Fundamentals of the Adhesion Mechanisms at the Plexar® Tie-Layer Resin/EVOH Interface

lyondellbasell

FUNDAMENTALS OF THE ADHESION MECHANISMS AT THE PLEXAR® TIE-LAYER RESIN/EVOH INTERFACE

Maged G. Botros, Ph.D., Equistar Chemicals, LP

(*This article originally presented at FUTUREPAK, November 17, 1994.*)

ABSTRACT

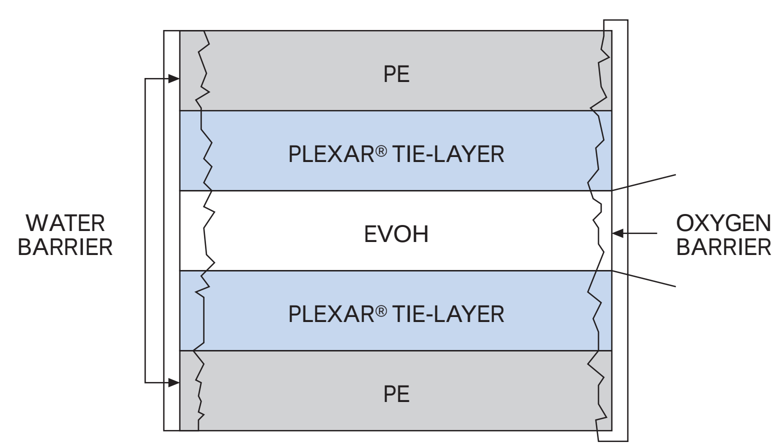
Plexar tie-layer resins are used in multi-layer films to bond non-polar polyolefin moisture barrier layers to polar oxygen barrier layers such as ethylene vinyl alcohol (EVOH). The mechanisms of adhesion at the Plexar tie-layer/EVOH interface were investigated on model systems using Fourier Transform Infrared (FTIR) spectroscopy. The results indicate that Plexar tie-layers react rapidly upon coextruding with EVOH, forming a significant number of covalent bonds. This fast reaction is followed by a similar but much slower reaction. Other types of bonds are also involved in the reaction, e.g. hydrogen bonding (H-bonding) and dipole-dipole interactions. Tie-layer resins with different rates of bond formation and adhesion mechanisms were also examined.

INTRODUCTION

Tie-layer resins are used in multi-layer film production [1,2]. The tie-layer's function is to bond dissimilar resins in composite structures, e.g. oxygen and moisture barrier layers in food packaging applications (Figure 1).

Tie-layer resins are synthesized mainly by modifying polyolefin resins through the addition of functionality. Acid or anhydride molecules are added to polyolefins through grafting or direct synthesis of copolymers or terpolymers [3-8]. Plexar tie-layer resins were some of the first materials of this type introduced to the market in 1976. Plexar tie-layers form very strong adhesive bonds to EVOH and polyolefins in multi-layer coextruded films. This paper deals with the adhesion mechanisms of Plexar tie-layer resins and ways of improving adhesive properties of coextruded, multi-layer films.

Figure 1. A multi-layer coextruded film with a Plexar tie-layer between layers of EVOH and polyethylene (PE)



EXPERIMENTAL METHODS

The Fournier Transform Infrared (FTIR) spectrometer (single-beam Nicolet 6000 instrument) was purged with dry air to eliminate water vapor and used to record the IR spectra. Film samples of Plexar-A, Plexar-B, Plexar-C, EVOH copolymers and their blends were used to obtain the transmission IR spectra.

The attenuated total reflection (ATR) spectra were also collected using multi-layer films with Plexar tie-layers and EVOH layers in contact with one another.

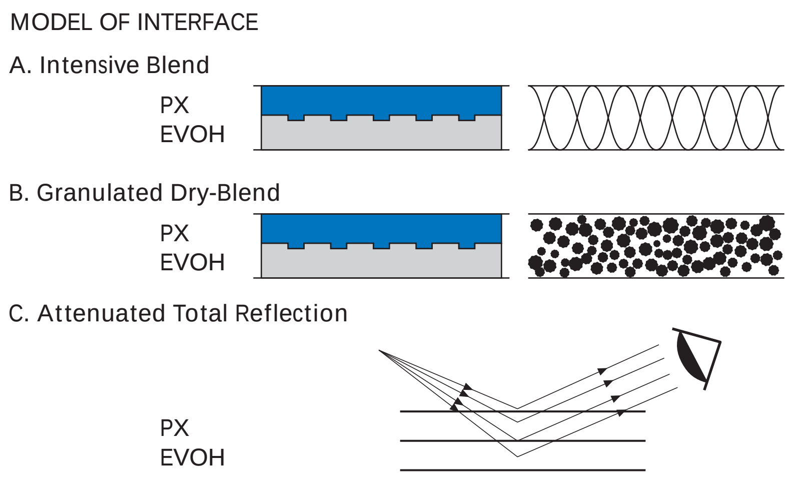
The reaction time and temperature of the film samples were monitored by using a heating chamber with a variable temperature controller inside the IR spectrometer.

MODEL SYSTEMS

In order to investigate the chemical interactions at the interface between Plexar tie-layers and EVOH, two model systems were designed together with an actual multi-layer film sample (Figure 2), using transmission as well as ATR-FTIR techniques.

The first system studied was the "intensive blend" model, in which Plexar resin and EVOH were thoroughly mixed in a single screw extruder at 210°C for a residence time of one minute. In the second system, Plexar resin and EVOH were ground to 35 mesh and pressed into a film at 210°C for a "granulated dry-blend" model. A multi-layer film sample of Plexar resin/EVOH/Plexar resin was also examined using the ATR-FTIR technique.

Figure 2. Model systems used to investigate the interactions at the Plexar resin (PX)/EVOH interface



RESULTS AND DISCUSSION

Figure 1 shows the two interfaces in the proposed multi-layer film structure. At interface 1, the "compatible interface," bonding occurs by chain entanglement, Van der Waals forces and co-crystallization. This interaction is affected by the chemical composition, the melt index and the elasticity of the coextruded films. At interface 2, the "incompatible interface," bonding occurs by chemical reactions, H-bonding and dipole-dipole interactions.

The FTIR technique was used to detect and characterize the interactions between Plexar resin and EVOH at interface 2. The bands in the IR spectra arising from the functionality in the Plexar resin disappear completely after mixing in the intensive blend system, indicating that a very fast reaction takes place between the Plexar resin and EVOH.

With the granulated dry-blend system, the dynamics of the interactions at the interface could be studied. In this case, the Plexar resin functionality band took about two minutes at 210°C to disappear. The decrease in the intensity of this band in the first two minutes of the reaction suggests the formation of covalent bonding at the Plexar resin/EVOH interface.

This decrease in functionality band intensity was accompanied by a corresponding formation of an ester band and a gradual increase in its intensity. The increase in the ester band intensity is due to the interaction between the functionality in the Plexar resin and the OH groups in EVOH.

COVALENT BONDING IN PLEXAR RESIN/EVOH SYSTEMS

From the previous results it can be concluded that the fast reaction taking place in Plexar resin/EVOH systems is due to covalent bonding. This conclusion is also supported by the depletion of the Plexar resin functionality over time at 210°C in the Plexar resin/EVOH mixture (Figure 3). In addition, plotting the intensity of the ester band formed due to the interaction of Plexar resin and EVOH further supports the conclusion of covalent bond formation (Figure 4). Figure 5 combines the results of both plots in the same time frame.

Figure 3. Depletion of functionality of Plexar-A/EVOH between 0 and 1.5 minutes at 210°C

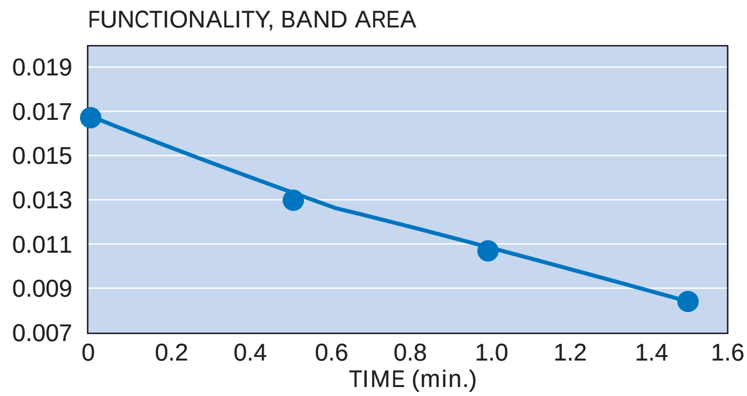


Figure 4. New band formation due to interaction between Plexar-A and EVOH between 0 and 1.5 minutes at 210°C

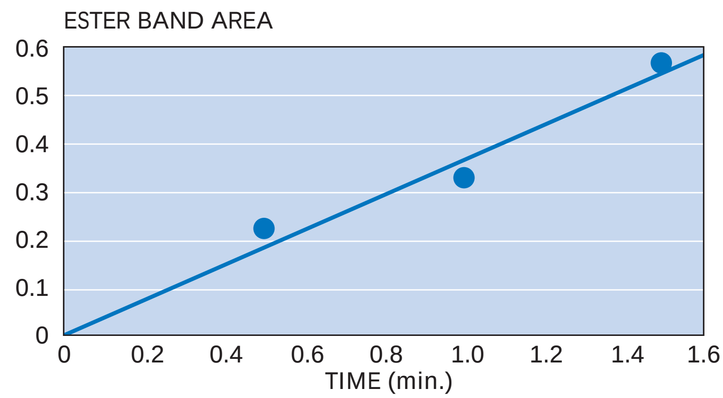
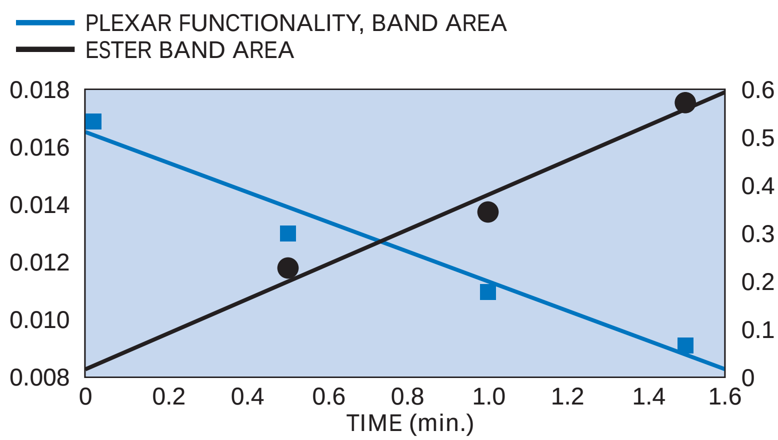


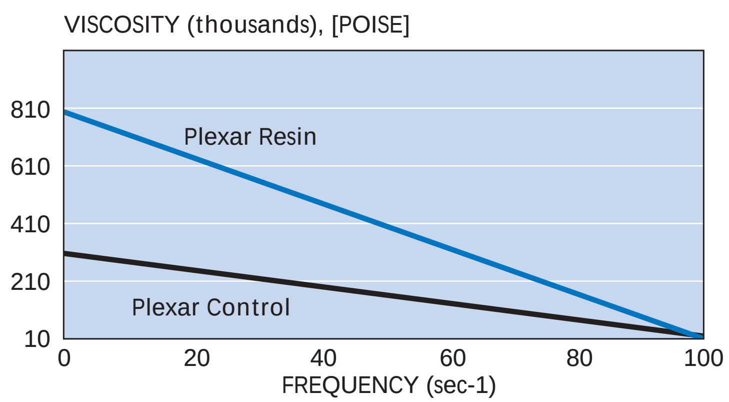
Figure 5. Depletion of functionality and new band formation in the first 1.5 minutes of reaction time in the Plexar-A/EVOH system at 210°C



To confirm these results, melt rheology measurements were conducted on a 50:50 melt blend of Plexar resin/EVOH and a non-functionalized Plexar resin analog with EVOH.

Figure 6 shows that the apparent viscosity of the Plexar resin/EVOH blend is higher than that of the non-functionalized Plexar resin/EVOH blend. This increase in viscosity in the Plexar resin/EVOH blend is due to interchain covalent bonding, yielding a higher molecular weight block polymer of Plexar resin/EVOH. Since the non-functionalized Plexar resin analog cannot chemically react with EVOH, no bonding with concurrent increase in viscosity is observed.

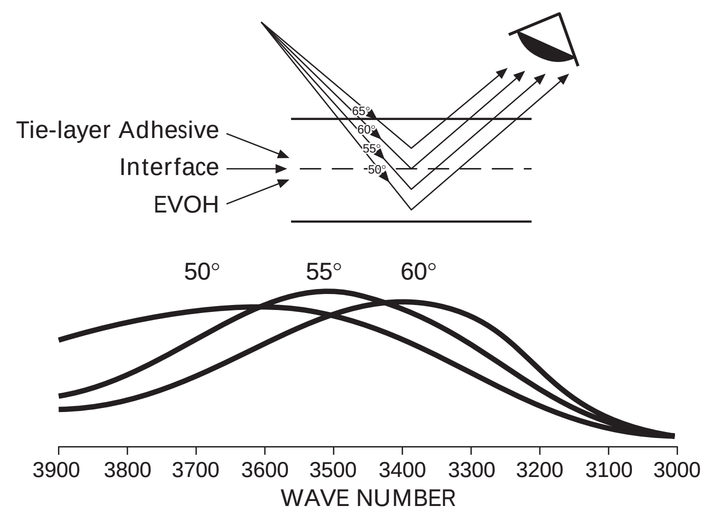
Figure 6. Rheological measurements on a 50:50 melt blend of Plexar resin/ EVOH and a blend of a non-functionalized Plexar resin analog and EVOH.



DETECTION OF H-BONDING IN PLEXAR RESIN/EVOH SYSTEMS

H-bonding was detected at the Plexar resin/EVOH interface using the ATR-FTIR technique. Sample films of Plexar resin/EVOH/Plexar resin were used as model systems. By changing the angle of incidence of the IR beam, the depth of penetration can be controlled. As seen in Figure 7, when this angle is varied from 60° to 50°, the OH stretch band of EVOH changes position from lower to higher wave numbers. This behavior indicates the presence of different types of H-bonds. At the interface (in this case reached at 60°), inter-molecular H-bonds predominate and exist at low frequencies. When the sample layers are penetrated more deeply by the IR beam (leaving the interface towards the EVOH layer), the OH band shifts to a higher frequency. This shift is due to the existence of more free and intra-molecular H-bonds in the EVOH layer compared to the number of inter-molecular H-bonds at the interface [9,10].

Figure 7. An ATR-FTIR study of the intermolecular H-bonding at the Plexar resin/EVOH interface



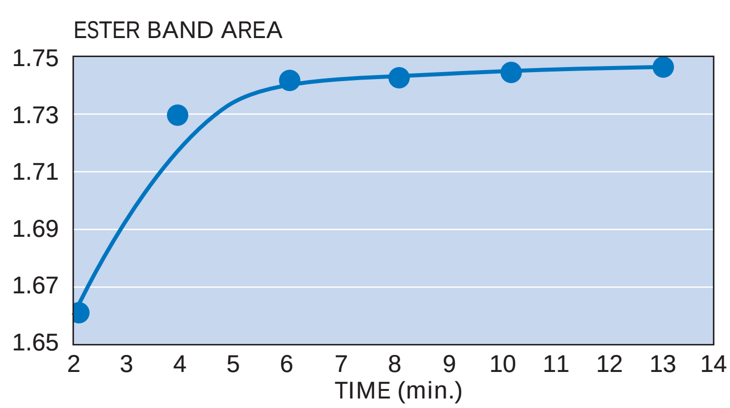
REACTION KINETICS

To investigate the reaction kinetics in Plexar resin/EVOH systems, the intensity of the ester band formed upon interaction was normalized and then plotted against reaction time. This study included three resins: Plexar resin-A, Plexar resin-B and Plexar resin-C. The results obtained follow.

Plexar resin-A

This Plexar resin showed two reaction rates using the granulated dry-blend model system (Figure 8). The first rate is caused by a very fast reaction occurring in the first four minutes at 210°C. This initial rate of reaction was 17 times faster than the second rate which began after the first four minutes.

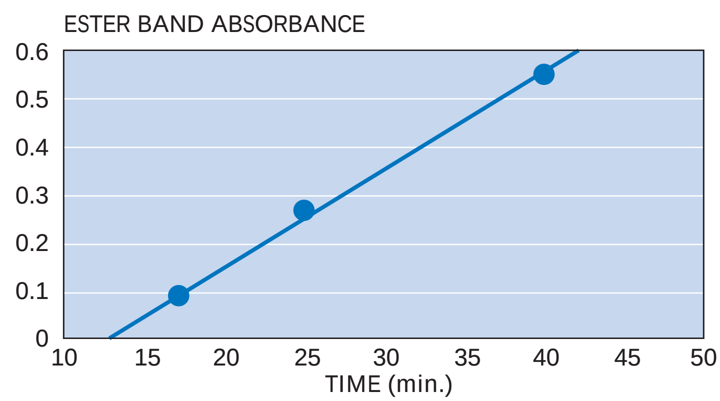
Figure 8. Detection of two reaction rates in the Plexar-A/EVOH system



Plexar resin-B

The interaction of Plexar resin-B with EVOH was studied in the same way as Plexar resin-A. Figure 9 shows that no interaction could be detected in the first 17 minutes, indicating that this combination resulted in a very slow reaction as compared to the Plexar resin-A/EVOH system. However, it is very important to note that the time frames given here do not reflect the reaction times obtained when actually coextruding Plexar resin and EVOH. The experimental time frames only indicate the differences between the systems. In actual practice, the bonding reaction between the Plexar resin and EVOH would be much faster, as indicated by the intensive blend model system discussed earlier.

Figure 9. Detection of one reaction rate in the Plexar-B/EVOH system

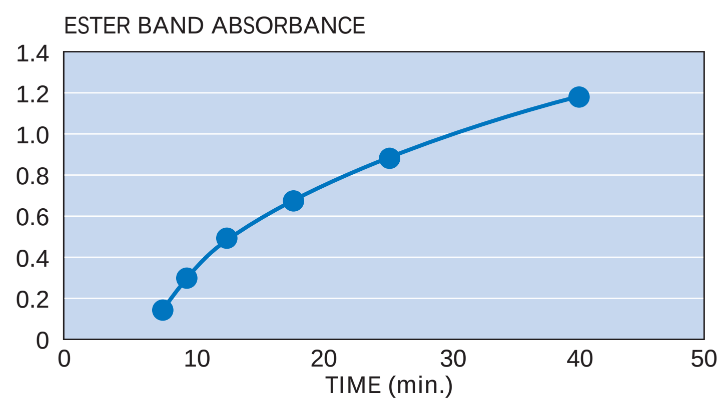


Plexar resin-C

The interaction of Plexar resin-C with EVOH was studied in the same manner as done with Plexar-A and B and results are shown in Figure 10. The Plexar-C/EVOH system had reaction behavior similar to that of the Plexar-A system. To further illustrate the mechanism of interaction in the Plexar-C/EVOH system, the decrease of the intensity of the Plexar-C functionality band was plotted between 0 and 150 minutes at 210°C (Figure 11). This information provides support for the results shown in Figure 10.

Comparing the three systems – Plexar-A/EVOH, Plexar-B/EVOH and Plexar-C/EVOH – the intensity of the new ester band formed upon interaction is plotted

Figure 10. Plexar-C/EVOH system reaction profile as indicated from the new band intensity-reaction time study



against time in Figure 12. It can be concluded that Plexar-A has the highest rate of interaction with EVOH followed by Plexar-C and then Plexar-B.

Figure 11. Plexar-C/EVOH system reaction profile as indicated from the depletion of the Plexar-C functionality band intensity versus reaction time

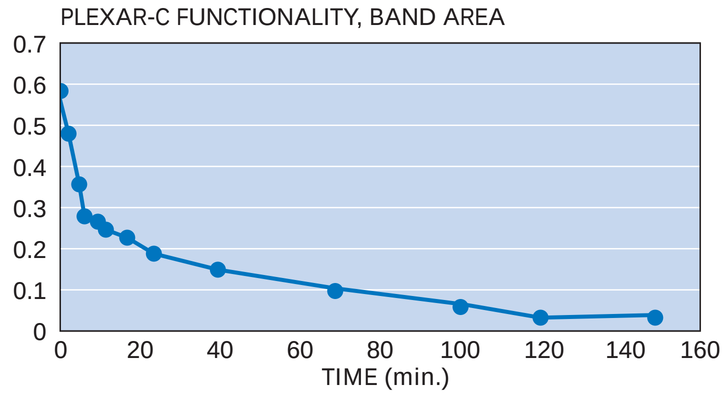
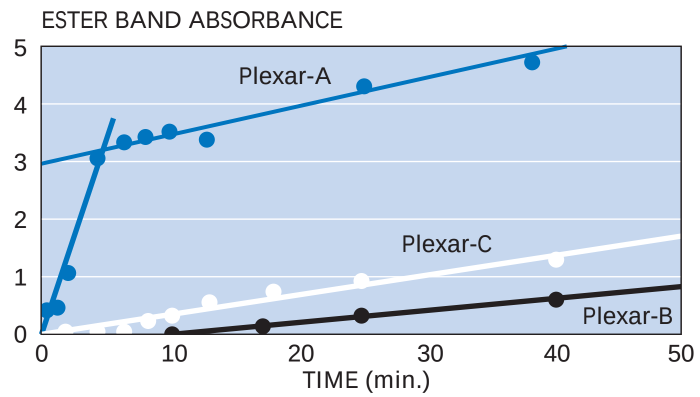


Figure 12. Comparison of reaction profiles in Plexar-A, Plexar-B and Plexar-C mixtures with EVOH



CONCLUSIONS

Methods of sample handling, model systems and techniques using FTIR have been shown to be very useful in following the interactions in Plexar tie-layer /EVOH systems. The following points can be concluded from this study:

1. Covalent, as well as H-bonding, has been detected in Plexar tie-layer/EVOH systems.
2. A very fast reaction, with evidence of covalent bonding, has been detected in Plexar-A and Plexar-C systems. This fast reaction is followed by a much slower secondary reaction.
3. Plexar-B has shown a different mechanism of bonding to EVOH with a much slower reaction rate than Plexar-A and Plexar-C.
4. The control of adhesion mechanisms in Plexar tie-layer resins and ways of improving adhesive properties of coextruded multi-layer films were demonstrated.

REFERENCES

[1] William C.L. Wu, Lawrence J. Krebaum, and John Machonis, Jr., U.S. Pat. 3,873,643, 1975.

[2] James W. Moriarty, Jr., U.S. Pat. 4,668,571, 1987.

[3] William C. Drennan, **Plastics Packaging**, 32, Sept., 1988.

[4] David A. Bivans and Gray L. Duncan, U.S. Pat. 4,064,315, Dec. 20, 1977.

[5] Charles R. Ashcraft and Michael L. Kerr, U.S. Pat. 4,650,721, Mar. 17, 1987.

[6] Duane A. Krueger and Thomas W. Odorzynski, U.S. Pat. 4,361,628, Nov. 30, 1982.

[7] Duane A. Krueger and Thomas W. Odorzynski, U.S. Pat. 4,552,714, Nov. 12, 1985.

[8] Duane A. Krueger and Thomas W. Odorzynski, U.S. Pat. 4,617,240, Oct. 14, 1986.

[9] T. Akahane, Y. Kazusa, and H. Nakaysu, **Kobunshi Ronbunshu**, 37 (5), 383-387, 1980.

[10] L.J. Bellamy, **The Infra-red Spectra of Complex Molecules**, N.Y.: John Wiley & Sons, Inc., 1958.

LyondellBasell Industries
P.O. Box 3646
Houston, TX 77252-3646
United States

www.LYB.com

7636/0715