

New Fast Curing Aliphatic Laminating Adhesives Reduce Waste and Energy Consumption

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Abstract: Two-component solventless urethane laminating adhesives are used in high speed converting of film-to-film laminations for food, industrial goods and lawn and garden packaging. Aliphatic urethane adhesives are typically used instead of aromatic urethane adhesives in applications requiring good uv stability and meeting FDA compliance for cook-in-bag and retort applications. Current commercial aliphatic urethane laminating adhesives either cure too fast or too slow. The faster curing systems typically contain a catalyst giving full cure of the laminated structure in an acceptable timeframe, but has the deficiency of having a short mixed pot-life. The short pot-life causes more frequent shutdowns and clean up of the converting equipment. Low or no catalyst containing systems have slow reaction rates giving favorable long pot-life and requiring fewer shutdowns to clean up. However, the laminated structure containing these adhesives takes several days to up to two weeks to fully cure. To circumvent the slow cure rate, converters use hot-rooms to force cure the adhesive in a reasonable time. This is an added step to their process which requires additional storage space, adds cost, and may be unacceptable for some heat sensitive films.

New technology has been developed in solventless aliphatic urethane laminating adhesives to provide long pot-life with faster full cure. This reduces machine down time due to slower viscosity build and also provides fully cured laminates in a shorter time at ambient temperature.

Introduction:

Flexible packaging laminating adhesives are used to bond two or more films, paper or foil together to protect the graphics of the package and/or add utility to the package. For example, a stand up food pouch may consist of reverse printed polyester film (PET) adhesively bonded to polyethylene film (PE). The PET film provides high gloss and scuff resistance to protect the printed graphics, while the PE film provides a surface that can be heatsealed to form a food containing pouch or bag. The adhesive must have good adhesion to the films and ink, good appearance, good heat resistance, does not scavenge slip from the film and have good resistance to the ingredients being packaged.

Solventless, otherwise known as 100% reactive, adhesives are an excellent choice for laminating adhesives. Typical features and properties of solventless adhesives include:

- Two-components
 1. Polyisocyanate (usually MDI-based)
 2. Curative (mixture of polyols)
- Low initial mixed viscosity (1,000 – 3,000 cps); reaction begins immediately after mixing the two components
- Slightly over-indexed with isocyanate
- Low-to-zero green bond off-line; requires high tension control coater
- Cure rate is typically 1-3 days

Two-component solventless adhesives have been commercially successful due to the following advantages:

1. Versatility in formulating polyurethanes that meet FDA compliance, price and performance.
2. Smaller capital investment for converters (i.e., lower cost equipment, no oven, no incinerator)
3. Less energy consumption due to no ovens or incinerator
4. Lower adhesive coat weight compared to solvent and water-based adhesives
5. Higher production line speeds
6. No solvent costs or VOCs
7. Smaller floor space requirement

However, solventless laminating adhesives do have disadvantages or limitations. Here are few limiting the broader success of this technology:

1. Low-to-zero green bond; unable to laminate and slit in-line
2. Poor adhesion with some laminations using water-based inks
3. Poor balance of long pot-life and fast full cure; especially for aliphatic urethane adhesives.

Aliphatic urethane adhesives are typically used instead of aromatic urethane adhesives in applications requiring good uv stability and meeting FDA compliance for cook-in-bag and retort applications. Current commercial aliphatic urethane laminating adhesives either cure too fast or too slow as shown by control 1 and 2, respectively in Figure 1. The faster curing systems typically contain a catalyst giving full cure of the laminated structure in an acceptable timeframe, but has the deficiency of having a short mixed pot-life. The short pot-life caused by fast reaction results in more frequent shutdowns and clean up of the converting equipment. Low or no catalyst

containing systems have slow reaction rates giving favorable long pot-life and requiring fewer shutdowns to clean up. However, the laminated structure containing these adhesives takes several days to up to two weeks to fully cure. Figure 2 shows the differential scanning calorimetry results for controls 1 and 2. Both adhesives take 4+ days to fully cure. To circumvent the slow cure rate, converters typically use hot-rooms to force cure the adhesive in a reasonable time. This is an added step to their process which requires additional storage space, adds cost, and may be unacceptable for some heat sensitive films.

Figure 1. Initial viscosity profiles of current aliphatic isocyanate laminating adhesives.

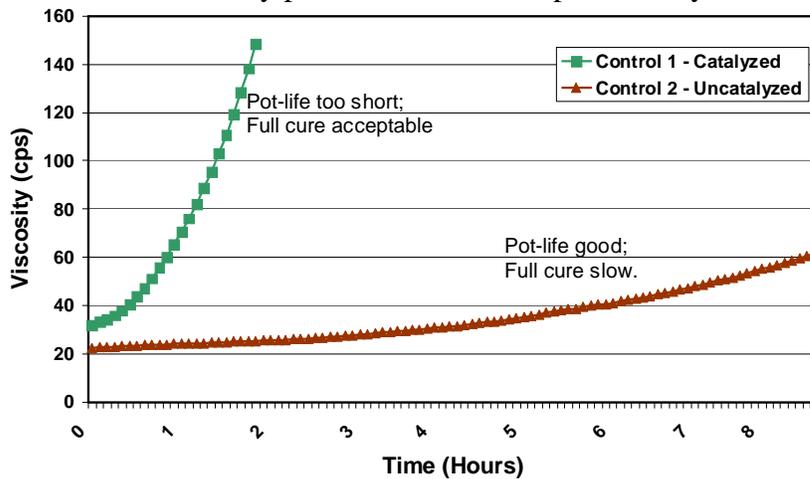
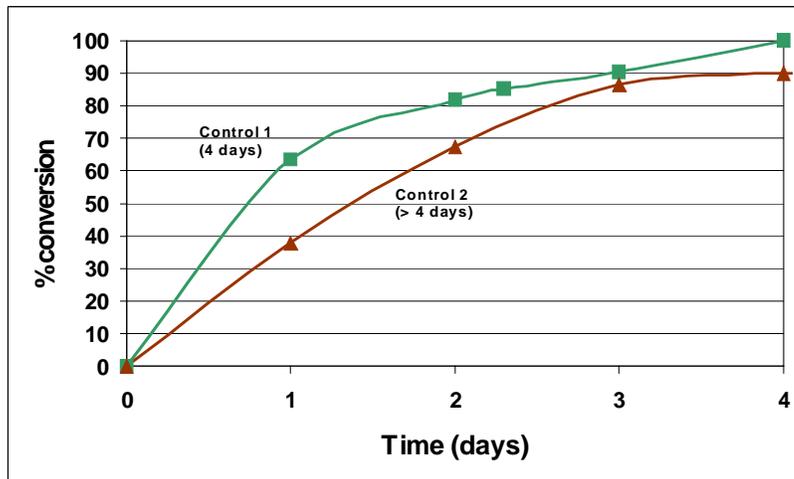


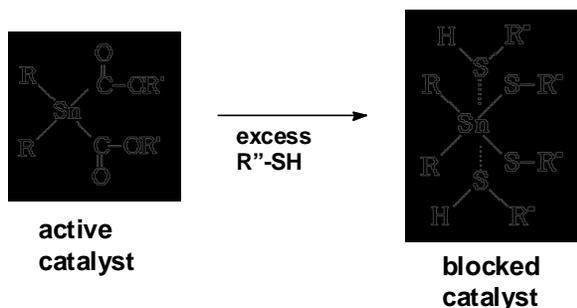
Figure 2. Differential Scanning Calorimetry of current aliphatic laminating adhesives.



New Development for Aliphatic Isocyanate Adhesives

New aliphatic laminating adhesives with long pot-life and faster full cure without the use of a hot-room were developed to improve efficiency and reduce waste in the lamination process. This paper shares our discovery in achieving this accomplishment by use of a blocked urethane catalyst. Figure 3 shows the proposed structure of the blocked catalyst.

Figure 3. Proposed blocked catalyst



Since aliphatic laminating adhesives are significantly used in food packaging, most of the testing included raw materials with FDA compliance and low-to-zero extractability. The blocking agents included in this paper are a monofunctional mercapto-silane and a trifunctional mercaptan. The catalyst is dibutyltin dilaurate.

Variable affecting the catalyst pot-life and full cure

Figure 4 shows that as the amount of blocking agent increases, the pot-life of the adhesive is extended as expected. The type of blocking agent gave similar results as long as the mole ratio of mercaptan to tin was held constant. Figure 5 shows that at storage temperature of 40°C, the open time of the adhesive gradually increases with time. For the specific formulation tested, this equilibration at 40°C took 5-6 weeks. Testing was continued through 3 months, but the open time results were similar to those at week 5 and 6. Based on the affect time had on extending the pot-life at 40°C, testing was completed at elevated temperatures to determine if blocking could be completed within a few hours. Figure 6 shows test results for pre-treating the blocked catalyst curative to different elevated temperatures. Essentially heating resulted in providing a fast option to fully block the catalyst.

Figure 4. Ratio affect of blocking agent to catalyst on open time.

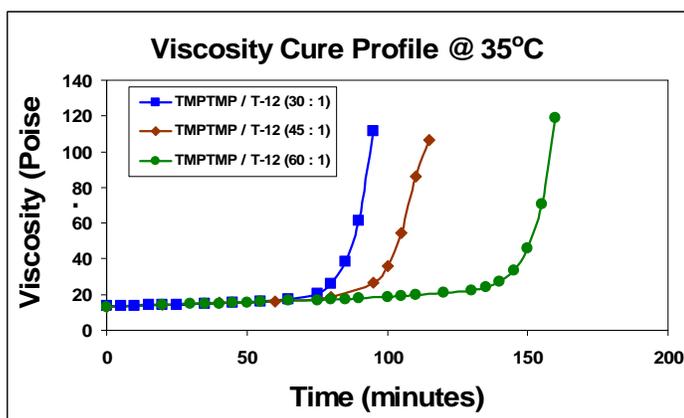


Figure 5. Adhesive pot life increases with age of blocked catalyst curative

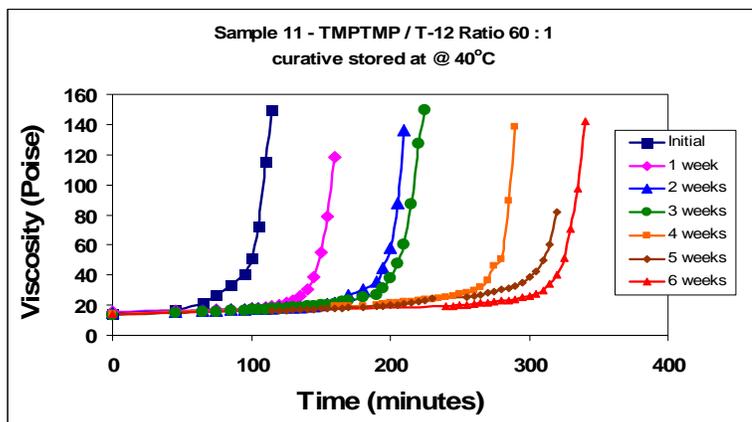
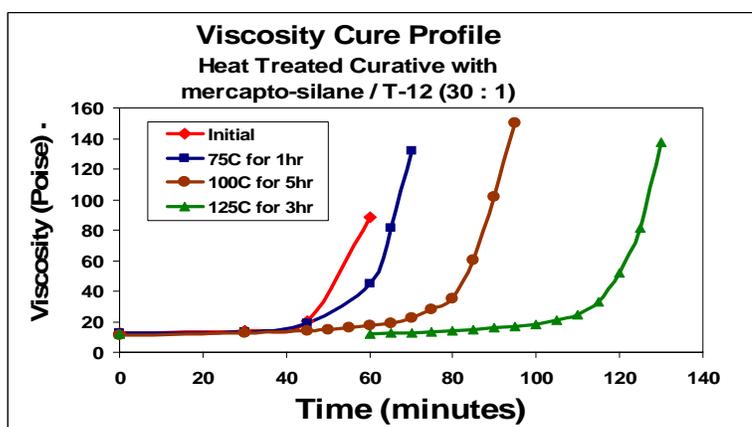
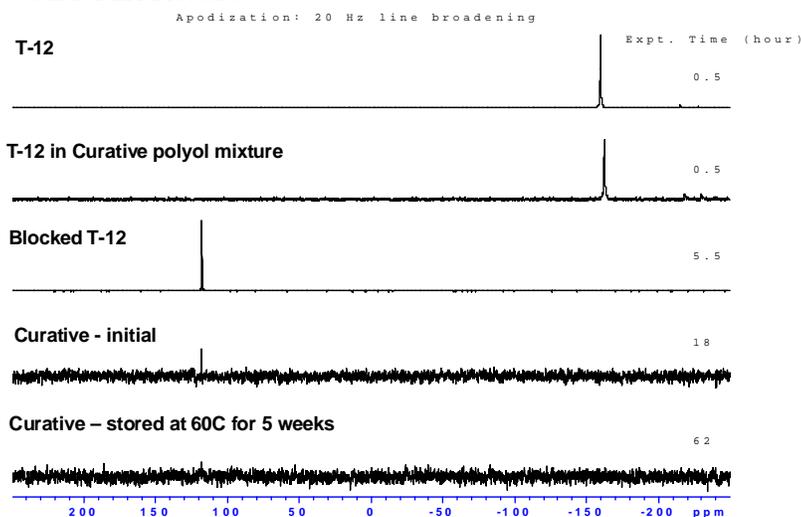


Figure 6. Temperature treatment of blocked catalyst curative and affect on adhesive open time.



Due to affect time and elevated temperature had on increasing the open time of the adhesive, analysis attempts were made to look at the chemical nature of the tin during each step. Figure 7 shows the ^{117}Sn NMR results for the pure catalyst, the pure catalyst in the polyol curative, the blocked catalyst mixture, and the blocked catalyst in polyol both initially and over 5 weeks at 60°C . The tin peak is very clean for the pure forms and the mixture of blocking agent and catalyst, but once formulated the peak disappears. The signal of the blocked tin catalyst in the polyol mixture becomes severely attenuated and / or dispersed with aging and heat.

Figure 7. ^{117}Sn NMR Results



Summary

The technology development of long pot life with fast full cure for solventless aliphatic urethane laminating adhesives was successful. Figure 8 shows the long pot life of two new formulations compared to the controls. Figure 9 shows the improved cure #2 formulation which has a very long pot life fully cures in two days at ambient temperature. Addition of a hotroom further reduces the cure time to about one day.

Figure 8. Pot life stability of new improved cure technology compared to controls.

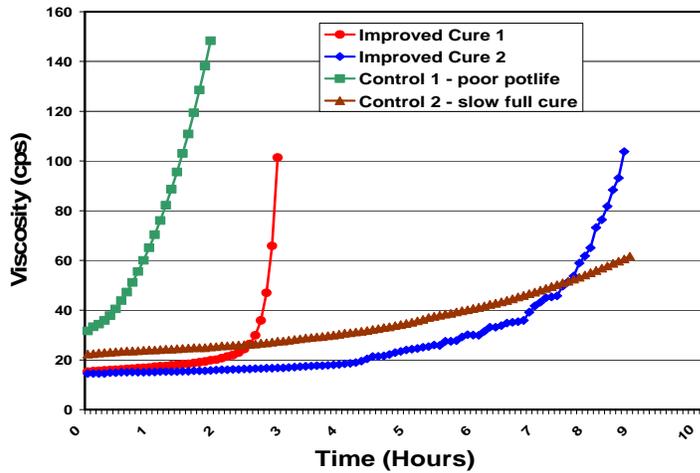
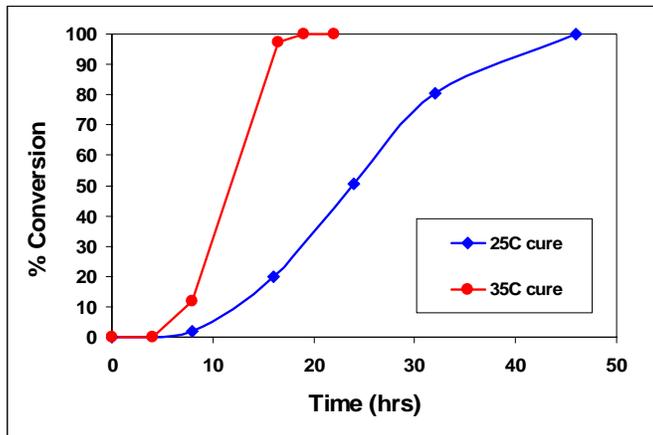


Figure 9. DSC cure of Improved Cure Formulation 2 at 25°C and 35°C.



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