**New Developments in Plexar® Tie-Layer Adhesives**

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**ABSTRACT**

Plexar® products were the first tie-layer adhesives developed in North America. These products are tailored for targeted applications and processes and are designed to give controlled adhesion at the interface in multilayer co-extruded structures. Typical structures include a barrier layer, such as ethylene vinyl alcohol (EVOH) or polyamide, and a polyolefin, such as polyethylene or polypropylene. Other structures include polystyrene, high impact polystyrene or their combinations.

This paper is aimed at introducing new high performance tie-layer adhesives. Performance is studied in several extrusion processes and in different applications. Applications cover a wide range of uses including food packaging, metal lamination, multi-layer pipe, and wire and cable.

The new adhesives are designed to give improved adhesion, while maintaining high clarity in multi-layer barrier applications. In highly demanding applications, such as orientation and thermoforming, the new adhesives are designed to dissipate the interfacial stresses in order to maintain high bond strength. Correlation between macro-scale performance and molecular structure was accomplished using newly developed analytical techniques.

**INTRODUCTION**

Tie-layer adhesives have been used in co-extruded and laminate structures for decades. Their main function is to bond dissimilar layers such as polar and non-polar resins primarily in co-extrusion processes. Most notably, tie resins are used in barrier co-extrusions of ethylene vinyl alcohol (EVOH) or polyamide with polyolefins.

Tie-layer adhesives are synthesized mainly by modifying polyolefin resins through the addition of functionality. This is achieved by incorporating acid or anhydride molecules to polyolefins through grafting or direct synthesis of copolymers or terpolymers. The most widespread use of anhydride modified tie-resins is in co-extruded blown and cast film structures. As with thicker rigid packaging and industrial applications, tie resins are primarily used to bond polar and non-polar layers of the structure.

The first section of this paper discusses the impact of tie resins on film transparency. New developments with improved transparency and adhesion are compared to standard adhesives. The effect of barrier material, such as EVOH or polyamide, on clarity was also investigated. The presence of polyamide next to the die resulted in a detrimental effect on film transparency. Special tie-layer grade was developed for such structures for which high adhesion and clarity were simultaneously achieved. An in-depth rheological and atomic force microscopy investigation was performed to determine the main parameters controlling clarity in multi-layer co-extruded films. A new rheological technique was developed and used to predict the effect of tie-layer adhesives on film clarity. The new technique is also used in designing new adhesives with controlled reaction kinetics tailored for specific applications.

The second part of the paper discusses the development of a new high performance tie layer designed to give outstanding adhesion in polystyrene barrier applications. In contrast to current adhesives for polystyrene, the new adhesive is linear low density polyethylene (LLDPE) based and not ethylene vinyl acetate (EVA) based. The new adhesive maintains high adhesion even after thermoforming.
Experimental Techniques

Narrow Angle Scattering Measurement (ASTM D1746)

The Zebedee CL-100 clarity meter was used for Narrow Angle Scattering (NAS) measurements. Multi-layer film specimens were cut into 10 cm x 10 cm squares and adhered to the test unit in front of the light source by air suction. Films were oriented in the same direction and tested in the same fashion to minimize testing variables. A minimum of six specimens were run for each sample.

Rheological Testing

Linear viscoelastic data (dynamic frequency data) and steady-shear viscosity data were obtained with an ARES and an INSTRON rheometer, respectively, at 250°C. Nylon samples were dried at 90°C for at least twenty-four hours prior to rheological testing, to avoid complications due to varying initial moisture content in the polymer. When the dynamic and shear data was available, the Leonov model was fitted for each resin of interest, in order to provide the viscosity and normal stresses as a function of shear rate.

Rheological Probing of the Nylon/Tie Interface

A test was devised to rheologically probe the interaction at the nylon/tie interface. The test was performed on an ARES rheometer in the parallel plate mode (50mm diameter plates), at 10% strain, frequency of 1 rad/sec and temperature of 250°C. Two disks of nylon (bottom) and tie (top) were placed in the gap. The disks had approximately the same thickness and the total gap was about 2.8-3.0 mm. The test consisted of a time sweep at a constant frequency and strain for 30 minutes. Monitoring the dimensionless increase factor of elastic modulus as a function of time, i.e., $G'(t)/G'(0)$, was thought to provide an indication of the interaction at the nylon/tie interface and the kinetics of such interaction.

Atomic Force Microscopy

Atomic Force Microscopy (AFM) was performed on a Veeco (Santa Barbara, CA) MultiMode Scanning Probe microscope. The AFM was operated in Tapping Mode with silicon probes with nominal radius of curvature of less than 10 nm, resonance frequency 300 KHz and force constant 40 N/m. Height (topographic) and phase contrast images were acquired simultaneously. Five micrometer square images required about 4 minutes to acquire at scan rate of 1 Hz. The AFM images are displayed with the height image on the left with light areas being high and dark areas being low and the phase contrast image on the right with light areas being hard and dark areas being soft.

Sample Preparation

Samples were cut in a Leica Ultracut UCT® ultra-microtome with a EMFCS™ cryo-stage (Leica Mikrosysteme GmbH, Vienna, Austria). Samples were held at cryogenic temperatures of -50°C to -90°C during microtoming, depending on sample brittleness. An initial cut was made with a glass knife in order to produce a flat face on the sample. Subsequently a diamond knife was used to microtome the finished smooth face on the thicker samples or to cut cross-sections of thin multilayer films. In the case of thicker samples, such as sheet, a smooth face was cut and AFM done directly on this smooth face. In the case of thin samples, such as film, thin cross-sections (approximately 250 nm in thickness) were cut, collected, mounted in adhesive and AFM done on the cross-section faces.

RESULTS AND DISCUSSION

(1) New Tie-Layer Developments for High Clarity Multi-Layer Applications

A. EVOH Barrier Application
In barrier co-extrusion, covalent bonds are formed at the tie-resin interface with EVOH or polyamide while the two polymers are in the melt phase. A detailed investigation of this reaction and correlation to tie-layer performance could be found in a previous TAPPI proceeding by Botros et al. While this interfacial bonding reaction is necessary for adhesion, it can lead to film clarity problems. If the polymers are flowing at different velocities or viscosities, the bonds do not allow the polymers to slip by each other or dissipate stresses. The result can be a non-uniform surface which gives the film a grainy appearance. In an extreme case, the film appears to have gels. These gels are actually the barrier resin being pulled into the tie resin. This type of problem is different from the traditional rheology mismatch between two non-reacting polymers. At these interfaces, the distortions appear to be more like waviness and not as random. For tie-resin barrier interfaces, viscosity mismatch becomes more critical in film transparency.

It is important to note that many factors can dramatically affect interfacial stress and thus film transparency. For instance, identical film structures run on different film lines can have excellent or poor transparencies. Tie resin structure has a lot to do with film transparency. In general, the higher the adhesion is, the lower the transparency. Transparency is measured in this paper by a technique called Narrow Angle Scattering (NAS). In this technique, clarity refers to the optical distinctness with which an object can be seen when viewed through a film. In the manufacture of sheeting or film, the quantitative assessment of clarity is just as important as that of haze. Clarity depends upon the linearity of the passage of light rays through the material. Small deflections of light, caused by scattering centers of the material, bring about a deterioration of the image. These deflections are much smaller than those registered in haze measurements. While haze measurements depend upon wide-angle scattering, clarity is determined by small-angle scattering. Wide and narrow angle scattering are not directly related to each other. Thus, haze measurements cannot provide information about the clarity of the specimen and vice-versa. This method was developed specifically for multi-layer structures for film and sheeting applications.

To further clarify this point, Figure (1), indicates the NAS and adhesion values of LLDPE and multi-layer films with relatively high adhesion and low adhesion to barrier layer. The barrier layer used was EVOH and total film thickness was 125 micron. It is evident from the Figure that clarity, as measured by NAS, is lower in multi-layer films compared to mono-layer LLDPE film. Also, the higher the adhesion at the tie / barrier interface, the lower the measured NAS. Lower transparency (see-through clarity) is not desired especially in food packaging applications. To overcome this problem, new tie-layer adhesives were recently developed that were designed for high clarity and high adhesion at the same time. Figure (2) reveals the performance of a new development labeled Tie-Clarity1 compared to a commercial tie-layer in five-layer cast film with EVOH barrier. The total film thickness was 125 micron and layer distribution is as follows: 43% LLDPE/4%tie/6% EVOH/4% tie/43% LLDPE. It is apparent that the NAS and the adhesion values are much higher than standard tie-layer adhesives used in this application. This new development is a LLDPE-based tie with 1.1 MI and 0.92 density. Figure (2) also shows the results of a higher performance tie resin labeled in this paper as Tie-Clarity2. It also has very high transparency, but a much higher level of adhesion at 16 N/15 mm. This grade was designed for more demanding applications like thermoformed or oriented films.

These new grades were specifically designed for EVOH blown film co-extrusions for which excellent adhesion and transparency are required. They are able to provide high transparency in blown film co-extrusions with EVOH in the core layer for several reasons. They have:

- Good rheological match with most blown film EVOH grades.
- Optimized anhydride content for adhesion and transparency.
- Unique graft architecture.
- Designed with the ability to absorb and dissipate interfacial stresses.

To summarize the problem of NAS transparency loss in barrier co-extrusions there is a tendency for co-extruded barrier films to have low optical transparency due to an apparent instability at the tie-barrier interface. Film descriptors for this phenomenon include ground glass, graininess, or orange peel appearance.

The cause is an uneven interface between the tie layer and barrier layer caused by a cross-linked network of covalent bonds. This cross-linked network amplifies interfacial stresses that lead to nanometer or visible
light wave distortions. To help improve clarity in barrier film co-extrusions, new adhesives were developed having specific designs for targeted structures

B. Polyamide Barrier Application

I. Rheological Investigation

In prior work on multilayer co-extrusion and the interplay of rheology and optical properties, Mavridis and Shroff\(^9\), identified the interfacial shear stress and elasticity ratio at the interface as critical parameters. A similar analysis was undertaken in the present work and was found to be inadequate in capturing or explaining the experimental observations. As will be discussed further below, it is conjecture that such inadequacy was due to the neglect of chemical interactions at the nylon/tie interface. Preliminary experimental results on a rheological test appear to support this conjecture and moreover, to provide a laboratory screening tool for tie resin performance.

Table 1 summarizes clarity results for a three-layer blown film co-extrusion with nylon/tie/LDPE (18/10/72). Film clarity was measured via NAS (ASTM D1746). Two sets of results are presented, the only difference being the tie resin used. The clarity is acceptable (24.2%) for Tie-A, but rather poor and unacceptable (0.3%) for Tie-B2. It is evident that some sort of interfacial instability sets in for Tie-B2.

Table 2 summarizes a similar set of clarity results for a five-layer cast film co-extrusion with nylon/tie/LLDPE/tie/nylon (20/4/52/4/20). Again, two sets of results are presented, the only difference being the tie resin used. Clarity is now good for both tie resins (Tie-A and Tie-B3), although there is a measurable difference between them (59% vs. 50.2%)

To understand the above findings, a modeling and simulation exercise was undertaken, as previously described\(^9\). Typical results are shown graphically in Figures (3) and (4), corresponding to Table 1. Specifically, Figure (3) shows the calculated profile of melt flow velocity in the die, while Figure (4) shows the profile of shear stress. The position of the nylon/tie interface is indicated by the dashed line. The results of these simulations include the calculated shear stress at the nylon/tie interface, the values of the viscosity and elasticity ratio (elasticity characterized by the first normal stress difference) and the interface velocity (Table 1). The corresponding calculations for the five-layer cast film case are summarized in Table 2.

Examination of the results of Tables 1 and 2 shows that:
- Interfacial stress alone (see Schrenk et al\(^13\)) does not explain the clarity results as Figure (5) illustrates by the lack of a common correlation between clarity and interfacial stress.
- Viscosity ratio in Figure (6) or elasticity ratio in Figure (7) are similarly insufficient: they do not correlate with clarity data.

Therefore, it was thought that perhaps an interfacial interaction at the nylon/tie interface, namely a chemical reaction, manifests itself rheologically in the time scale of the coextrusion process and influences correspondingly the interface behavior and thus clarity. If such a scenario was the case, any analysis that did not account for the kinetics of the interfacial interaction would be insufficient to capture and explain the experimental findings.

The rheological test described in the Experimental Section for probing the nylon/tie interface was employed and results are shown in Figure (8). The plots of Figure (8) consist of the time evolution of the increase in the elastic modulus of a nylon/tie structure measured in the rheometer. It shows that the time evolution in the case of nylon/Tie-A is a rather slowly rising curve, particularly at early times. The curve for the nylon/Tie-B3 case is flat very early but then rises faster than that for nylon/Tie-A. Finally, the curve for nylon/Tie-B2 rises the fastest and it corresponds to the case of worst clarity. Therefore, the rheological test for interfacial probing appears to capture faithfully the observed experimental trends. It is thus being used for screening candidate tie-layers in high clarity multilayer structure applications. More work on this matter will be pursued and reported in the future.
II. Atomic Force Microscopy Investigation

Effect of Nylon Layer Thickness and Tie-Layer on Clarity of Polyamide Multilayer Structures

Figure (9) shows the nylon layer in the 20% nylon Tie-B3, nylon/tie/LLDPE/tie/nylon multilayer. The crystalline morphology of the nylon may be readily observed in the phase contrast image. Crystalline “spherulites” of approximately 0.5 µm diameter were detected. The layer structure, as shown in Figure (9), was used in the AFM analysis to determine the location of the various layers of interest. As previously discussed, Tie-A multi-layer exhibited good clarity in Killion-prepared films with 10% and 20% nylon. The Tie-A film interface with 10% nylon is shown in Figure (10). The interface is smooth and exhibits virtually no disruption. In fact the interface between the tie and nylon is not easily discernible. These results confirm that Tie-A works well and exhibits good clarity even under high interfacial stress manifested by thinner polyamide layer thickness. Similarly, Tie-B3 multilayer exhibited good clarity in Killion-prepared films. The Tie-B3/nylon interface is shown in Figure (11). The interface is smooth and exhibits no disruption. These interfaces are exhibiting good adhesion to the nylon layer and good clarity at the same time.

Further, nylon layer thickness did not have an effect on clarity when using the above-mentioned tie adhesives (A and B3), which are designed for high clarity applications. On the other hand, Figure (12) shows the NAS data for adhesives (A and B4), indicating good clarity when using Tie-A irrespective of nylon layer thickness. In contrast when using tie adhesive not designed for clarity applications, such as Tie-B4, nylon layer thickness had a significant, deleterious effect on NAS, as nylon layer thickness decreased, as seen in Figure (12).

AFM results clearly show the interfacial instability in films prepared with Tie-B4. Figure (13) shows the interface for the 10% nylon structure while Figure (14) is for the 20% nylon using Tie-B4. A gap (approximately 0.2 µm in width) running vertically in the phase contrast image may be observed in Figure (13). A gap (approximately 0.4 µm in width) running vertically in the phase contrast image may be observed in Figure (14). These gaps in the adhesion of the tie/nylon interfaces apparently are one contributing factor to the poor clarity observed. In Figures (13) and (14) mixing of the tie and nylon may be indicated by the vertical lines observed. These vertical lines apparently indicate a successive layering of the two polymers (Tie-B4 and nylon) near the interface. Both effects of micro delamination and interlayer mixing contribute to the reduced clarity (NAS) of films made with Tie-B4.

In conclusion, the new tie-layer developments were carefully designed to simultaneously obtain optimum interfacial adhesion and high clarity. To achieve this goal, several rheological parameters as well as controlled reaction kinetics were taken into consideration.

(2) New Tie-Layer Developments for Polystyrene Multi-Layer Sheet and Thermoforming Applications

Many food packaging applications utilize a container formed from a multi-layer extruded laminate where polystyrene is one of the layers. In general PS constitutes at least 80 to 85% of the total structure. Polystyrene could be used alone or could be blended with high impact polystyrene (HIPS) at different percentages to improve the overall mechanical properties of the container. One typical structure of single-serve shelf stable container is made of an extruded laminate of polystyrene/tie-layer/EVOH/tie-layer/polyethylene. The polystyrene is desirable as an outer layer in that it is heat formable, being formable in a non-molten state at a temperature above glass transition temperature. Polyethylene (PE) is advantageous inner layer in that it is inert and has desirable organoleptics (taste/odor properties). PE also serves as an effective heat seal layer. EVOH as an inner layer is known for its excellent gas barrier properties. Furthermore EVOH acts as a chemical barrier, inhibiting the flow of chemicals, such as polystyrene plasticizing oils. Other barrier layers could be used such as polyamide.

The new tie-layer development is designed to work in extrusion applications to adhere polystyrene resins used in food packaging to polar resins such as EVOH or polyamide and non-polar resins such as polyethylene. Currently typical adhesives used in this application are EVA-based. The main reason is that
EVA is somewhat compatible with polystyrene and imparts moderate adhesion between PS and other layers in the laminate. Several examples exist in literature for EVA-based tie-layer adhesives used in PS co-extruded structures. Moreover, there are several disadvantages of using EVA-based tie layer adhesives in such systems. One main drawback is that EVA gives off an odor when extruded at high temperatures. EVA resins are known for their low temperature stability. They degrade at high processing temperatures, contaminate the extrusion system, and create gels and black specks in the laminates. Also they prevent the use of the laminate in high temperature filling applications. In addition, EVA remains soft or stringy after thermoforming, compromising the ease of processing by die cutting. The new adhesive, on the other hand, is LLDPE-based. It provides high temperature stability and superior die cut-ability. The difficulty of developing tie-layer adhesives that are PE-based for PS structures is that PE is known to be incompatible with PS. Despite the difficulty of such development, the new tie-layer proved to give adhesion to PS providing greater than 100% of that found in current adhesives.

To illustrate the high performance of the new development, a series of experiments were conducted and explained in the following section. In the first experiment, a heat seal test was developed in which 125 micron thick films of the adhesive and the PS/HIPS blends were heat sealed at 260 °C, 40 PSI and 3 seconds dwell time. Figure (15) shows the adhesion to 50:50 blends of PS/HIPS. Several blends of PS and HIPS were used to illustrate the utility of the new adhesive with different resins. Results indicate that the new adhesive labeled as Adh-PX bonds with four times the strength of reference tie. Similarly, Figure (16) shows the same performance when the blend ratio of HIPS to PS varied to 75:25. Adh-PX was then tested versus two other tie-layer adhesives in a commercial trial to produce a five-layer sheet with the following structure: 85% HIPS+PS/2% tie/3% EVOH/2% tie/8% PE. The total sheet thickness was 1100 micron. Adhesion results shown in Figure (17) clearly illustrate the superiority of the new adhesive over standard tie-layers currently used in this application. The outstanding performance of Adh-PX provide the opportunity for down gauging of tie-layer thickness for potential cost savings. In order to demonstrate the advantage of the new development in high temperature application, adhesion of the produced sheets was performed at high temperature. Two sets of data were developed at 50 °C for a dwell time of three and five minutes. Results shown in Figure (18) demonstrate the utility of the new development in high temperature applications such as hot fill application. Moreover, adhesion to EVOH was maintained at very high level at which no delamination was observed at the EVOH interface in all tests performed using Adh-PX. The sheet samples produced were then thermoformed into round cups having the dimensions 8.4 cm diameter x 7.9 cm depth. Figure (19) reveals the high performance of the new development after thermoforming.

The following section will clearly demonstrate the difference between the performances of different adhesives in thermoforming application. A new AFM study was performed on the sheet and the thermoformed samples tested above.

**Effect of Tie on PS Adhesion in Multilayer Sheet Application**

Sheets of PS+HIPS/tie/EVOH/tie/PE multilayer were analyzed to determine the quality of adhesion of the tie to the PS layer. Details are shown in Figures (20) and (21). In Figure (20) Ref-2 exhibited poor adhesion to the PS layer, as indicated by the large gap running vertically in the middle of the phase contrast image. The delamination of this interface was indicated by the large depth (on the order of greater than 1 µm) of this gap. Ref-2 adhesion to the EVOH layer was also somewhat poor, but the gaps observed by AFM (not shown) were not as deep (on the order of less than or equal to 0.3 µm). This was interpreted to signify that Ref-2/EVOH adhesion was somewhat poor, exhibiting some delamination, that was not as severe as in the case of the Ref-2/PS interface. However, the new development, Adh-PX, exhibited excellent adhesion with no interfacial delamination as shown in Figure (21).

**Effect of Tie on PS Adhesion in Thermoformed Cups**

Thermoformed cups prepared from the previously tested multilayer sheets were analyzed to determine the quality of adhesion of the tie to the PS layer. Figure (22) shows Ref-2/PS interface. A large gap running vertically in the middle of the phase contrast image indicates the poor adhesion of Ref-2 to PS. The high orientation of the material near the tie-PS interface may also be observed in Figure (22). The high orientation of the polymer is manifest by a fibrillar (fibrils are about 25 to 50 nm in thickness) morphology.
running vertically, in the direction of orientation, in the phase contrast image in Figure (22). In contrast, Figure (23) shows the tie-PS interface with Adh-PX in the multilayer thermoformed structure. In this Figure, good adhesion of the new tie, Adh-PX, to PS is readily observed. Again, high orientation of the material near the tie-PS interface may also be seen but did not adversely affect the adhesion at the interface between the tie and PS as previously seen with Ref-2. Similar high orientation was observed where vertical fibrils of about 25 to 50 nm in thickness were detected in the morphology in the phase contrast image in Figure (23).

CONCLUSIONS

The effect of adhesion on multi-layer film clarity was investigated. Analysis of current tie-layer grades show that higher adhesion typically leads to lower clarity. By carefully controlling the reaction kinetics and rheological characteristics of tie-layers, Equistar Chemicals, a Lyondell Company, was able to develop new Plexar® adhesives that maintained high clarity and high adhesion at the same time.

The effect of interfacial shear stress and elasticity ratio at the interface of nylon/tie multilayer film structures were found to be insufficient parameters to explain the optical properties measured experimentally. It was predicted that such inadequacy was due to the neglect of chemical interactions at the Nylon/Tie interface. A new test was devised to rheologically probe the interaction at the nylon/tie interface. Monitoring the dimensionless increase factor of elastic modulus as a function of time provides an indication of the interaction at the nylon/tie interface and the kinetics of such interaction. Results gave a direct correlation between reaction kinetics and optical properties. It was concluded that slower initial reaction rate imparts high clarity in barrier multi-layer co-extruded films. In addition, AFM technique was used to correlate adhesion to clarity. High clarity films were found to have smooth undisturbed interface while lower clarity films were found to have interfacial delamination.

A new high performance LLDPE-based tie-layer adhesive was developed for polystyrene barrier application. The new adhesive proved to have superior performance in sheet and thermoforming applications. AFM technique was used to investigate performance on a micro scale. Results indicate that higher initial adhesion is required to maintain adhesion and container integrity after thermoforming. The new development provides a potential for cost savings where down gauging of the adhesive layer could be achieved while maintaining high adhesion.

The techniques employed in this investigation were used as tools in developing high performance tie-layer adhesives that are targeted for specific applications.

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Figure (1) Adhesion versus Clarity in Standard Multi-Layer Films with EVOH Barrier

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Figure (6) Attempt to Correlate Interfacial Viscosity Ratio with Clarity
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Figure (10) AFM Images in the 10% Nylon with Tie-A Multi-Layer Structure. Continuous and Undisturbed Tie/Nylon Interface Is Shown.
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Table (1) Computer Simulation Results for a Three-Layer Blown Film Co-Extrusion (Nylon/Tie/LDPE)

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Calculated Values at Nylon/Tie Interface

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Table (2) Computer Simulation Results for a Five-Layer Cast Film Co-Extrusion (Nylon/Tie/LDPE)

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Calculated Values at Nylon/Tie Interface

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