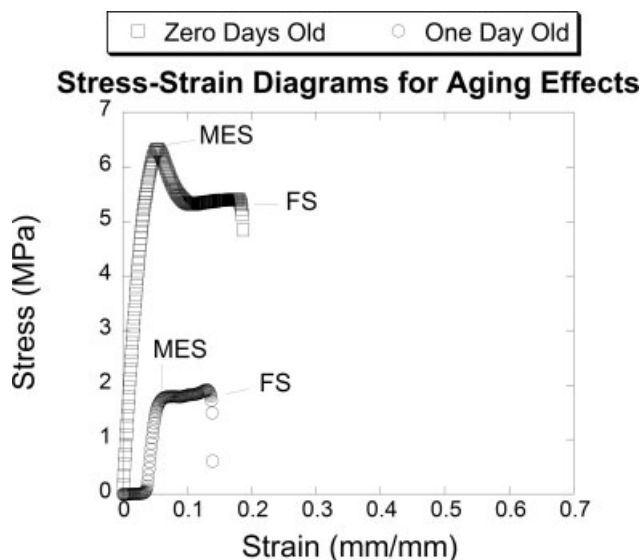


Figure 7 Representative plot showing the effect of Aging on the material properties of construction material with 5% crosslinker. The maximum elastic stress is labeled with the acronym MES and the fracture stress is labeled FS.

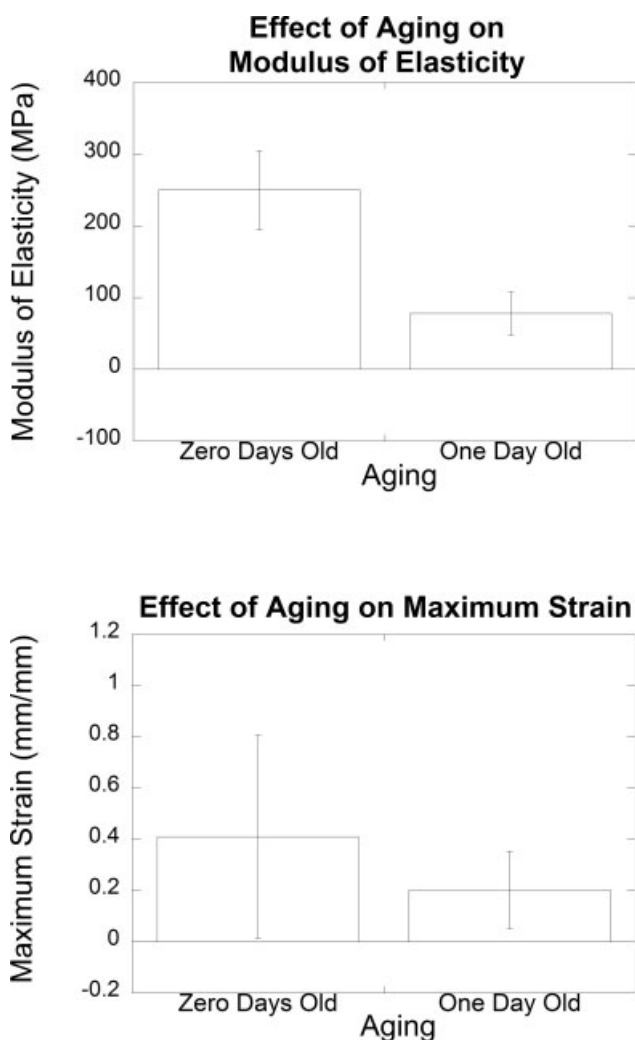


Figure 8 Histograms showing the effect of aging on modulus of elasticity (top) and strain (bottom).

immediately used. This may not be as significant of a problem for channel walls or the bulk of the device as it is for movable parts, posts, or other components within the channels where there is fluid flow.

Material inhomogeneity and curling

Aging can also be observed in samples through curling (Fig. 2). Curling of a sample always takes place away from the side closest to the UV source, regardless of which side it is resting on or the media that surrounds it. A possible explanation is that there is less excess monomer on that side of the sample because it has had more direct contact with the UV and it has undergone more polymerization. On the other side of the sample, there may be slightly more excess monomer, and shorter polymer chains. As time passes, the excess monomer can evaporate and the material experiences shrinkage on the side with shorter polymer branches causing curling. Some of

this monomer evaporation may be the cause of the decreases in modulus and elongation, although from the tensile tests employed it is difficult to study this anisotropic behavior. It is possible that having short polymer chains on one side causes the sample to have low elasticity and begin to crack on that side, given that it does not have much freedom to stretch uniformly and for chains to slip past each other.

A simple gravimetric test was carried out to evaluate if indeed there was excess monomer in the sample susceptible to evaporation. Samples of the material were placed in a 70/30 methanol/hexane solvent mixture for the monomer that was chosen through a thin film chromatography experiment. The samples were placed in this solvent and weighed on an analytical balance over a period of 24 h. It was found that the mass of the polymer sample did decrease to $(95 \pm 3)\%$ total of its original mass. This loss of monomer occurred within the first hour of aging. Aging experiments done in air are expected to also have monomer loss, but at a slower rate.

Another possible cause for curling in the material could be the absorption of water. It has been seen in other polymeric materials that absorption of water has decreased the modulus of elasticity.¹⁸ To test this hypothesis the samples were studied in different humidity levels. No observable differences were found in samples aged in very humid air (RH 90%), samples aged in a chamber with desiccated air (RH 16%), and samples aged in the local lab air (RH 30%). The criteria used were speed of curling, degree of cracking, and texture. All samples behaved in the same manner, curling at the same times and cracking at the same times after curing (data not shown).

The curling observed with aging also occurred as a function of the intensity of the UV light at which it was cured. As stated previously, the material curls in the direction opposite to the side that is closest to the UV light source, the likely cause being a gradient in polymerization across the thickness. Since these samples have a thickness of only 250 μm , material must absorb a significant amount of UV light for such a gradient to form. Experiments were performed to gauge the amount of absorption taking place through the thickness of the sample while it is polymerizing. In this experiment, the intensity of the UV light shined on the sample was measured under the curing stack, through the glass, mask, and Melinex sheet without the prepolymer mixture and then with the polymer mixture.

It was found that by the time the UV light reaches the opposite side of the material, its intensity was $\sim 14\%$ less than in the initial intensity when using high intensities. If a low intensity is used it was $\sim 55\%$ less. Thus, as the intensity decreases, the degree of curling increases. This can be observed qualitatively in Figure 9, where specimen cross

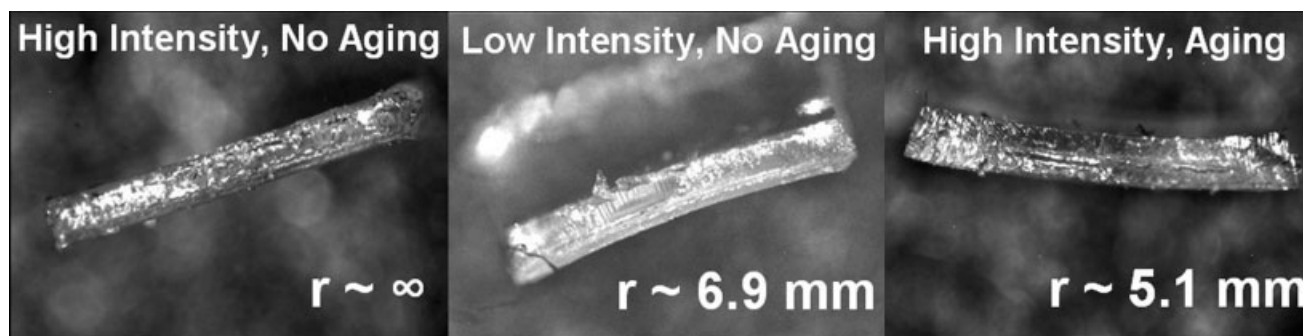


Figure 9 Left: Cross section of sample specimen cured at a high intensity and no aging. There is no curling in the cross section. Center: Cross section of sample specimen cured at a low intensity and no aging. Although the sample has not been aged, there is evidence of curling due to the nonuniformity of the UV intensity through the depth of the sample. Right: Cross section of sample specimen cured at a high intensity and subjected to aging. A specimen that started out comparable to sample on the left has begun to curl with the passage of time. Radius of curvature, r , indicated for each. Curling in these samples has taken place in air less than 30 min after release from storage methods described in Material and Methods.

sections that have been cured with different intensities are shown.

Not only does the intensity vary with depth, but as the reaction progresses and vitrification of the polymer advances, the intensity also decreases. This was determined by performing the experiment above and taking measurements at 5 s and at 10 s of curing and determining how much the intensity decreased. Therefore there are two factors influencing the reduction of intensity, depth of the material in the sample thickness, and progression of the reaction.

This lack of uniformity of intensity through the thickness causes the sample to develop different properties in different locations in the sample, making it inhomogeneous and anisotropic. In addition to IBA, other photopolymers used in microdevices are

also subject to this inhomogeneity caused by decrease of intensity as the UV light travels through the material and the polymerization progresses.

Although the mechanical properties of the material are greatly affected by aging, it should be noted that the curled geometry of the specimen does not affect the material properties investigated. Under the sample preparation conditions reported here, the curvature of the sample cross section (as seen in Fig. 9) was relatively subtle.

Appreciating this phenomenon is important for device design. For the practical matter of device performance, securely fixing a feature within the device may hinder or at least delay curling in the same manner as clamping did when storing the tensile test samples. For instance, walls, one of the most

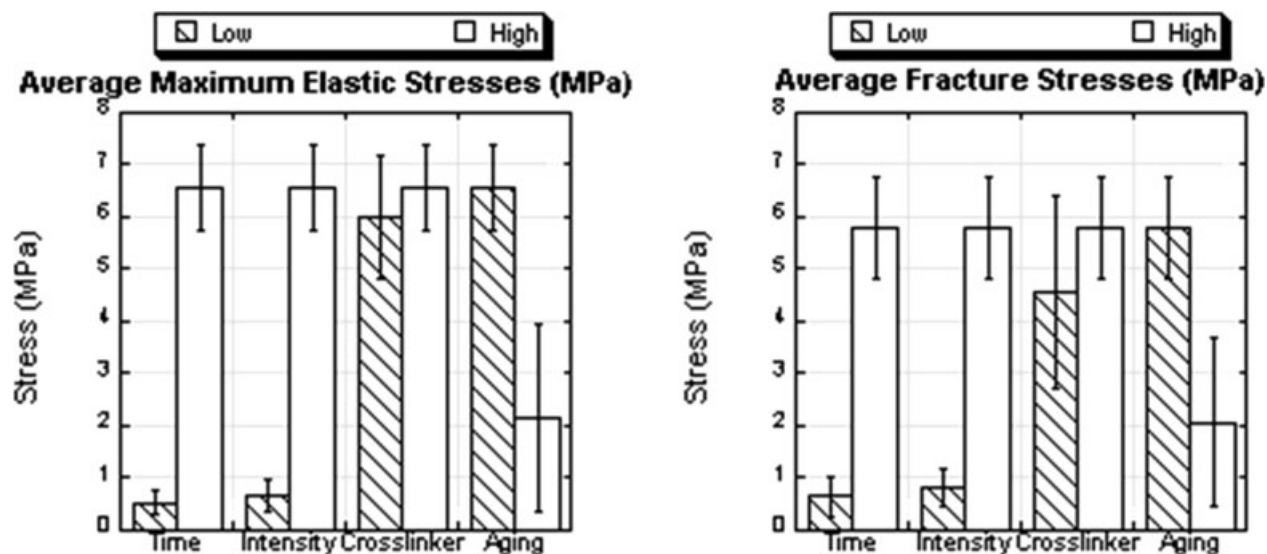


Figure 10 Effect of UV intensity and UV exposure time on the material properties of IBA with 5 wt % crosslinker in the prepolymer mixture.

reliable features in microdevices, are usually surrounded by glass and polycarbonate on five out of six sides. Extremely thin posts that are fixed only on one side have been seen to suffer bending. This can be due to the phenomenon described here. In cases like this, it may be necessary to use a different material or take measures to evade the problem during fabrication.

Maximum elastic and fracture stresses

The maximum elastic stress and fracture stress is also affected by variations in fabrication parameters. Figure 10 shows how these two stresses vary with exposure time, intensity, crosslinker concentration, and aging. For a decrease in the first two parameters, maximum elastic and fracture stresses decrease. This is additional support for the similarity in the impact on material properties of exposure time and intensity. A small part in a microfluidic device made from this material will be more resistant to forces if a combination of high time and high intensity is used to fabricate it. The effect is a difference in strength in order of magnitude. It can also be observed from the charts that fracture occurs more commonly at a lower strength, before the onset of yielding. Therefore, the devices will firstly begin to fail by plastic deformation, although the phenomenon may be subtle enough that it may not be noticed until the material begins to crack. Aging decreases maximum elastic and fracture stresses in a similar way that time and intensity does. After just one day of aging, the strengths decrease considerably.

CONCLUSIONS

The material properties of microfluidic devices made from IBA construction material can be greatly affected by changes in parameters during fabrication. The parameters tested were exposure time, intensity, and aging. If time or intensity is reduced, elasticity, maximum elastic stress, and fracture stress is reduced significantly, weakening the material. Variations in UV intensity and exposure time cause similar effects on the material properties of construction material. To obtain stiffer, stronger polymers, intensity of UV and exposure time should both be

increased. The lowering of either one of the parameters will cancel out the strengthening effect of the other parameter. Therefore, when reporting curing factors, it is not enough to speak of energy dose, the individual parameters of intensity and time should be stated. Aging causes weaker, brittle samples. It was found that aging and decrease in modulus may be caused by evaporation of excess monomer. Other studied effects such as humidity and curvature have no effect on the decrease in modulus. Curling is a result of aging as well as the intensity and rate of reaction. If higher intensities are used curling will decrease, increasing the shelf-life. These results provide guidance to device designers enabling fabrication protocols that will produce the desired properties in the final device.

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