

Dynamic and static crosslinking of polyvinyl butyral with a silane agent

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Chemical modification of polyvinyl butyral, with vinyltrimethoxysilane, increases its resistance to organic solvents through dynamic and static crosslinking.

Polyvinyl butyral (PVB) is an amorphous random terpolymer that consists of vinyl butyral, vinyl alcohol, and residual vinyl acetate, and that is prized for its toughness, flexibility, and optical clarity.^{1,2} PVB is used primarily in the automotive industry in laminated safety glass, which is a sandwich of PVB film (typically containing 10–35% w/w of plasticizers^{3,4}) between two glass sheets. To date, however, wider application of PVB has been limited owing to its solubility in the types of organic solvents commonly used in industry. Increasing the solvent resistance of PVB without sacrificing its favorable properties is therefore critical to enhancing its utility.

The solvent resistance of PVB can be increased by creating crosslinking bonds in the polymer. However, most crosslinking PVB processes are carried out in solution, which is neither economically attractive nor environmentally friendly on an industrial scale. In contrast, chemical modification in the molten state would be attractive, provided it could be suitably adapted. One promising approach in this regard is melt mixing PVB with a silane agent to generate the desired crosslinking.⁴

Our main objective in this work was to expand the application of PVB, by improving its solvent resistance through industrially suitable crosslinking reactions. We also wished to determine the optimal chemical modification process parameters for preserving the elasticity and toughness properties of solvent-resistant PVB. Finally, we hoped our investigation would lead to a better understanding of the crosslinking reactions that occur between PVB and the silane agent.

The PVB we used in this study was a recycled laminate glass material from the automotive industry. As a silane agent, we chose vinyltrimethoxysilane (VTMS), which is regularly used in the chemical modification of polyethylene.⁵ VTMS is a bifunctional organosilane

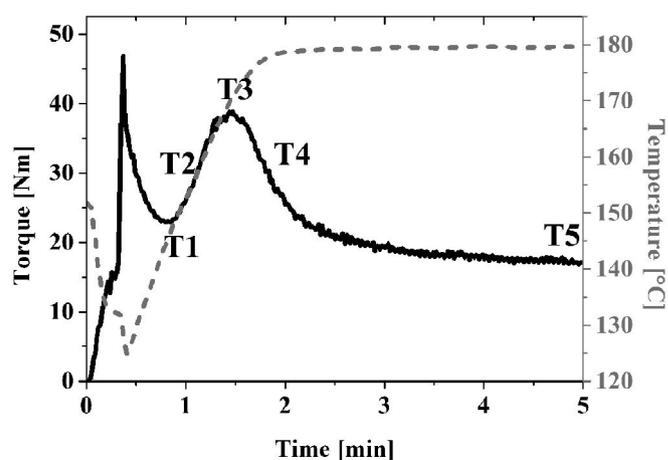


Figure 1. Torque (solid line/left axis) and temperature (dashed line/right axis) monitoring curves showing typical variation as a function of time. The five mixing times (T1–T5) used in the study are indicated.

with a reactive vinyl group and a hydrolyzable trimethoxysilyl (alkoxysilane). We performed the melt mixing of PVB and VTMS in an internal mixer, and we obtained five samples from five different mixing times (T1–T5), as shown in Figure 1. After mixing, the five samples were compression molded at 180°C, at a load of 10 tons for 10 minutes. We then subjected all the samples and the neat PVB to Soxhlet extraction, using ethanol as the solvent. Mixing in this way gives rise to three types of reaction: grafting (on initial reaction of VTMS with PVB chains); dynamic crosslinking (which occurs between the grafted VTMS groups during mixing of PVB and VTMS); and breaking off of hydroxyl (–OH) groups from PVB chains (due to temperature and shear). The most probable grafting mechanism is the reaction of an –OH group (from PVB) with alkoxy silane, which is a result of a difference in electronegativity brought about by transesterification.^{4,6} The

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grafted alkoxy silane then reacts with another –OH group of the polymer chain, thus creating a crosslinked structure.⁴ In contrast to dynamic crosslinking, which occurs during mixing of PVB with VTMS, static crosslinking is induced by compression molding of the PVB-VTMS sample.

We set our five mixing times (T1–T5) based on torque and temperature monitoring curves (see Figure 1). T1 represents the time it takes for grafting/crosslinking formation to be initiated (known as the gel time).⁷ As the crosslinking reactions become more intense, the viscosity and torque increase and more crosslinked clusters (i.e., highly crosslinked regions in the bulk material) are broken or dispersed (chain scission), until the maximum rate of crosslinking is reached at T3. Thereafter, the viscosity and shearing of the melt are so high that the clusters are broken up, which causes the melt viscosity and torque to decrease.^{7–9} With the decrease in viscosity, chain scission is less intense and equilibrium between chain scission and crosslinking is thus achieved (represented by a stable torque at T5). The T2 and T4 mixing times represent intermediate stages.

Gel content (see Figure 2) is a measure of the efficiency of crosslinking under dynamic and static conditions. During dynamic crosslinking, we found that the gel content of our samples increased with mixing time, until T3-M (i.e., at the maximum crosslinking rate) and that the gel content was then constant from T3-M to T5-M (despite the reduction in viscosity and torque). In the equilibrium between chain scission

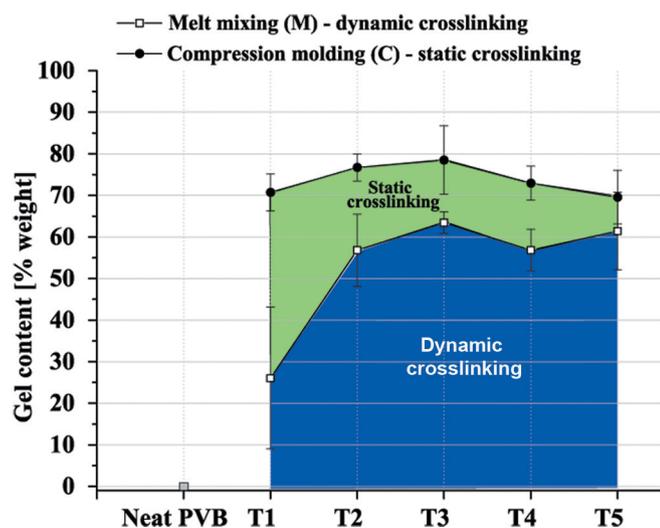


Figure 2. The gel content of the neat polyvinyl butyral (PVB) and the PVB-VTMS (vinyltrimethoxysilane) samples (labeled T1–T5) after they were subjected to Soxhlet extraction (with an ethanol solvent). Results are shown for dynamically crosslinked and statically crosslinked (through compression molding at 180°C) samples.

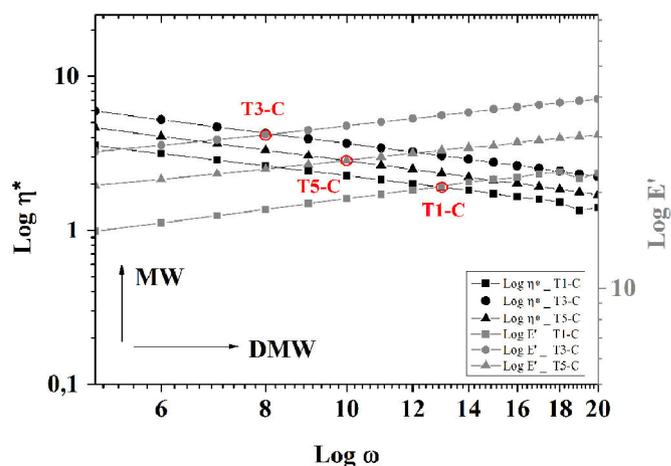


Figure 3. Frequency (ω) scan, obtained from dynamical mechanical analysis of samples that have approximately the same degree of crosslinking, indicating the molecular structure generated by different mixing times. η^* : Complex viscosity. E' : Storage modulus. MW: Molecular weight. MWD: Molecular weight distribution.

and crosslinking, the gel content was approximately 60% (the maximum gel content achieved under all the conditions in our study). Our results also show that static crosslinking through compression molding significantly increased the degree of crosslinking (caused by the absence of shear and chain scission). Indeed, with the T1-M sample (i.e., from the shortest mixing time) we achieved a gel content of 26% after mixing, but this value increased to 70% after compression molding (T1-C). Our other samples also showed similar behavior. Static crosslinking thus ensures maximum gel content, regardless of the degree of crosslinking achieved in the previous dynamic crosslinking step. Moreover, the gel content of the neat PVB was approximately zero, indicating that it was completely dissolved in ethanol.

Mixing time also affects the formation of the crosslinked structure.⁸ During dynamic crosslinking, shear and temperature cause clusters that have formed to break and disperse (without significantly impairing gel content). A crosslinked structure comprises both unmodified chains and larger, high-molecular-weight clusters, and it can be thought of as a continuum of different-sized clusters. These structures also allow the processing of crosslinked PVB, where the unmodified chains and micro-sized clusters act as a thermoplastic phase.⁸ During compression molding, static crosslinking occurs all over the PVB, and causes the formation of connections between clusters, and thus gives rise to a different structure. Depending on the mixing time, the ratio of dynamic and static crosslinking may vary and result in different final structures.

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Samples that contain larger crosslinked clusters have higher molecular weights (MWs). In addition, samples with a greater variation in cluster size have a larger polymer MW distribution (MWD). The structure of modified PVB can therefore be assessed with a dynamic mechanical analysis (DMA): see Figure 3.^{10,11} In DMA, the crossover point between the storage modulus and the complex viscosity can be related to the polymer MW and MWD.^{10,11} Although we find that the degree of crosslinking among the compression-molded samples is similar, the T3-C sample has a higher MW and a lower MWD than T1-C (T5-C represents an intermediate value). These results indicate that the T1-C sample (i.e., at the gel point) exhibits small, different-sized, clusters (i.e., low MW, high MWD) that grow to form larger and more uniform clusters (high MW, low MWD) at T3-C. The shear inside the mixer then breaks and disperses these large clusters, resulting in an intermediate structure in the T5-C sample. Our results thus illustrate that melt mixtures of PVB-VTMS could be produced in an extruder without excessive crosslinking or increased viscosity, which would allow subsequent molding, as desired, with a maximum degree of crosslinking.

In summary, the objective of this study was to increase the organic solvent resistance of PVB through chemical modification (via the use of a silane agent in the molten state), based on the assumption that crosslinks formed by VTMS would prevent solubilization of PVB. We also wished to understand how chemical modification develops during both dynamic and static crosslinking. We find that the ideal mixing time for the PVB and the silane agent in the molten state should be set so that mixing is complete before the maximum crosslinking rate is achieved (i.e., to avoid excessive degradation). The maximum solvent resistance of approximately 80% is assured because the degree of crosslinking that can be achieved before the torque peak is not high enough to affect post-processing (and because the crosslinking reactions continue during molding). The possibility of modifying PVB in traditional industrial processes, such as extrusion (melt mixing) and compression/injection molding (static crosslinking), is a significant contribution to expanding the applicability of PVB. In the future we plan to use modified PVB to obtain flexible, natural-fiber-reinforced polymeric composites with high solvent resistance.

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