Alternative Test Methods for Quantification of Elastic Behaviors in UV/EB Cured Oligomers



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Digital light projection (DLP) and stereolithography (SLA) printing technology has created the ability for end users to rapidly generate custom—fabricated 3—dimensional objects used in a wide range of applications. As this industry has matured, the focus has shifted from rapid prototyping to the production of finished goods. The highly cross—linkable range of thermoset UV—curable materials is ideal for creating rigid 3D—printed structures, but creating flexible or elastic parts with excellent print definition can be challenging, particularly due to viscosity limitations of the mainstream UV—curable printing processes.

Formulators commonly understand that the physical properties of UV-curable materials are directly influenced by the composition and structure of the oligomers and monomers used in the system¹ - the bulk properties of the cured resin are primarily a function of the oligomer structure, while the fine tuning of other formulation parameters can be achieved by careful selection of monomers and additives. In flexible thermoset systems, the higher molecular weight oligomer component plays a stronger role in the overall formulation properties by providing the necessary reduction in crosslink density that typically corresponds with elastic or flexible final properties. Because elastic, high rebound systems derive most of their properties from the backbone oligomer, it is crucial to understand the impact of backbone material selection, crosslinking chemistry, and overall molecular weight on the final properties of the cured resin.

Common techniques for measuring the elastic properties of polymers have been developed over the years such as tensile set (ASTM D412) and rebound resilience (ASTM D7121 and ASTM D2632). Both test methods are adequate for quantifying the amount of elastic rebound a material exhibits after stressed, however, neither test addresses how quickly that response occurs. For this study, thin film dynamic mechanical analysis (DMA) was used to determine the cured system's elastic behaviors exceeding the limited set of information accessible via other test methods. The DMA can consecutively collect stress and strain data by first applying a stress to a set strain and then releasing the stress to record the recovery. This feature allows the total elastic rebound, reported as strain recovery, along with the rate of recovery to be quantified in one test.

This investigation will explore common structures used in oligomer synthesis to discern the structure-property relationships as it pertains to elastic behavior in the form of strain recovery and rate of recovery. Furthermore, this study will evaluate the ability to model strain recovery from other commonly measured properties, such as tensile properties.

Testing

Model formulations (see Table 1) were mixed until all solid components were dissolved, and the mixture was homogeneous. Cured test specimens of each formulation were prepared according to the relevant test methods identified below and cured with a broad spectrum Dymax 2000–EC flood curing unit for 2 minutes per side. The irradiance was measured at approximately 50 mW/cm². Specimens were allowed to rest for at least 12 hours at ambient temperature before testing.

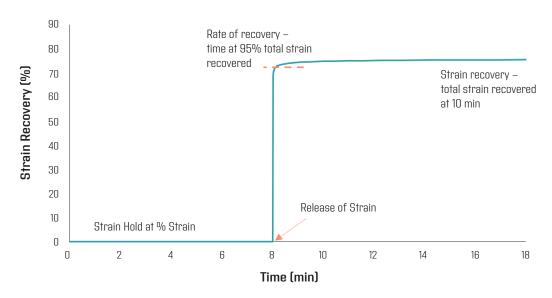
Table 1. Model Formulation

Component	Weight (g)
Oligomer	98
Omnirad 184	2

Strain recovery testing was performed on TA instruments DMA Q800 with single screw thin film clamp in stress relaxation mode. Rectangular films with nominal dimensions of 10 mm by 20 mm by 0.5 mm were tested. A normal force of 0.001 N was applied to the films before the sample's initial length was measured. The temperature for this testing was held constant at 25°C. After the initial isotherm, a stress was applied to maintain a constant strain for 5 minutes. Next, the stress was released, and the sample was allowed to recover for ten minutes. Percent strains explored for this work were 25% and 50%. Although the strain recovery values vary at different strains, the trends seen are consistent, regardless of the amount of strain applied to the system. The data collected at 50% strain was selected to be presented due to the larger differences seen in strain recovery between the variables studied. Strain recovery was calculated with the following equation:

 $\frac{(strain\ under\ stress) - (strain\ after\ recovery)}{Strain\ under\ stress})X100$

Figure 1. Representative graph of strain recovery response from DMA



For this study, speed of recovery is defined as the amount of time the sample took to return to 95% of its maximum strain recovery. The maximum strain recovery value for this testing is the amount of recovery observed at the end of the ten—minute recovery time.

Molecular weight of the oligomers was determined by gel permeation chromatography (GPC) in accordance with ASTM D5296–19. GPC analysis was done using a Shimadzu gel permeation chromatography instrument with a refractive index detector. THF was used as the mobile phase at a flow rate of 1 mL/min. Oven temperature was set to 40°C and separation occurred using an Agilent ResiPore 3µm HPLC column.

Glass transition temperature (Tg) and storage modulus were assessed using a DMA per ASTM D648. Specimens were tested using a TA instruments Q800 with a dual cantilever geometry in multi–frequency strain mode at 1 Hz frequency while strained to 0.2%.

Durometer hardness testing was performed according to ASTM D2240. Durometer readings were done using an Asker CL-150 constant loader tester attached to an A-scale durometer.

Type IV "dogbone" specimens were cast and cured for tensile mechanical testing. Tensile properties of all specimens were obtained using an Instron tensile tester and related software according to ASTM D638. Specimens were extended at a strain rate of 25 mm/min.

Tear testing was done in accordance with ASTM D624.

Rectangular samples with a thickness of 3 mm were cured and tear test samples were punched out using a "type B" die

on a hydraulic press. Specimens were extended at a strain rate of 500 mm/min on an Instron tensile tester.

Results and Discussion

In general, UV-curable urethane oligomers are the product of the following reactants: 1) a hydroxy-functional capping agent containing at least one olefin capable of undergoing free radical polymerization, 2) a diisocyanate, and 3) a polymer backbone containing at least one but most commonly two hydroxyl groups. The molecular weight of the final oligomer can be modified by one of three ways: 1) increasing the molecular weight of the starting raw materials, most often the polyol, 2) manipulating the diisocyanate to polyol ratio and/or 3) introducing low molecular weight hydroxyl functional chain extenders. All oligomers presented in the following work are designated with a generic name PU followed by a number. To make comparisons clearer, the independent variable being explored is identified within parentheses directly following the oligomer identifier.

I. Capping Reagents

Acrylate and methacrylate chemistries are the two most common capping agents present in UV-curable urethane oligomers, which will be the first variable discussed in this investigation of strain recovery. Four oligomers were compared to determine the effect that capping chemistry has on strain recovery. PU-1 (A) and PU-2 (MA) are almost identical except for the capping reagent and inhibitor used in synthesis. As inhibitor has not historically been shown to significantly alter cured mechanical material properties, the capping reagent can be considered to be the only significant difference. With PU-3 (A) and PU-4 (MA), only the capping reagent was changed.

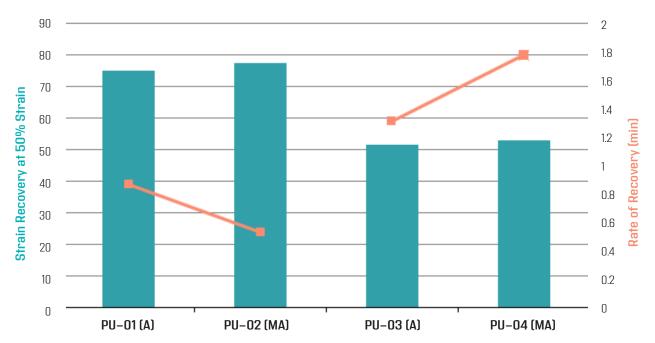
The capping chemistry does not appear to have a significant impact on strain recovery (Figure 2). The standard deviation between individual runs was approximately 5%, making observed differences in strain recovery insignificant.

Table 2. Strain recovery and rate of recovery for the different capping chemistry

Oligomer	Capping Chemistry	Rate of Recovery (min)	Strain Recov- ery (%)
PU-01	A	1.30	51.5
PU-02	MA	1.78	52.9
PU-03	A	0.84	75.4
PU-04	MA	0.53	77.3

The rate of recovery of different capping chemistries was also similar within an analogous series. In general, the methacrylate (MA) systems recovered their strain slightly slower than the analogous acrylate (A) system (Table 2). In most cases, the time difference between capping chemistries was small, less than 30 seconds.

Figure 2. Strain recovery and rate of recovery of acrylate (A) and methacrylate (MA) capped oligomers.



II. Diisocyanate structure

To evaluate the effect of diisocyanate structure on strain recovery, PU-05 was used as the control and the diisocyanate structure was varied. Diisocyanate structures probed were cycloaliphatic (CA), aromatic (AR), and linear aliphatic (LA), while all other variables were held constant.

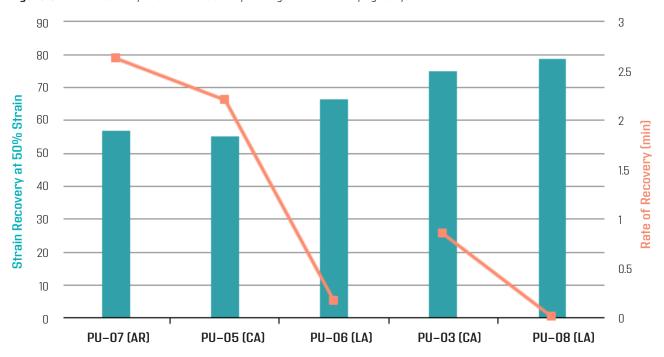
Unlike capping chemistry, there is an observable difference with regards to strain recovery and disocyanate structure (Figure 3). The systems containing ring structures showed approximately 15% less recovered strain than the corresponding linear aliphatic system. One possible explanation for this phenomenon is the rigid, bulky ring structures present in the cycloaliphatic and aromatic urethane linkages provide steric hindrance against the system returning to its original geometry². Furthermore, the aromatic and cycloaliphatic structures showed similar strain recoveries, seen in Figure 3.

Table 3. Strain recovery and rate of recovery varying isocyanate structures

Oligomer	Diisocyanate	Rate of Recovery (min)	Strain Recovery at 50% Strain (%)	
PU-05	Cycloaliphatic (CA)	2.06	55.1	
PU-06	Linear aliphatic (LA)	0.17	66.3	
PU-07	Aromatic (AR)	2.63	57.0	
PU-03	Cycloaliphatic (CA)	0.84	75.4	
PU-08	Linear aliphatic (LA)	0.01	77.6	

PU-03 (CA) and PU-08 (LA) share the same polyol backbone, with different diisocyanate structures, cyclic and linear aliphatic, respectively. As seen with the 1st set of comparisons in this section, the linear diisocyanate structure showed a higher strain recovery compared to the cycloaliphatic. In this case, the difference in strain recovery was not as dramatic as it was with PU-05 (CA) compared to PU-07 (LA). The molecular weight of the polyol used in PU-03 (CA) is approximately twice that of the polyol backbone used in the PU-05 (CA).

Figure 3. Strain recovery and rate of recovery for oligomers with varying isocyanates.



As the molecular weight of the polyol increases, the ratio of diisocyanate required to keep the same stoichiometry decreases. This could explain the smaller difference in strain recovery observed between the different data sets.

The rate of recovery can also be tied to the diisocyanate structure (Table 3). Oligomers with cyclic diisocyanates, aromatic and aliphatic, recovered slower than linear aliphatic systems. Despite PU-03 (CA) and PU-08 (LA) presenting similar strain recoveries, the linear aliphatic diisocyanate rate of recovery was significantly faster. Similarly to the total recovery, the steric hinderance of the bulky ring structures creates resistance for the movement of polymer chains, thus slowing the recovery rate.

III. Polyol Backbone Chemistry

Backbone chemistry theoretically plays a significant role in final oligomer performance, specifically the polyol. Several oligomers, with polyols of similar molecular weight and varying chemistries, were synthesized. These products were compared to commercially available products to evaluate the effects of different polymer chemistry backbones on strain recovery, listed in Table 4. Synthetic processes/procedures, diisocyanate identity and stoichiometry were held constant to yield oligomers with similar molecular weights. Due to the complexity of the comparison, the following discussion will focus on one molecular weight range. Since acrylate and methacrylate chemistry have proven to be an insignificant variable, it was not necessary to keep the capping reagent constant.

Generally, the backbone chemistry of the polyol appears to have little effect on total strain recovery of the cured system

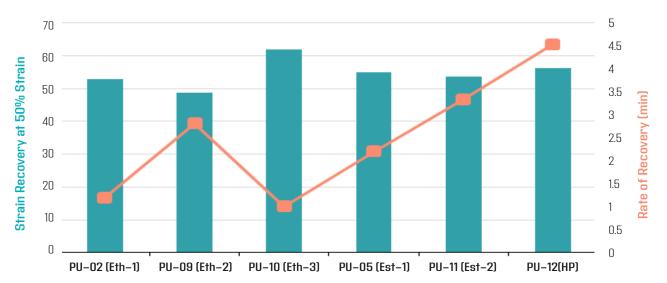
when strained to 50% (Figure 4), although an effect on rate of recovery is observed. PU-10 (Eth-3) showed a higher strain recovery compared to all other polyol backbones. The polyol for this oligomer is analogous to a Bomar 300 series polyether oligomer. Interestingly, PU-09 (Eth-2) showed the least strain recovery despite containing a polyether backbone. The remaining backbones evaluated, a mix of esters and ethers, showed similar strain recovery, around 50% recovered.

As noted above, a small dependence of polyol chemistry was observed for the rate of recovery (Table 4). A general trend can be seen which indicates polyethers will recover faster than polyesters, except for PU-09 (Eth-2) type structures. Polyester and hydrophobic backbones along with the PU-09 (Eth-2) structure recovered the slowest. A more involved study of rate of recovery would need to be conducted to fully elucidate the mechanism behind strain recovery speed and backbone chemistry.

Table 4. Strain recovery and rate of recovery for varying polyol backbones.

Oligomer	Oligomer Backbone Chemistry		Strain Recovery at 50% Strain (%)	
PU-02 (Eth-1)	Polyether, type 1	1.78	52.9	
PU-09 (Eth-2)	Polyether, type 2	2.81	48.8	
PU-10 (Eth-3)	U-10 (Eth-3) Polyether, type 3		61.8	
PU-05 (Est-1)	Polyester, type 1	2.06	55.1	
PU-11 (Est-2)	Polyester, type 2	2.83	53.6	
PU-12 (HP) Hydrophobic		2.87	53.6	

Figure 4. Strain recovery and rate of recovery of oligomers with varying polyol backbones.



IV. Polyol Molecular Weight

A library of oligomers using the polyether type 2 and type 3 polyol structures were synthesized using a varying of different polyol molecular weights, with keeping diisocyanate, capping and synthetic process constant.

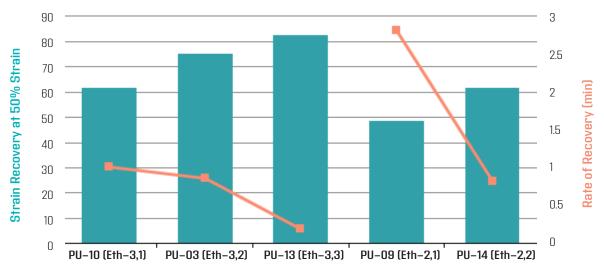
Molecular weight of the polyol does have an apparent effect on the resulting strain recovery as seen in Figure 5. This is likely due to varying the stiffness of the polymer network. Urethanes are often thought of as containing hard (urethane linkages) and soft (polyol regime) segments. As the molecular weight of the polyol increases, the concentration of the urethane linkages in the matrix decreases, holding stoichiometry constant. The

increase in flexible segments allows the material to recover more strain compared to oligomers with more urethane linkages. A similar trend can be seen in the PU-09 (Eth-2,1) and PU14 (Eth-2,2) type oligomers, where the molecular weight of the polyol in PU-14 (Eth-2,2) is greater than PU-09 (Eth-2,1). With a higher overall molecular weight, PU-14 (Eth-2,2) recovers more strain in comparison to PU-09 (Eth-2,1) (Figure 5). The rate of recovery can also be correlated to the molecular weight of the polyol (Table 5). Higher molecular weight oligomers can recover displaced energy quicker compared to the lower molecular weight counterparts. Since these materials are not fully entangled polymers, higher molecular weights will yield more mobility in the system when crosslinked.

Table 5. Strain recovery and rate of recovery of different molecular weight oligomers.

Oligomer	Backbone Identity	Relative Backbone Mw	Rate of Recovery (min)	Strain Recovery at 50% Strain (%)	Storage Modulus at 50°C (MPa)
PU-10	Eth-3	1	0.94	61.8	4.93
PU-03	Eth-3	2	0.84	75.4	1.17
PU-13	Eth-3	3	0.01	82.4	1.20
PU-09	Eth-2	1	2.81	48.8	8.51
PU-14	Eth-2	2	0.82	61.8	3.48

Figure 5. Strain recovery and rate of recovery of oligomers over a range of polyol molecular weights



V. Oligomer Molecular Weight

Starting with higher molecular weight raw materials is not the only way to build molecular weight in urethane synthesis. Adjusting other variables, such as stoichiometry, order of addition or the introduction of a small molecule chain extender can also manipulate the polymer's observed molecular weight. A variety of oligomers, using the same raw materials (type 1 polyester polyol and cycloaliphatic diisocyanate) were synthesized in a range of molecular weight, PU–16 (1.5xMW)> PU–15 (1.5xMW) >> PU–17 (1xMW)> PU–05 (1xMW), as can be seen on GPC in Figure 5b.

The highest molecular weight oligomers showed the greatest strain recovery, as seen in Figure 6a; a trend discussed in the previous section. Interestingly, there is a significant difference in the strain recovery between PU-05 (1xMW) and PU-17 (1xMW), despite the oligomers being close in molecular weight. The GPC in Figure 6b shows a lower molecular weight species, indicated by the red arrow, which is often referred to as the diadduct peak. This low molecular weight species is formed when both sides of the diisocyanate are reacted with the capping reagent used in synthesis. By concentration, there is

approximately double the diadduct in PU-05(1xMW) compared to PU-17 (1xMW) and minimal present in PU-15 (1.5MW) and PU-16 (1.5xMW).

A higher concentration of a small molecule diacrylate (or dimethacrylate) species will increase the crosslink density of the cured system. This crosslink density increase can be seen via the storage modulus in the rubbery plateau in Table 6. The drastic change in crosslink density helps explain the difference in strain recovery observed for PU-05 (1xMW) compared to PU-17 (1xMW), despite having similar overall molecular weights.

The force required to strain the cured oligomers to 50% can also indicate differences in the crosslink density. In Table 6, it can be seen the force required to strain the sample to 50% follows the same trend as storage modulus, as it increases, the crosslink density also increases. The difference in force can be attributed to a lack of chain mobility due to a more densely crosslinked network. The effects of crosslink density also affected the rate of recovery, PU–05 (1xMW) had the slowest rate of recovery and highest storage modulus, while PU–15 (1xMW) and PU–16 (1.5xMW) had the quickest rates of recovery, and lowest storage moduli.

Figure 6. a) Strain recovery and rate of recovery for oligomers of different molecular weights. b) GPC chromatogram of compared oligomers.

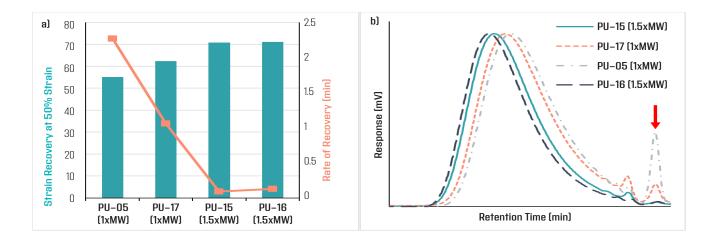


Table 6. Strain recovery and rate of recovery of different crosslinked systems.

Oligomer	Rate of Recovery (min)	Strain Recovery at 50% Strain (%)	Force Required to Strain 50% (N)	Storage Modulus at 50°C (MPa)
PU-05 (1xMW)	2.06	55.1	8.15	10.10
PU-17 (1xMW)	0.98	62.4	6.9	6.16
PU-15 (1.5xMW)	0.07	70.8	5.37	3.17
PU-16 (1.5xMW)	0.13	71.1	3.14	2.72

MODELING ELASTIC BEHAVIORS IN UV-CURABLE MATERIALS

Given strain recovery appears to be directly associated to the oligomer microstructure and equivalent weight, it was investigated to see how other physical properties could be correlated to strain recovery. Tensile testing, tear strength, durometer hardness and Tg were evaluated on the oligomers used previously and compared to strain recovery at 50% and 25% strain. By plotting other physical properties with strain recovery, a variety of trends appear.

In Figure 7, a clear correlation between tensile strength and Young's modulus to strain recovery can be seen. Tensile strength is often thought of as a function of structure and crosslink density. The R^2 correlation is slightly better with

modulus compared to ultimate tensile strength. This greater correlation could be contributed to the modulus measurement being collected within the linear viscoelastic regime (LVR). It is assumed within the LVR, all energy inputted into the system is recovered, leading to little or no plastic deformation. By eliminating plastic deformation, the elastic response is primarily seen. Furthermore, at ultimate tensile strength, the system is stressed until the sample fractures. Minor defects in the sample can make the material prematurely fail, causing the data to being skewed. The minor defects will have negatable effects on the modulus at low strains yielding a better correlation. This is further evident when looking at strain recovery at 25% strain (Figure 8). When plotting the strain recovery at 25% compared to Young's modulus the R² correlation increases to almost 0.6, indicating a better fitting line. It appears that the % strain applied will influence the accuracy of the model.

Figure 7. Correlation of strain recovery at 50% strain with a) tensile strength and b) Young's modulus.

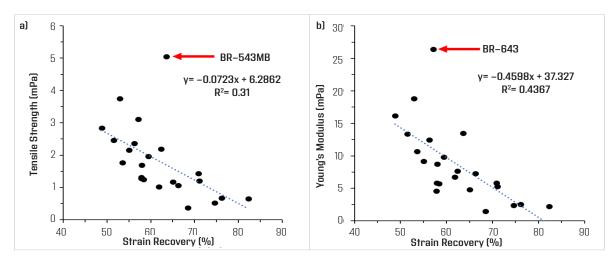
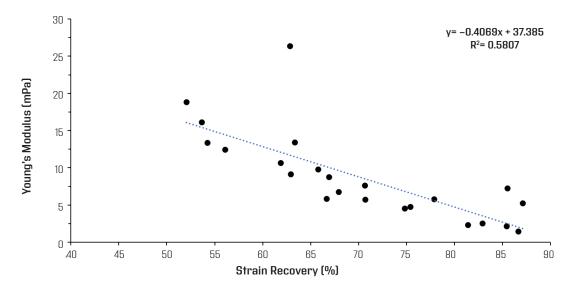


Figure 8. Correlation of strain recovery at 25% strain and Young's modulus.



Tear strength also correlates with strain recovery. A strong correlation was observed between tear strength and ultimate tensile strength (Figure 9a), thus the relationship of tear strength to strain recovery was investigated (Figure 9b). The correlation of tear strength to strain recovery shows parallel response as strain recovery and Young's modulus. The relationships of hardness and Tg with respect to strain recovery were investigated. There was no discernible correlation between Tg and strain recovery. A weak connection between hardness and strain recovery ($\mathbb{R}^2 < 0.1$) was observed, thus both graphs is excluded.

Elucidating a correlation between rate of recovery and other physical properties were not as apparent. There was no apparent relationship between any mechanical properties measured and rate of recovery. The recovery can be thought of as a fluid response, so the focus of investigation was shifted to a rheological study. A DMA temperature sweep was used to determine the storage modulus for each oligomer at 25°C, the same temperature strain recovery was tested at. The Tg for all the studied oligomers was less than 25°C and only BR-1043MB has Tg greater than 0°C, thus all data points were collected within the rubbery plateau.

Figure 9. Correlation of tear strength to a) tensile strength and b) strain recovery @ 50% strain.

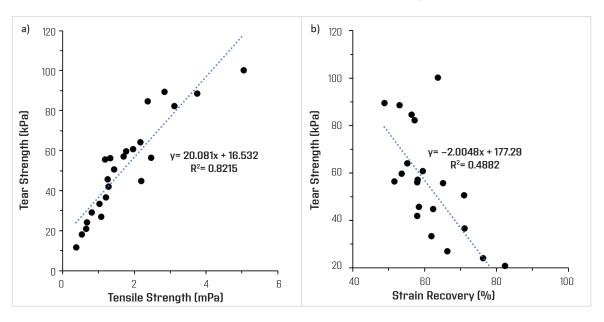
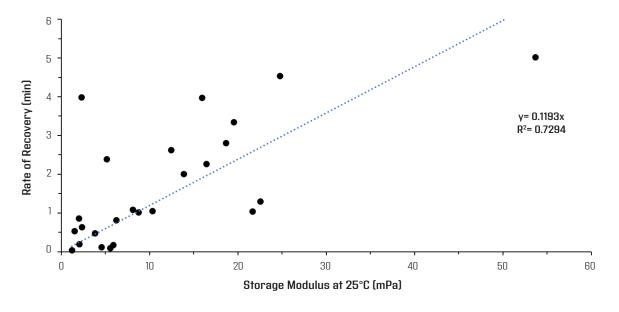


Figure 10. Correlation of Storage Modulus and Rate of Recovery



As seen with Young's modulus and strain recovery relationship, there appears to be a similar correlation between rate of recovery and storage modulus (Figure 10). The storage modulus can be considered as elastically stored energy, which can resist deformation. Lower storage modulus indicates a lesser ability to store the deformation energy which can be given back to the system quicker, indicating a faster rate of recovery.

The strain recovery parameters have successfully been modeled and theoretically can be used to predict the strain recovery of cured oligomers. To determine the efficacy of the model, the following formulation (Table 7) was examined for strain recovery along with tensile, tear, and rheological testing. The material was cured in the same manner as the samples previously discussed.

Table 7. A modified elastic formulation from Bomar's 3DP literature.

Raw Materials	Weight (g)
BRC-4421	50
IBOA	17.5
EOEOEA	32.5
Irgacure 184	2.0

Using the correlations in Figure 7b and Figure 8, the theoretical strain recovery of the elastic formulation at 50% and 25% strain should be about 70% and 82.5%, respectively. The measured strain recovery of the elastic formulation at 50% and 25% strain was 81.2% and 96.4%, respectively. Interestingly, the predicted 25% strain recovery shows about the same percent error (13%) as the 50% strain recovery prediction, despite the R² being higher for 25%. The 13% error is acceptable as the formulation tested contains less than 50% oligomer, while the model was derived from neat oligomer measurements. The rate of recovery for the elastic formulation was predicted to be 1.23 min and the observed rate was 0.95 min. The model derived for the rate of recovery has a higher percent error than the total strain recovery model, even though having a nearly doubled R² value. To obtain a more accurate predictive model for strain recovery and rate of recovery for fully formulated products, a more robust study would need to be conducted.

Lastly, the tear strength of the elastic formulation was predicted using the tensile strength and tear strength correlation, Figure 9a. The predicted tear strength was calculated to be 220 kPa and the observed tear strength was 203 kPa, a percent error of 8%. Given the strong correlation between tear strength and tensile strength, it is not a surprise the predicted value is almost within the percent error of the test.

Table 8. Predicted and measured strain recover and rate of the elastic formulation.

	Strain Recovery at 50% Strain (%)	Rate of Recovery at 95% Recovered Strain (min)	Tear Strength (kPa)
Predicted Value	70.55	1.23	220.22
Actual Value	81.17	0.95	202.77
Percent Difference	13.08 %	22.76 %	8.18 %

OLIGOMER DIFFERENTIATION

Formulators often look for a variety of properties. The data displayed and discussed through this study has only focused on strain recovery, with little comparison to other physical properties. Therefore, the set of oligomers discussed previously along with several commercial products were fully evaluated to determine which of those displayed the best balance of properties. The oligomers in this study were comparatively rated on the following properties: greatest recovery at 50% strain, fastest rate of recovery, greatest modulus of toughness at 25% strain, greatest tear strength, and lowest viscosity. Modulus of toughness (the area under the stress–strain curve) was determined through 25% strain to ensure full inclusion of all samples. The results are displayed in Table 9.

The highest scoring products, indicating the best balance of physical properties, were BR-643 and BR-345. BR-643 was not discussed previously in the paper due to the unique polyol backbone and limited molecular weights commercially available. BR-643 is the only oligomer in the top five that is not an ether-based polyol backbone. Furthermore, referring to Figure 7b, BR-643 deviated higher than the predicted trend line of strain recovery based upon modulus, but was one of

the slowest oligomers to recover strain. BR-345 showed the greatest amount of strain recovery and one of the fastest rates of recovery but showed poor tensile properties and tear strength. BR-543MB and BR-1043MB both displayed a good balance of strain recovery, as well as, tensile strength, tear strength and lower viscosity. BR-543MB also showed a much greater tensile strength given its strain recovery as seen by the predicted trend line in Figure 7a. The individual application needs will determine which of these oligomers would be best suited.

There were a few experimental oligomers that showed promise that are included in Table 9. XCAC-31-134 displayed the highest score among all the compared oligomers. This oligomer showed one of the highest strain recoveries along with low viscosity. However, the tensile and tear strength were considerably low. Another oligomer included was XHNF-17-140. This oligomer displayed an average recovered strain, along with the highest amount of tear strength recorded in this study but has a comparatively slow rate of recovery and a high viscosity.

Table 9. Comparative physical property data.

Oligomer	Reference	% Strain Recovery @ 50%	Rate of Recovery (min)	Modulus of Toughness @ 25% Strain (kPa)	Tear Strength (kPa)	Viscosity @ 60C (cPs)	Sum of the Scores
BR-643	PU-13	7.13	0.02	10.00	8.22	0.99	26.37
BR-345	None	10.00	10.00	1.40	2.09	2.85	26.34
BR-1043MB	PU-02	5.92	0.04	6.61	8.94	3.31	24.83
BR-543MB	PU-09	6.42	0.06	7.50	8.86	1.21	24.04
BR-344	PU-03	9.15	0.12	1.33	1.82	8.50	20.92
BR-543	PU-01	6.25	0.08	5.77	5.65	1.30	19.04
BR-7432GB	PU-15	8.59	1.41	3.15	5.07	0.19	18.42
BR-374	None	9.24	0.16	1.53	2.43	4.83	18.19
BR-1044MB	PU-14	7.50	0.12	3.04	4.57	1.41	16.64
XCAC-31-134	PU-08	9.42	10.00	1.23	2.91	8.89	32.45
XHNF-17-140	None	7.71	0.03	5.70	10.00	0.37	23.81

CONCLUSIONS

In this research, the effects of oligomer's microstructure were investigated regarding the strain recovery and rate of recovery. Acrylate and methacrylate capped oligomers appeared to perform similarly, and polyol backbone chemistry did not play a significant role in total strain recovery, with Bomar 300 series backbone being a notable exception. However, backbone polyol chemistry was shown to have a significant impact on rate of recovery. Diisocyanate structure and functional equivalent weight were determined to be significant factors in strain recovery and rate of recovery. Systems containing cyclic structures in the diisocyanate showed lower strain recoveries and recovery rates. Crosslink density and molecular weight affected strain recovery; matrices with a lower crosslink density and higher molecular weight were observed to yield higher strain recoveries and faster rates of recovery.

Being able to predictively screen materials for strain recovery could be useful for formulators wishing to achieve elastic type properties in UV-curable materials. This research discussed the direct correlation to strain recovery and Young's modulus, where a lower modulus insinuates a greater strain recovery. Rate of recovery was also determined to have a correlation to the storage modulus, as a lower storage modulus will allow for a faster recovery rate.

Bomar oligomers, BR-345, BR-643, BR-543MB and BR-1043MB, are excellent candidates for achieving elastic-like behaviors, based upon the research conducted within this study. Two experimental oligomers, XCAC-31-134 and XHNF-17-140, also show promise and may outperform current commercial products. With two industry standard tests, a dogbone tensile data set and DMA temperature sweep, the strain recovery and rate of recovery can be estimated without knowing the intimate details of the oligomers structure. Being able to derive how much and how quickly a system can recover to an unperturbed state when stressed will provide valuable insight into the material's performance.

REFERENCES

- 1. Khudyakov, Igor V., Kenneth W. Swiderski, and Robert W. Greer. "Structure property relations in UV curable urethane acrylate oligomers." Journal of applied polymer science 99.2 (2006): 489–494.
- 2. Jiang, Lei, et al. "Synthesis and structure/properties characterizations of four polyurethane model hard segments." Royal Society open science 5.7 (2018): 180536.

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