Structure-Property Investigation of Functional Resins for UV-Curable Gaskets

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The main purpose of this work was to use polymer design (via living radical polymerization) to gain a better understanding of how the resin structure in UV-curable gaskets influences key properties such as compression set. In the design of UV-curable sealants, an important means of controlling a product's physical properties is through selection of the reactive resin in the sealant formulation. Such resins conventionally may have a broad range of molecular weight, functionality and backbone composition. For the purposes of this study, telechelic polyacrylate terpolymers were synthesized via a process called Single Electron Transfer-Living Radical Polymerization (SET-LRP).[1,2]

The SET-LRP process allows for very precise control of the three resin characteristics cited above. Specifically, the molecular weight of the product polymer is determined by the monomer-to-initiator ratio; the functionality of the polymer is controlled by the choice of initiator as well as (possibly) by choice of capping agent; and the backbone composition can be tailored by selecting from a wide variety of (meth)acrylate monomers that can be copolymerized with controlled incorporation ratios.

It is worth noting, as well, that polymers prepared via living radical polymerization characteristically have very narrow molecular weight distributions, with polydispersities on the order of 1:1 or less. The broad capabilities of SET-LRP are key to achieving the project goal of investigating the relationship between polymer structure and sealant performance.

The relative importance of various sealant performance parameters will obviously vary depending upon the desired application. To keep the scope of this study suitably narrow, we focused on a single application type, UV-curable, mold-in-place compressive gaskets. For compressive gaskets, a key performance parameter is the compressive sealing force, which can be at least qualitatively assessed by compression set measurements.

Additional parameters on which the resin will have an impact include glass transition temperature (desirably less than room temperature for most gasketing applications), and tensile and elongation properties. Generally, low molecular weight resins will contribute toward better (lower) compression set, but also high hardness and low elongation. Higher molecular weight resins give

TABLE 1

Resins prepared via SET-LRP

Resin name	Target functionality	Measured functionality	Molecular weight (g·mol-1)
Resin 1	2	1.9	30,000
Resin 1b	2	1.7	30,000
Resin 2	1	0.8	30,000
Resin 3	2	1.8	10,000
Resin 7	3	2.9	30,000

better elastomeric properties, but higher compression set. This project was designed to investigate the fundamental relationship between telechelic resin design and resulting physical properties. Specifically, this work has studied the impact of the resin functionality (mono-, di-, tri-), molecular weight (10K g/mol to 30K g/mol), and bimodality (controlled mixtures of resins with different functionality and/or molecular weight) on compression set; tensile strength and elongation at break; and glass transition temperature.

Experimental

Bromine-terminated acrylate prepolymers were prepared by random copolymerization of a fixed feed ratio of butyl acrylate, methoxyethyl acrylate and ethyl acrylate via SET-LRP.[1,2] These materials were functionalized by reaction with methacrylic acid in the presence of potassium carbonate to substitute the bromine with methacrylate functionality. A summary of the resulting telechelic polymers that were prepared is given in Table 1. Note that all of the polymers used for this study were linear terpolymers and had the same backbone composition; variations were only made in molecular weight or functionality.

For evaluation of sealant performance, the resins listed in Table 1 were formulated—both singly and in blends—into a simple model sealant composition. The model composition consisted of 73 wt% resin or resin blend, 20% reactive monomer, 5 wt% inorganic filler, 1 wt% antioxidant and 1 wt% photoinitiator. Formulations in which the 73 wt% resin component was made up of a single resin from Table 1 were designated as controls. For compositions in which the 73 wt% was comprised of a blend, two variables were defined:

- For compositions with resins of differing molecular weight (e.g., Resin 1 + Resin 3), the "Average Molecular Weight in Blend" (AMWB) was defined according to Equation 1.
- For compositions with resins of differing functionality (e.g., Resin 1 + Resin 2 or 7), the "Average Functionality in Blend" (AFB) was defined according to Equation 2.

Once each formulation was effectively mixed, 5 X 5 X 0.075-inch test sheets were prepared and cured by UV irradiation (9 J/cm^2, Fusion H bulb). Compression set was measured according to ASTM D395 Method B, using stacks of discs pressed by a die from the cured test sheets. The test specimens with initial thickness t_i were compressed by 25% (compression thickness, t_c) in steel jigs and placed in an oven at either 70° or 150°C for a period of 70 hours. Upon removal from the oven, the specimens were released from compression, cooled to room temperature and then measured for final thickness (t_f). Compression set was then reported according to the following equation:

$$C_s(\%) = \frac{t_i - t_f}{t_i - t_c} \times 100$$

Note that low compression set values are desirable for gasket applications. Other performance parameters that were evaluated for each composition include tensile strength and elongation at break,[3] and glass transition temperature (dynamic mechanical analysis).[4]

Results and Discussion

Performance According to AMWB

To understand the influence of polymer molecular weight on sealant performance, as well as to explore the difference between narrow-polydispersity polymers (the control formulations) and bimodal blends, model sealant formulations as

Equation 1

$$AMWB = \frac{MW(resin1) * wt\%(resin1) + MW(resin3) * wt\%(resin3)}{wt\%(resin1) + wt\%(resin3)}$$

Equation 2

$$AFB = \frac{Functionality(resin1) * wt\%(resin1) + Functionality(resin2) * wt\%(resin2)}{wt\%(resin1) + wt\%(resin2)}$$

TABLE 2

AMWB of blends prepared from Resins 1 and 3

Resin ratio		
Resin 1	Resin 3	AMWB (g·mol⁻¹)
0	1	10,000
1	4	14,000
1	2	16,667
1	1	20,000
3	1	25,000
5	1	26,667
1	0	30,000

described in the experimental section were prepared, with each composition containing 73 wt% total resin content. For the AMWB study, two control model sealant compositions were prepared from Resin 1 (30,000-molecular weight, difunctional) and Resin 3 (10,000 molecular weight, also difunctional). Analogous compositions containing five different blends of Resins 1 and 3 were then prepared, with average molecular weights as shown in Table 2. In each composition, the total resin content was maintained at 73 wt%. For example, a composition designed to have AMWB = 20,000 g/mol would contain 36.5 wt% each of Resin 1 and Resin 3.

Each of the compositions prepared according to Table 2 was tested for compression set, tensile strength, elongation at break and glass transition temperature. The data are summarized in Table 3. The results for compression set agreed well with expectations; lower molecular weight polymers result in higher crosslink density, which contributes to lower (more desirable) compression set. However, lower molecular weight also contributes—undesirably—to lower elongation at break and higher glass

transition temperature. An interesting result can be noted in the tensile and elongation data in Table 3. Tensile strength and elongation at break both increased with increasing AMWB—with one interesting exception. The control composition containing only the 30,000-molecular weight resin had significantly lower tensile strength and elongation than the "blend" compositions with AMWB of 25,000 or 27,000. Testing of several replicates confirmed this result.

An increase in performance with molecular weight was not unexpected, since greater polymer entanglement at the higher molecular weights can greatly enhance tensile performance. Regarding the higher tensile strength and elongation observed with the bimodal blends versus monomodal controls, it was found that a "bimodal reinforcement effect" has been noted previously for polysiloxanes (for example, see Viers and Mark[6]). A possible explanation for the effect is reinforcement by micro- or nano-structures formed by the lower molecular weight component. We have not yet pursued this topic further to confirm if the explanations offered for polysiloxanes might also hold for these polyacrylates.

TABLE 3

Test results for sealants with varied AMWB

AMWB	Compression set* (%)	Tensile Strength (MPa)	Elongation at break (%)	T_g (°C)
30,000	38	3.0	190	-25
27,000	37	5.0	230	-24
25,000	35	4.5	220	-24
20,000	25	3.5	150	-21
17,000	20	3.5	120	-21
14,000	20	3.5	120	-19
10,000	13	3.0	120	-16

*25% compression, 70 hours @ 70°C

TABLE 4

Resin blend ratios and corresponding AFB

Resin ratio (parts)			AFB
Resin 2	Resin 1	Resin 7	
Monofunctional	Difunctional	Trifunctional	
3	1	0	1.1
6	0	1	1.1
1	1	0	1.4
2.5	0	1	1.4
1	3	0	1.6
1.6	0	1	1.6
1	5	0	1.7
1.3	0	1	1.7
0	1	0	1.9
1	0	1.1	1.9
0	2.8	1	2
0	1	1.1	2.3
1	0	2.5	2.3
0	1	3.6	2.6
1	0	6	2.6
0	0	1	2.9

TABLE 5

Test results for gasket compositions of varying AFB

Resin blend components (functionality)							
Resin 2 (mono)	Resin 1 (di)	Resin 7 (tri)	AFB	Compression set (%)	Tensile Strength (MPa)	Elongation (%)	T_g (°C)
3	1	0	**1.1**	65	2.5	290	-27
6	0	1	**1.1**	63	1.7	150	-29
1	1	0	**1.4**	50	2.8	250	-27
2.5	0	1	**1.4**	54	3.5	180	-26
1	3	0	**1.6**	42	3.8	240	-26
1.6	0	1	**1.6**	43	4.3	175	-26
1	5	0	**1.7**	44	3.5	250	-25
1.3	0	1	**1.7**	42	4.8	190	-25
0	1	0	**1.9**	38	3	190	-25
1	0	1.1	**1.9**	37	4.7	180	-24
0	2.8	1	**2**	28	6.2	240	-24
0	1	1.1	**2.3**	25	6.4	220	-23
1	0	2.5	**2.3**	25	nd	nd	nd
0	1	3.6	**2.6**	23	5.2	175	-23
1	0	6	**2.6**	28	nd	nd	nd
0	0	1	**2.9**	22	4.2	190	-23

To summarize the result of the AMWB study—the most desirable compression set is achieved with lower molecular weight resins. However, to obtain the best overall balance of performance, a bimodal blend of resins with AMWB ~ 25,000 to 27,000 was found to be most effective.

Performance According to AFB

The study of AFB was conducted in much the same way as the AMWB study. Control compositions were prepared containing 73 wt% of a 30,000-molecular weight resin that was either di- or tri-functional (Resins 1 and 7, respectively, from Table 1). No control composition was prepared from Resin 2 (monofunctional) because its functionality is too low to provide measurable properties upon UV cure. The three resins were then blended in controlled ratios as shown in Table 4 to provide compositions with a specified average functionality. Since all three

resins had molecular weights of 30,000, the blended compositions maintained an average resin molecular weight of 30,000. As part of this study, several model gasket formulations comprising different polymer blends with the same average functionality were prepared. For example, a composition with AFB = 1.4 could be prepared by using a 1-to-1 blend of monofunctional and difunctional resins or by using a 2.5:1 blend of monofunctional and trifunctional resins.

Prototype gasket formulations containing 73 wt% of the blends shown in Table 4 were UV-cured and tested as described in the experimental section. The resulting data are summarized in Table 5.

As was observed with the AMWB study, compression set decreased with increasing crosslink density (i.e., in this case, increasing AFB). The compression set values (measured after 70 hours at 70°C and 25% compression) appeared to depend only upon the average blend functionality, not on the functionality of the component resins. For example, blends with 1.1 average functionality gave essentially the same compression set regardless of whether they were prepared from monofunctional +

trifunctional or monofunctional + difunctional polymers. T_g was relatively unaffected by AFB, with just a slight upward trend with increasing AFB. Tensile strength and elongation at break had rather more complicated behavior and will be addressed in some more detail.

To better explain the tensile strength and elongation results, the data are plotted in Figures 1 and 2.

Tensile strength, in general, increases with increasing AFB (Figure 1). This trend changes for the difunctional + trifunctional blends above 2.3 AFB. For higher AFB blends (including some data not reported), the observation that the failure point is at a lower stress even though the crosslink density is higher is most likely related to the effect of material hardness on crack propagation.

Typically, a softer material distributes stress more effectively during crack propagation than a hard material. A hard polymer accumulates all the stress in a small area close to the notch of a possible fissure and is, therefore, likely to fail earlier than a softer material in which the stress is distributed over a wider area. The difunctional-trifunctional resin blend

was less flexible and harder than the rest of the UV-sealant prototypes that were investigated, and above 2.3 AFB this hardness resulted in failure at lower tensile stress. Finally, as observed previously, blended resins demonstrated higher tensile strength than unblended controls (data point at 1.9 AFB).

Elongation data for the AFB study are shown in Figure 2. The blends of mono- + difunctional polymers and di- + trifunctional monomers showed the expected trend of decreasing elongation with increasing functionality. However, when a monofunctional resin is blended with a trifunctional resin, the elongation at break is almost constant and much lower than the other blends. The tensile strength behavior does not reflect the same trend and, in fact, is quite similar for mono- + tri-functional versus mono- + di-functional. Likewise, for the control compositions, elongation appears to be independent of functionality, even though tensile strength and modulus both increase with increasing functionality. For the blends of monofunctional and trifunctional resins, it was observed that too high a monofunctional content leads to polymers that feel "cheesy"; tensile strength is measured to be in a normal range, while elongation is low. As AFB increases for the mono- + tri-functional blends, monofunctional content decreases; this may explain why elongation appears to not decrease with increasing AFB as expected. However, this hypothesis fails to explain the result for the control compositions.

Conclusions

This project investigated key compression gasket parameters (compression set, tensile properties and glass transition temperature) and how they were impacted by controlling

FIGURE 1

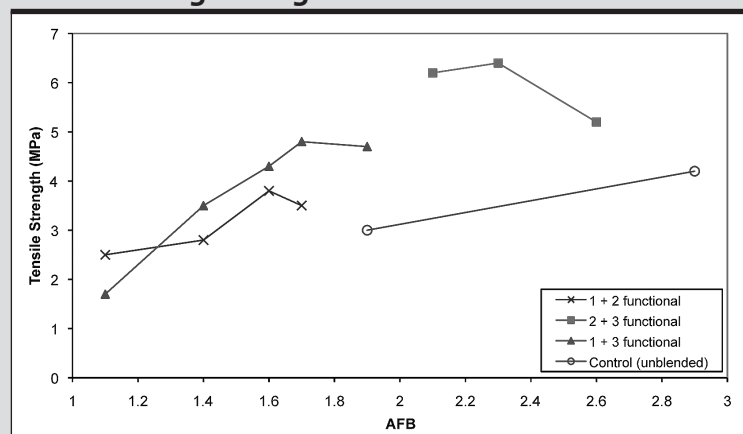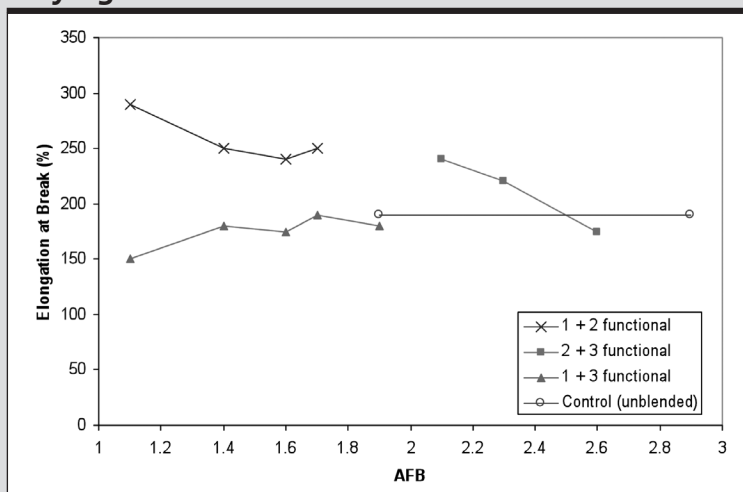**Tensile strength for gaskets with different AFB**

FIGURE 2

Elongation at break for gasket prototypes with varying AFB

formulation crosslink density by way of either resin molecular weight or degree of resin functionality. Controlled, narrow-polydispersity, methacrylate-functionalized polyacrylate terpolymers having molecular weights between 10,000 and 30,000 g/mol and functionalities between 0.9 and 2.9 were prepared by SET-LRP. These polymers and blends, thereof, were the basis for the model UV-curable gasket formulations used in all subsequent testing.

From the molecular weight variation study, one of the most significant results was that narrow-polydispersity functional polymers, when formulated without other resins, were inferior to bimodal and higher blends with regard to gasket performance. For difunctional polyacrylates, bimodal blends of two different molecular weight resins were found to have significantly better tensile properties than the monomodal control compositions. Lower molecular weight resins were found to be most desirable for low compression set, but at the expense of T_g (which increased

with decreasing molecular weight) and tensile properties. The best balance of properties was found with blends of polyacrylates having an average molecular weight around 25,000 g/mol.

For 30,000 g/mol polyacrylates with varying functionality, higher formulation crosslink density resulted in better (lower) compression set. Compression set was more strongly impacted by functionality than any of the other performance parameters studied. Polymer blends with the same average functionality gave the same compression set values, even if the component polymer functionalities were different. Glass transition temperature increased slightly with increasing functionality. Tensile strength generally increased with functionality up to an average functionality of 2.3, after which it decreased due to rapid crack propagation in the harder, higher-functionality cured gaskets. Elongation results were somewhat inconsistent and are not yet completely understood. Based upon all of the compiled data, an average functionality of about 2.3

is expected to give the best balance of low compression set and high tensile performance.

In summary, the best gasket performance under the conditions evaluated would be anticipated for a bimodal blend of polymers with average functionality 2.3 and average molecular weight around 25,000. Further improvement in any one performance parameter will most likely come at a cost. For example, compression set could be lowered by increasing functionality or decreasing molecular weight, but this would have an undesirable effect on tensile strength, elongation and T_g. Future work could investigate blends of polymers having both different molecular weights and different functionalities to identify the true optimum composition. ◗

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