

Photocuring of New Advanced Barrier Coatings

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Abstract: *A photopolymerized thiol-ene formulation with high barrier to oxygen was fabricated. This system was also investigated using DSC, DMA, and pencil hardness testing indicating a durable film with very narrow thermal and mechanical glass transition regions. The high oxygen barrier of this film is comparable, and in some cases superior, to those of typical barrier thermoplastic materials.*

Introduction

Flexible barrier films and coatings for these films are areas of keen industrial interest. With U.S. market sizes of over \$1 billion for high barrier films and over \$3 billion for flexible packaging that incorporate these barrier films, it is no wonder that breakthroughs are constantly being sought in the realms of barrier coatings and treatments, multilayer packaging, and active or scavenging materials.¹

Photocurable coatings feature several characteristics that make them attractive in the coatings industry today. They generally comprise 100% reactive components making these coatings environmentally acceptable. UV-curable are also extremely energy efficient compared to thermally processed coatings; they require only a fraction of the power used in thermal coatings. And perhaps most interestingly these coatings can be specifically tuned to meet property and application requirements by modifying the chemical structure of the monomers and oligomers or through the incorporation of additives.²

While these attributes apply mainly to multifunctional acrylate coatings, photopolymerized thiol-enes offer the distinct advantage of proceeding via a free-radical step-growth mechanism that is uninhibited by oxygen. These materials are also, like other UV-curable systems, easily administered as liquid systems and then cured rapidly by exposure to UV radiation.³ And as this research will show, the oxygen barrier properties of a certain thiol-ene formulation are actually competitive with that of current barrier polymers.

Experimental

Materials

The thiol monomer trimethylolpropane tris(3-mercaptopropionate) (3-Thiol) was supplied by Bruno Bock Thio-Chemical-S. Ene monomer 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) was obtained from Sartomer. All films of these monomers were initiated using the photoinitiator 2,2-dimethoxy 2-phenyl acetophenone (DMPA) obtained from Ciba Specialty Chemicals. All materials were used as received.

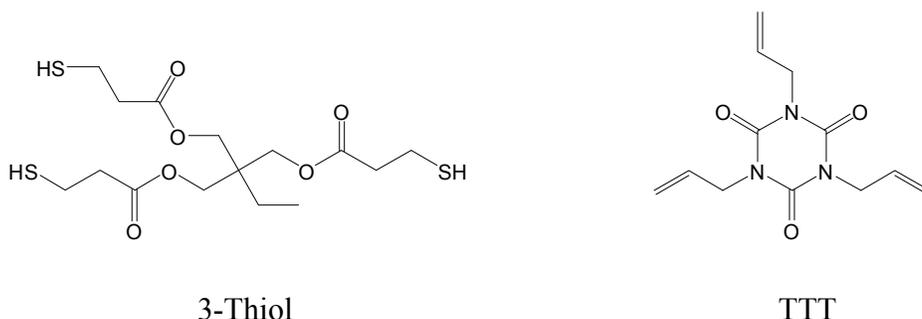


Figure 1. Structures of thiol and ene monomers.

Preparation of thiol-ene films

3-Thiol was combined with TTT at a 1:1 molar ratio. 1 wt% DMAP was added to the mixture and then sonicated for 10 minutes. This mixture was then drawn down onto a glass plate using drawdown bars of 2 different thicknesses (5 mils and 9 mils). Films were then cured using 10 passes at 10 ft/min feed speed under a Fusion UV curing line system with a D bulb (400W/cm² with belt speed of 10 feet/min and 3.1 W/cm² irradiance). All films were normalized in air for several days prior to testing. Annealing of films, although not a strict requirement to obtain high barrier properties, was investigated using an annealing procedure of 100 °C for 2 hours in air.

Characterization

Oxygen barrier properties were measured using a Mocon OX-TRAN[®] 2/21 oxygen permeation apparatus. The OX-TRAN[®] uses a continuous-flow testing cell method approved by the ASTM (D 3985). Oxygen is the test gas and inert nitrogen is used as the carrier gas. The sample is loaded into the testing cell and flushed with nitrogen gas to purge out excess gases and to develop a zero point for the test. Pure oxygen gas is introduced to one side of the test cell; the driving force for permeation is a difference in partial pressure of oxygen since the concentration of oxygen on the carrier side of the cell is maintained at essentially zero. Oxygen is carried away from the downstream surface of the film by the nitrogen carrier gas to a coulometric sensor.

Permeability P and diffusivity D are obtained by performing a two-parameter least-square fit of the experimental oxygen flux data to the solution to Fick's second law (Equation 1).⁴

$$J(t) = \frac{Pp}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-D\pi^2 n^2 t / l^2) \right] \quad (1)$$

Using the solution-diffusion equation (Equation 2), the solubility S is then calculated.

$$P = D \cdot S \quad (2)$$

Mechanical and thermal properties were also investigated. A Rheometric Scientific DMTAV was used to perform small-strain dynamic mechanical analysis at a frequency of 1 Hz using a temperature sweep of 5 °C/min. A TA Instruments Q1000 DSC was used to investigate thermal properties, namely the glass transition temperature. Samples were scanned at 10 °C/min. Pencil hardness values were obtained using a standard ASTM testing procedure.

Results and Discussion

A clear, uniform 3-Thiol+TTT film cured on a Fusion curing line equipped with a D bulb was removed from the glass substrate and prepared for gas barrier measurements on the Mocon system described in the Experimental section. An example of the experimental oxygen flux data generated during testing fit to the two-parameter model is shown in Figure 2 for the photocured 3-Thiol + TTT film with a thickness of 0.088 mm. The flux curves exhibited traditional Fickian behaviour, and it was thus possible to extract D and S values from the non-linear rise of the flux curve and P from the steady-state flux upon taking into account the film thickness. Oxygen permeability values for several different film samples of the 3-Thiol+TTT formulation, including values from an annealed film, are shown in Table 1. These values demonstrate a window of repeatability for the films and indicated no significant change due to annealing, at least under the regime used to process, store and evaluate the barrier properties.

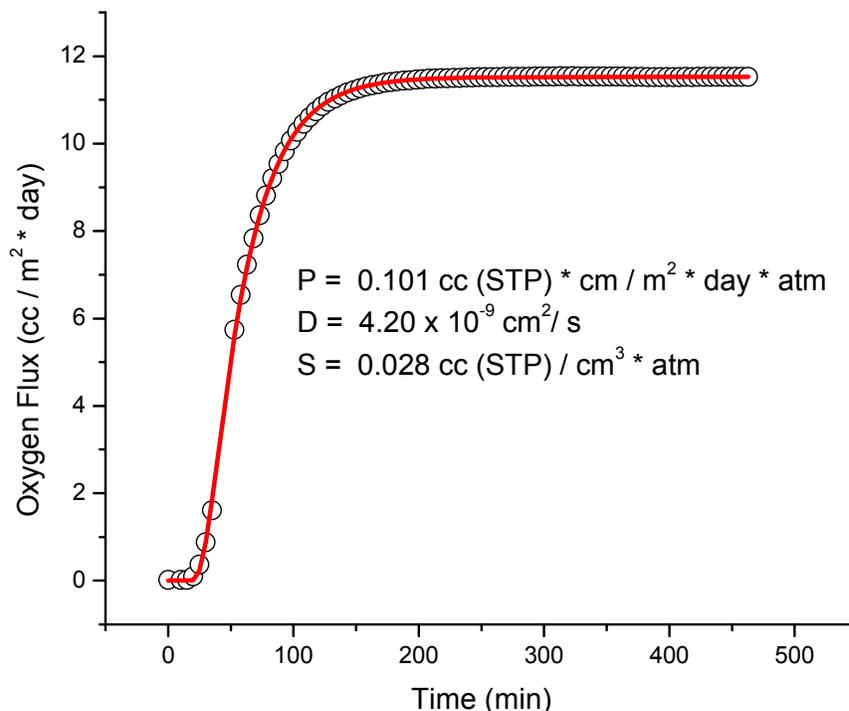


Figure 2. Experimental oxygen flux data with two-parameter fit curve (red) for 3T-TTT annealed film of 0.088 mm thickness with corresponding P, D, and S values.

Material	Oxygen Permeability	
	(cc (STP) * cm / m ² * day * atm)	
3T+TTT	0.081, 0.083	
3T+TTT (annealed)	0.104	

Table 1. Oxygen permeability results for multiple film samples of the 3-Thiol + TTT formulation.

Since traditional thermal processed high-oxygen barrier plastics are well-established, it is important to draw performance comparisons to these industrial standards. Figure 3 shows oxygen permeability values for styrene-co-acrylonitrile (SAN), poly(vinylidene chloride) (PVdC), nylon 6, and poly(ethylene terephthalate) (PET) at or near room temperature⁵ compared with results from one of the UV-curable thiol-ene barrier films presented in Table 1. It is obvious that the 3-Thiol+TTT photocured film exhibits barrier properties, corrected for film thickness, that is significantly better than typical polyethyleneterephthalate (PET) and nylon, and only 2-3 times that of a polyacrylonitrile-styrene copolymer and polyvinylidene chloride. This places it in the range of having reasonably good barrier properties.

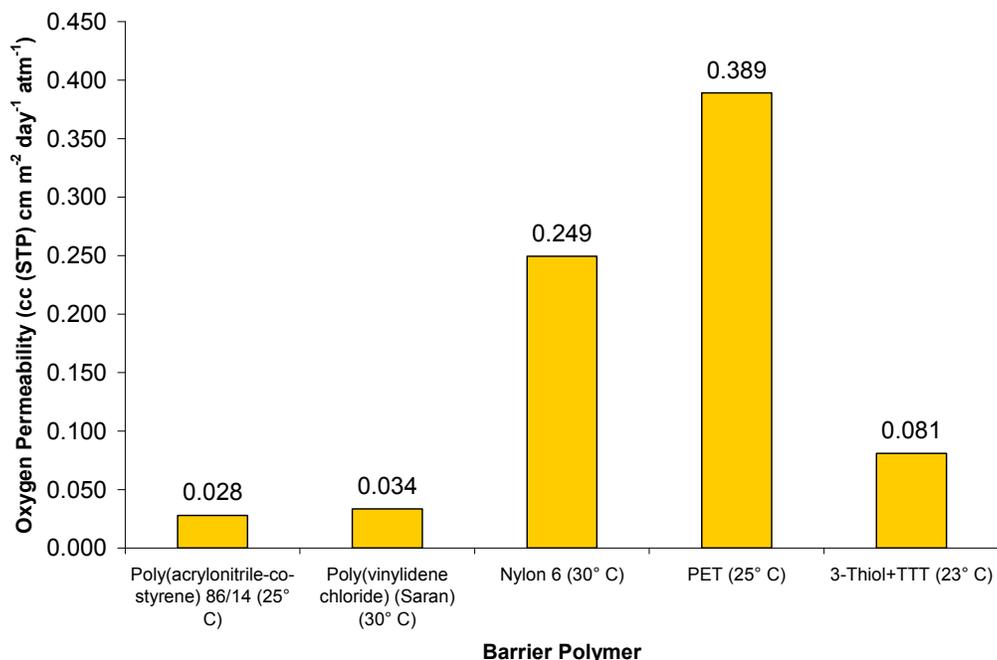


Figure 3. Permeability comparison of new thiol-ene barrier films to current barrier materials.

In addition to exhibiting a high barrier to oxygen transport, the 3-Thiol+TTT UV-cured film also maintains the unique advantages of thiol-ene photopolymerized network materials. These include, as mentioned in the introduction, polymerization in air due to no oxygen inhibition, and a highly uniform network with narrow glass transitions. 3-Thiol+TTT films also have 7H pencil hardness indicating a fairly robust coating. Figure 4a shows a tan delta plot obtained from dynamic mechanical analysis (DMTA) for a 3-Thiol-TTT film. The glass transition obtained from the DMTA results in Figure 4a are certainly consistent with a very narrow glass transition region (with peak maximum occurring at 54 °C) as indicated by the high peak tan delta curve and a base width of only about 30 °C. This type of narrow transition can be contrasted to the tan delta mechanical plots for films formed by photocuring typical multifunctional acrylates which can extend over temperature ranges as high as 150 to 200 °C. Figure 4b shows a corresponding DSC exotherm plot for the photocured 3-Thiol-TTT film. Since the corrected scanning frequency is much lower than used for the DMTA analysis, its glass transition region occurs at a lower temperature range. Nonetheless, the DSC scan has a very narrow transition region (no greater than about 20 to 25 °C) with some indication of sub- T_g relaxation occurring during scanning. The implications for designing materials with narrow transitions for gas barrier materials applications will be considered in the presentation.

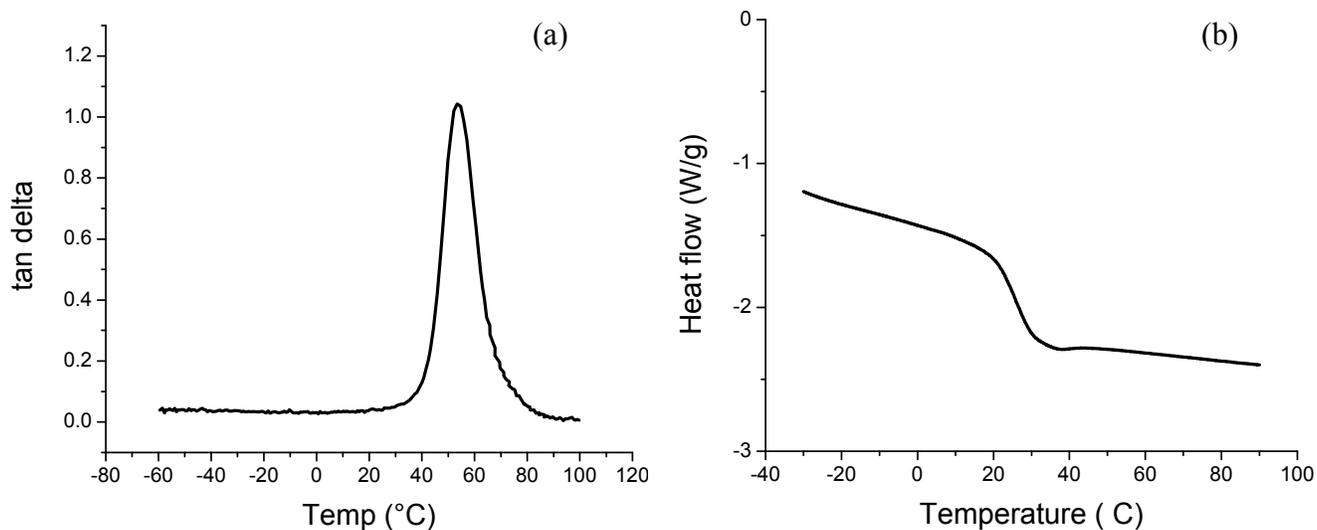


Figure 4. Tan delta plot via DMTA and heat flow exotherm via DSC for 3Thiol-TTT film.

Conclusions

UV-photopolymerized thiol-ene films comprising commercially-available monomers were fabricated and tested for oxygen barrier and mechanical properties. The system of 3-Thiol with TTT ene monomer showed remarkably high oxygen barrier performance. Other thiol-ene systems with structural variations are currently being evaluated and will be discussed in the presentation along with a description of structural parameters that may be important in general in designing photocurable gas barrier materials.

References

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