NEW DEVELOPMENTS OF PLEXAR®TIE-LAYER RESINS IN FLEXIBLE AND RIGID APPLICATIONS

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ABSTRACT

This paper discusses new developments at LyondellBasell in tie-layer adhesives for flexible and rigid applications. Two series of polyethylene and polypropylene based adhesives have been studied. The effect of adhesion on multi-layer film clarity was investigated. Newly developed adhesives maintain high clarity with high adhesion performance.

The relationship between adhesive molecular structure and performance was investigated in detail using Dynamic Oscillating Rheometer technique. Data generated were used to predict performance and processability in multi-layer film structures. The same techniques, together with Fourier Transform Infra Red spectroscopy (FTIR), were used to detect interactions between tie-layer adhesives and ethylene vinyl alcohol (EVOH). Good correlation between interaction at the interface and performance was found. Results were used to develop adhesives with high performance for targeted applications.

INTRODUCTION

Tie-layer adhesives have been used in coextruded and laminate structures for decades. Plexar resins were the first commercial tie-layer adhesives developed in North America in early 1970s.   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 coextrusions 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[1-6]. The most widespread use of anhydride modified tie-resins is in coextruded 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.

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The choice of tie resin for a given blown or cast film co-extrusion is usually based on adhesion requirements as well as many other factors. In thin films, tie-layer is an integral part of the structure and is required to enhance the overall value and properties of the structure. Some key considerations include:

1. Film physical and barrier properties:
   a. High tensile strength
      i. LLDPE or HDPE based tie resins usually preferred.
   b. Shrink films
      i. Tie resins with excellent memory.

2. Film optical and clarity properties
   a. Low Haze:
      i. EVA based tie resins usually preferred.
   b. Transparency or see-through clarity
      i. Tie resins designed for specific line and structure required.

3. Specific post manufacturing conditions or end-uses
   a. Film orientation. e.g. double bubble or machine direction orientation
      i. Tie-resin with high bond population and ability to absorb interfacial stresses.
   b. Thermal processing: Example cook-in meats, hot-fill pouches
      i. Tie resin with melt point above thermal processing temperature.

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. In the second part of the paper, the effect of polymer structure on adhesive performance in end application is studied using Dynamic Oscillating Rheometer technique. The last section is a detailed investigation in a molecular level aimed to detect interfacial interactions between tie-layer adhesives and ethylene vinyl alcohol (EVOH). Good correlation between interaction at the interface and performance was found. Results were used to develop adhesives with high performance for targeted applications.

EXPERIMENTAL TECHNIQUES

Narrow Angel Scattering (NAS) Measurement (ASTM D 1746):
The Zebedee CL-100 clarity meter was used for 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.

Dynamic rheological measurement:
Dynamic rheological measurement data were obtained with a Rheometrics ARES using parallel plates at 170°C for PE-based adhesives and at 230°C for PP-based adhesives, in the radian frequency range of 0.01 – 1000 rad/sec. The strain was employed below 20% but was verified to be in the linear viscoelastic region. All samples were stabilized with antioxidant before compression molding at 150°C of 25 mm diameter sample disks. The normalized relaxation spectrum were derived from storage modulus G' and loss modulus G" using a regularization procedure with quadratic programming[7].

Killion Film Adhesion test

Five layer co-extruded film samples were made in a Killion extruder having a structure of A/B/C/B/A where A is HDPE in case of PE-based adhesives and PP in case of PP-based adhesives, B is tie layer, and C is EVOH. Adhesion was measured by cutting 25.4 mm wide strips in the machine direction near the center of the film. Each strip was separated at the tie / EVOH interface. The force required to separate the film apart in a T-Peel configuration at 254 mm/min. was measured using tensile tester. The average of five specimens was recorded as the peel strength in Newton / 15 mm.

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR Nicollet spectrometer purged with nitrogen was used to record the IR spectra. Sixty-four scans of both the sample and the reference were collected at a resolution of 2 cm^{-1} with double precision throughout the range 4000 – 400 cm^{-1}.

RESULTS AND DISCUSSION

(1) FILM TRANSPARENCY

In barrier coextrusion, covalent bonds are forming at the tie-resin interface with EVOH or polyamide while the two polymers are in the melt phase. A detailed investigation of this reaction will be given later in this paper. 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 and 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 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 small-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 linear low density polyethylene (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 are designed for high clarity and high adhesion at the same time. Figure (2) reveals the performance of a new development labeled Tie-Clarity1compared to a commercial tie-layer in 5-layer cast film with EVOH barrier. The total film thickness was 125 micron and layer

distribution are 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 3.2 lbs. 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 where 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.

1. They have good rheological match with most blown film EVOH grades.
2. They have optimized anhydride content for adhesion and transparency.
3. Unique graft architecture.
4. Designed with the ability to absorb and dissipate interfacial stresses.

To summarize the problem of NAS transparency loss in barrier coextrusions: 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 coextrusions, new adhesives were developed having specific designs for targeted structures

The following section will shed some light on some of the parameters taken into consideration when developing new tie-layer adhesives with high adhesion performance.

(2) RHEOLOGICAL CHARACTERIZATION FOR TIE LAYER DEVELOPMENT

There are several rheological methods to characterize flow properties of polymer melts. The most common way of measuring rheological property is to utilize the dynamic oscillatory shear measurement based on a linear viscoelasticity theory and the steady-state shear using the rotational type (cone-and plate, parallel plates, and coaxial cylinder) and the capillary type for non-linear viscoelasticity. Each measurement show unique characteristic features to obtain useful information for industrial applications. For examples, the dynamic oscillatory shear measures G' (elastic modulus) and G" (loss modulus) as a function of frequency, ω which can be used to calculate very useful rheological parameters such as complex viscosity, zero shear viscosity, stress relaxation modulus, and melt elasticity number[8-12]. Those rheological parameters are very sensitive to small changes in molecular weight (Mw), molecular weight distribution (MWD) and long chain branching (LCB) of a material.

In dynamic rheological measurement, a sinusoidal strain is imposed on the melt under test. If the viscoelastic behavior of the melt is linear, the resulting stress will also vary sinusoidally, but will be out of phase with the strain. Thus the linear viscoelastic response can be converted into useful rheological parameters such as G' and G" as a function of frequency. Then complex viscosity (η^*), as a function of frequency, can be obtained from the relation, $((G'^2 + G''^2)^{1/2})/ \omega$. Also, normalized stress relaxation spectrum as a function of relaxation time can be obtained from G' and G" based on the linear viscoelastic theory[13]. The purpose of this section of the paper is to correlate rheological data to tie layer performance in Killion co-extruded cast films made with PE-based tie-layer compounds.

Two sets of PE-based tie layer compounds were employed for this investigation. The first set has three products labeled PE Tie-1, PE Tie-2 and PE Tie-3 with MI = 2.1 g/10 min. and density = 0.925 g/cc. The second set has three adhesives labeled PE Tie-4, PE Tie-5 and PE Tie-6 with MI = 1.0 g/10 min. and density = 0.918 g/cc. The compounds in each set contains almost identical amount of MAH functionality.

Figure (3) shows the complex viscosity versus frequency for the first set of PE-based tie layer compounds at 170°C. All samples showed very similar viscosities at low frequency range (< 1 rad/sec). However, there is difference in the viscosity at high frequency range (> 10 rad/sec): PE Tie-3 shows the lowest viscosity among samples, indicating the most shear thinning behavior. The increased shear thinning behavior is due to the presence of low molecular weight species, leading to rheologically broader molecular weight distribution (MWD).

Relaxation spectrum calculated from G' and G" as a function of frequency also provides an insight into the molecular structure of the compound. Relaxation time is a measure of the time taken for molecules to recoil after deformation. Thus molecules with differences in molecular structure would be expected to show difference in relaxation time because of variation in their molecular configuration during stress release. As shown in Figure (4), PE Tie-3 shows much longer relaxation time distribution compared to PE Tie-1as indicated by shifting the distribution to longer relaxation time zone. PE Tie-2 appears in between PE Tie-1 and PE Tie-3 in the relaxation behavior.

The behavior of the relaxation time distribution correlated well with the adhesion data of the 75 micron and 125 micron film samples as shown in Figure (5). In this family of adhesives studied, it was concluded that the tie layer compound with short relaxation time tends to show a higher film adhesion than that with longer relaxation. Compare film sample of PE Tie-1 to that of PE Tie-3. This means that adhesive relaxation behavior coupled with film extrusion process plays a major role in determining film adhesion. We are currently investigating a possible mechanism showing a good correlation between rheological relaxation behavior and film adhesion.

Figure (6) shows similar complex viscosity data for the set of PE-based tie layer compounds. In this case, the behavior of viscosity varies differently compared to the previous set (Fig. 3). All samples show very similar viscosities at high frequency range (> 100 rad/sec). However, there are some differences in viscosity at low frequencies (< 1 rad/sec). PE Tie-5 (1.0 MI) shows slightly higher viscosity than PE Tie-4 (1 MI) and much higher than PE Tie-6 (1.2 MI). An examination of the distribution of relaxation time indicates a dramatic increase in longer relaxation times for PE Tie-5 than for PE Tie-4 at the same MI (Figure 7). PE Tie-6 shows an intermediate relaxation time. Similarly we observed a good correlation between relaxation time and Killion film adhesion as shown in Figure (8). By comparison to Series-1, tie-layers of Series-2 also indicated that adhesives with longer relaxation give lower film adhesion.

(3) DETECTION OF INTERFACIAL INTERACTIONS BETWEEN TIE-LAYER ADHESIVES AND EVOH AND RELATIONSHIP TO PERFORMANCE

Previous sections covered the development of tie-layer adhesives for targeted applications and techniques that are used to guide such developments. Section 3 is aimed to go even deeper in the development / performance relationship. In this section, a detailed investigation of the interactions between tie-layer adhesives and barrier layers are studied. EVOH was chosen as a barrier since it is commonly used for such applications and it is harder to adhere to than polyamides. Tie layer products studied are all polypropylene based. New developments are labeled PP Tie-1 through PP Tie-3. Other commercial existing tie layers are used as a reference and are labeled as PP Ref-1 and PP Ref-2.

Tie layers were tested for performance in flexible and rigid applications. To detect the performance in flexible application, 75 micron 5-layer Killion films were made with 32 mol% EVOH as a barrier and PP skins. Layer distribution was 43% PP / 4% Tie / 6% EVOH / 4% Tie / 43% PP. For rigid applications, bottles were made on a Krupp line with similar layer distribution and 1000 micron total thickness. Figure (9) indicates the adhesion performance of various tie layers in flexible applications. PP Tie-3 shows by far the highest performance followed by PP Tie-2 then PP Tie-3. In general, PP tie references were lower in adhesion. The adhesion was tested once the products were made and also after one day. All adhesives showed enhancement of adhesion with aging.   The new products gave the largest increase especially PP Tie-3 where adhesion was doubled. Adhesives PP Tie-2, PP Tie-3 and PP Ref-1 were tested in bottle applications. The adhesion of 1000 micron structure is shown in Figure (10). New developments gave by far the best performance in thick gauge applications. A drop test was applied to 1 liter bottles of the previous structure. Bottles were filled with water and conditioned for 1 day before testing. Bottles were dropped at 30.5 cm increments. The average maximum height before breakage was reported. This test was repeated 15 times for each structure. Results are given in Figure (11) where PP Tie 2 and 3 give the best performance compared to Ref-1. Results indicate that higher adhesion is required for rigid applications where structure integrity is required.

In order to investigate performance on a molecular level, rheological as well as FTIR spectroscopic studies were developed for blends of PP and PP tie adhesives with EVOH. Figure (12) shows the complex viscosity of the different blends at 230°C. It is apparent that PP blend is separated from all other blends and has the lowest complex viscosity especially at low frequency below 0.1 rad/sec^{-1}.   The reason for this behavior is that maleic anhydride interacts with EVOH and creates covalent bonds. The formation of strong bonding between PP and EVOH increases the molecular weight significantly and restricts the motion of the molecules. It is interesting to notice that the viscosity curves followed exactly the performance behavior of PP tie products (compare Figure 9 to Figure 12). The highest adhesion and viscosity was observed for PP Tie-3 and the lowest for Ref-1. The same trend can also be observed in Figures 13 and 14 — the elastic modulus G' and the loss modulus G" respectively. Again PP Tie-3 shows the highest modulus and PP blend has the lowest values especially at low frequency. All rheological curves follow the same performance trend as in Figure (9). The loss modulus G" shows similar trend to viscosity at low frequency due to increased molecular weight of blends. The elastic modulus clearly shows the upturn at low frequency because it is related to the elastic behavior of the material or its solid state characteristics. The stronger the bonding in the blend the higher the upturn as is in PP Tie-3 blend. The restricted motion due to network formation can also be traced by plotting G' and G" versus frequency as in Figure (15). The crossover represents a fundamental change in material behavior. The more the elastic component is in the compound, the higher the solid like behavior and the higher the crossover.

A detailed FTIR spectroscopy investigation was employed in order to study the nature of interaction taken place at the tie / EVOH interface. For quantitative analysis, the spectra were normalized for thickness using an internal reference at 898.9 cm^{-1} as shown in Figure (16). The 899 cm^{-1} band in iPP is due to combination of CH_3 equitorial rock, CH_2 rock and CH equatorial bend. Figure (17) shows the spectra of all blends after normalizations. It is clear that two new bands are formed at 1710 cm^{-1} and 1740cm^{-1}. The first band is assigned to acid formation and the second is due to ester formation[15]. In our earlier research[15], we proved that the reaction between maleic anhydride in tie-layer adhesives and EVOH leads to ester formation detected at 1740 cm^{-1}. The ester band absorbance was measured for each blend and normalized as previously stated. Results are plotted in Figure (18) together with adhesion performance for all tie layers and PP reference. PP Tie-3 shows the highest ester formation followed by PP Tie-2, then PP Tie-1. Ref-1 has the lowest ester and PP with no ester formation. Results correlate very well with adhesion as seen in this last Figure. Also, these results confirm the earlier rheological results in Figures (12 – 15). The higher ester formation indicates more covalent bonding, higher molecular weight and network formation that make the resin to behave as a solid at low frequency range. In addition to ester formation, carboxylic acid is also formed due to ring opening of maleic anhydride. Figure (19) depicts the formation of carboxylic acid measured as absorbance of the 1710 cm^{-1}. Results

are normalized and plotted against adhesion. Similar to ester formation, acid formation followed the same performance trend of tie-layer adhesives studied.

In summary, by knowing the requirements for the application and the rheological and chemical behavior of tie-layer adhesives in the final structure, it is now possible to develop high performing adhesives for targeted applications.

CONCLUSIONS

The effect of adhesion on multi-layer film clarity was investigated. It was concluded that the higher the adhesion, the lower the clarity. LyondellBasell has developed new Plexar adhesives that maintain high clarity and high adhesion at the same time.

A correlation between the dynamic rheological data and tie-layer film adhesion for PE-based compounds was developed. It was found that the rheological relaxation time showed an excellent correlation with film adhesion. Tie layer compounds with shorter relaxation times gave higher film adhesion in multi-layer structures.

Interactions between tie-layer adhesives and EVOH were thoroughly investigated using rheological as well as spectroscopic techniques. It was concluded that covalent bonding are formed due to the reaction between maleic anhydride and OH groups in EVOH. The higher the bonding is, measured as ester formation, the higher the adhesion between tie layers and EVOH.

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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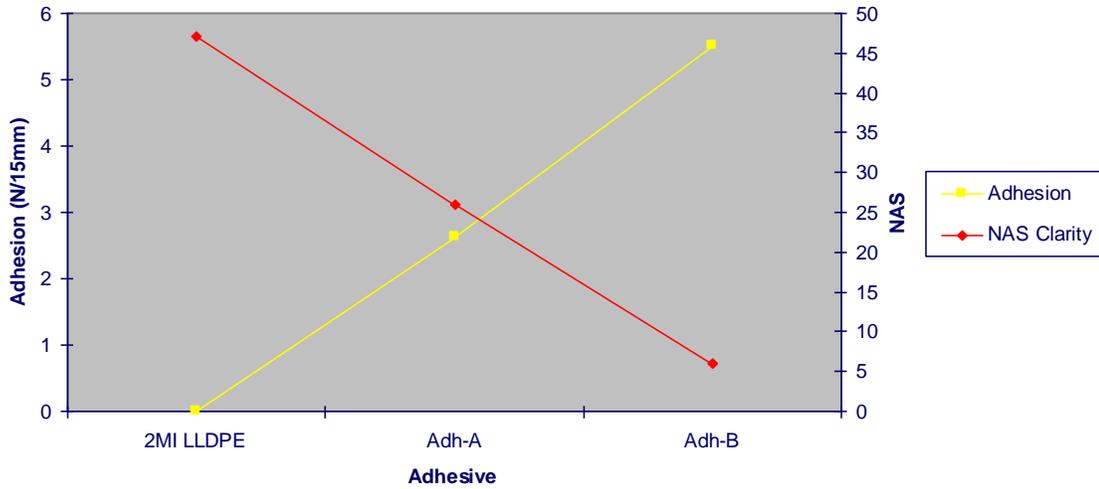
Figure 2:   Adhesion versus Clarity in Multi-Layer Films with EVOH Barrier for New Tie-Layer Developments
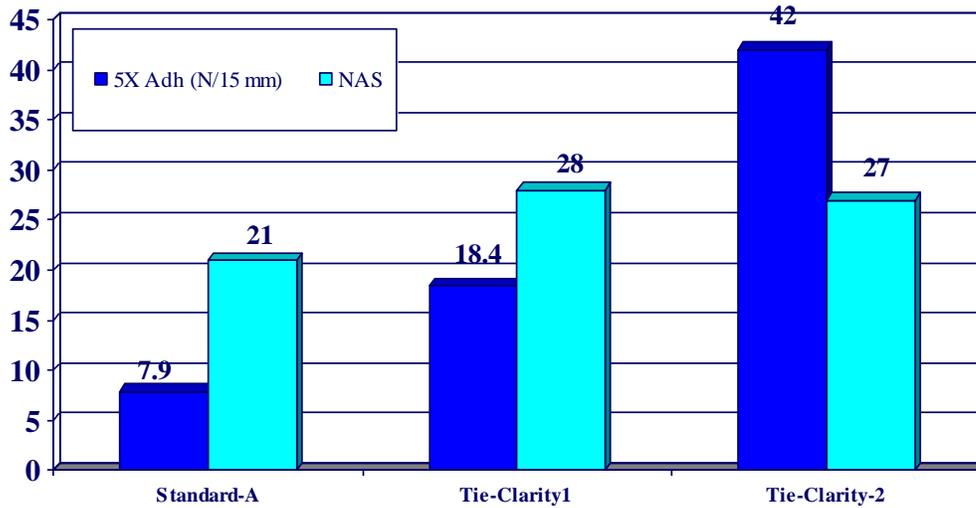
Figure 3: Calculated Complex Viscosity versus Frequency for PE-Based Tie (Series-1)

Calculated Complex Viscosity vs. Frequency
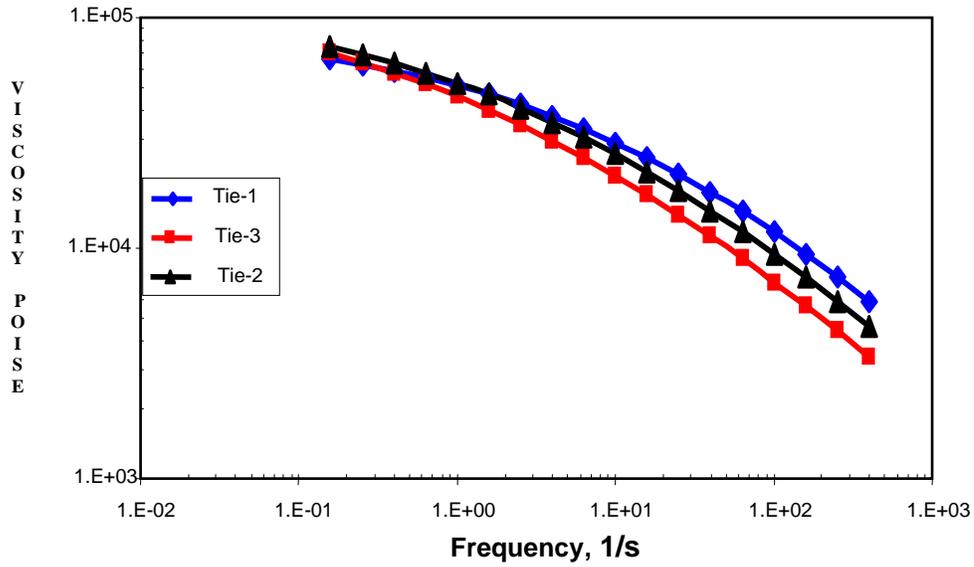
Figure 4: Normalized Relaxation Spectra versus Relaxation Time for Series - 1
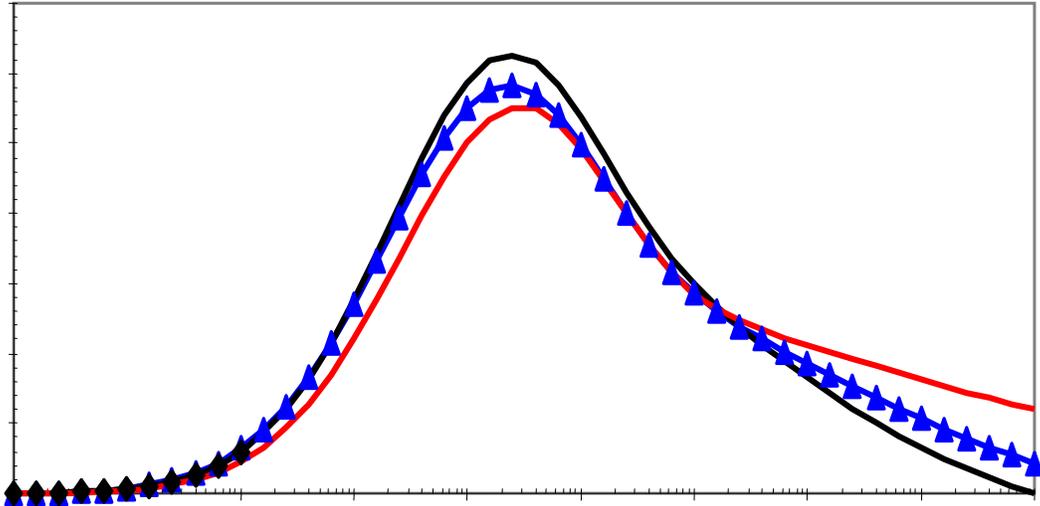
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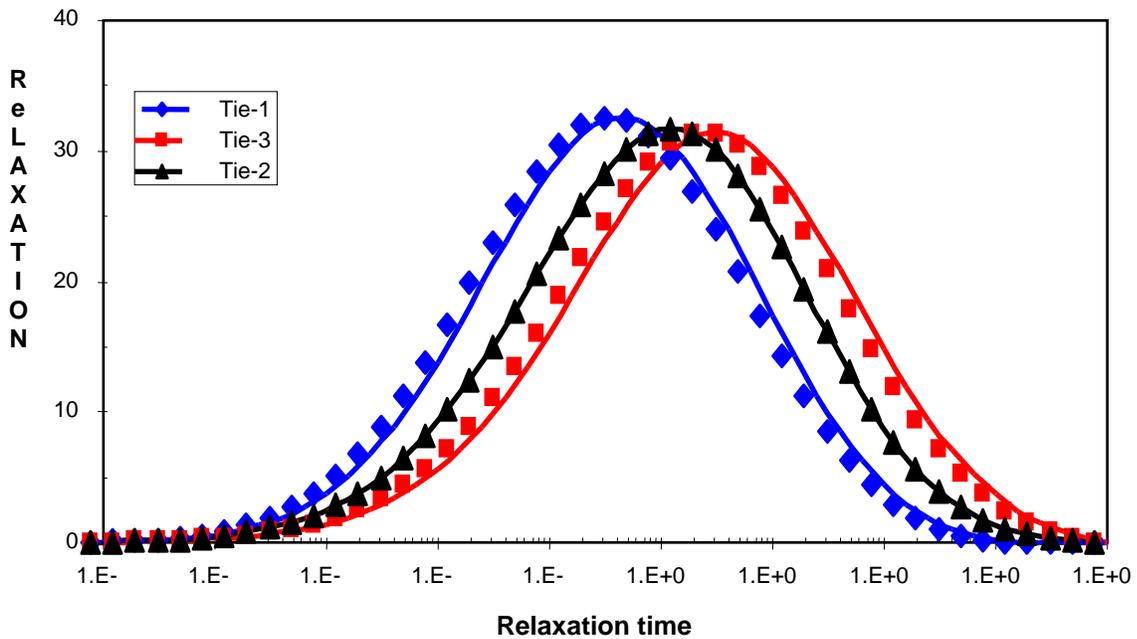
Figure 5: Adhesion at Tie-Layer / EVOH Interface for PE Based Tie Layers of Series - 1
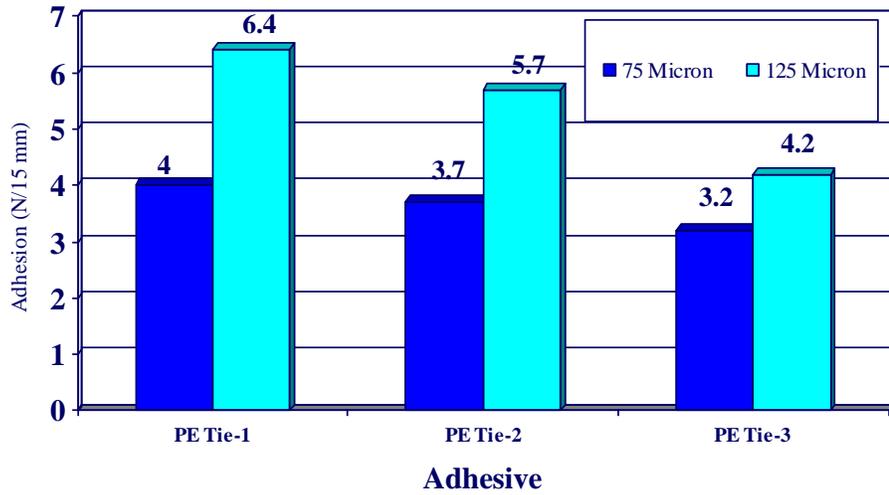
Figure 6: Calculated Complex Viscosity versus Frequency for PE-Based Tie (Series-2)

Figure (6)
Viscosity Comparison
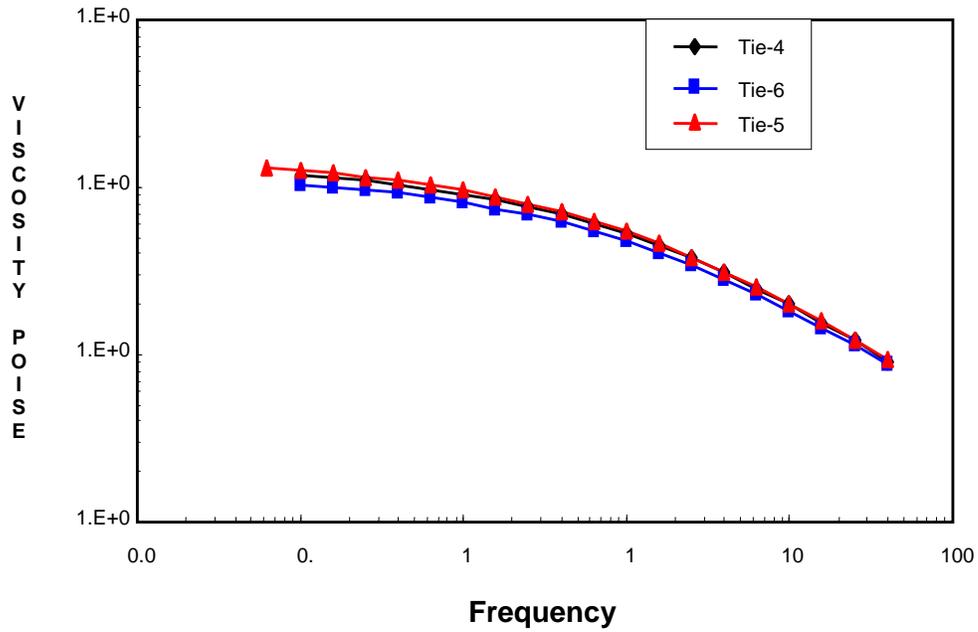
Figure 8: Adhesion at Tie-Layer / EVOH Interface for PE Based Tie Layers of Series - 2
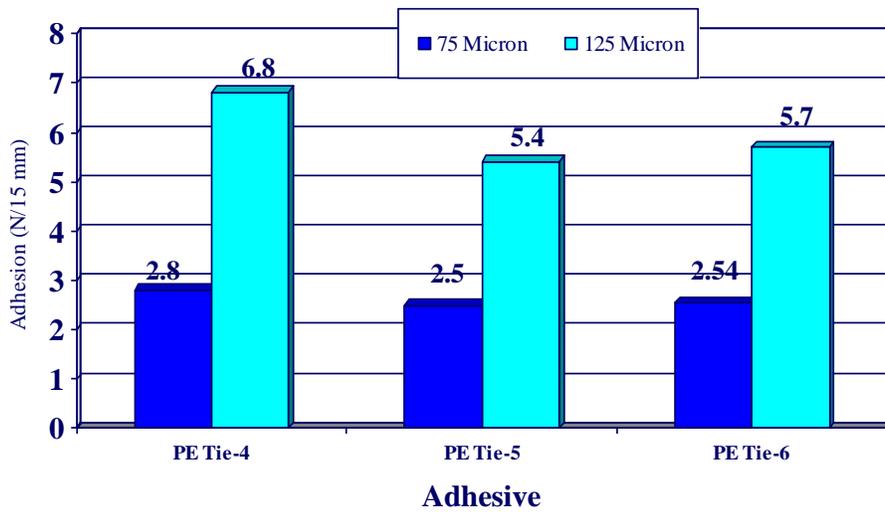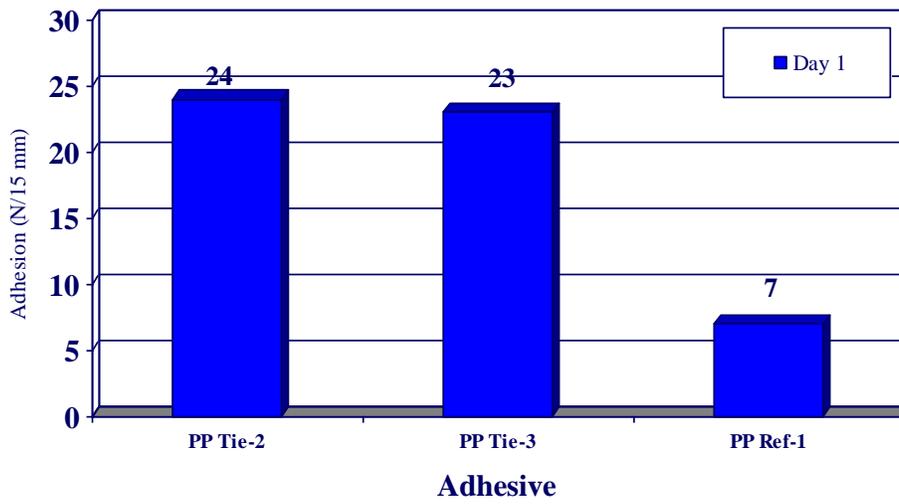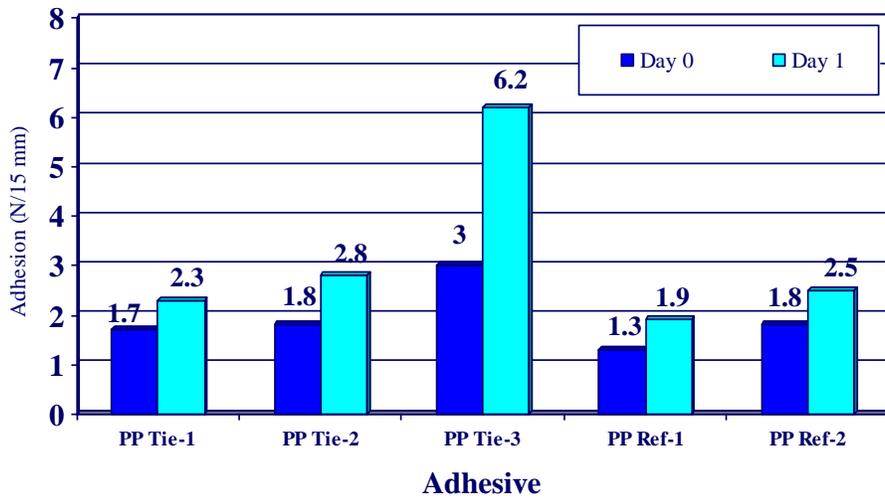
Figure 11: Drop Test Results for PP Based Tie Layers in Bottle Applications
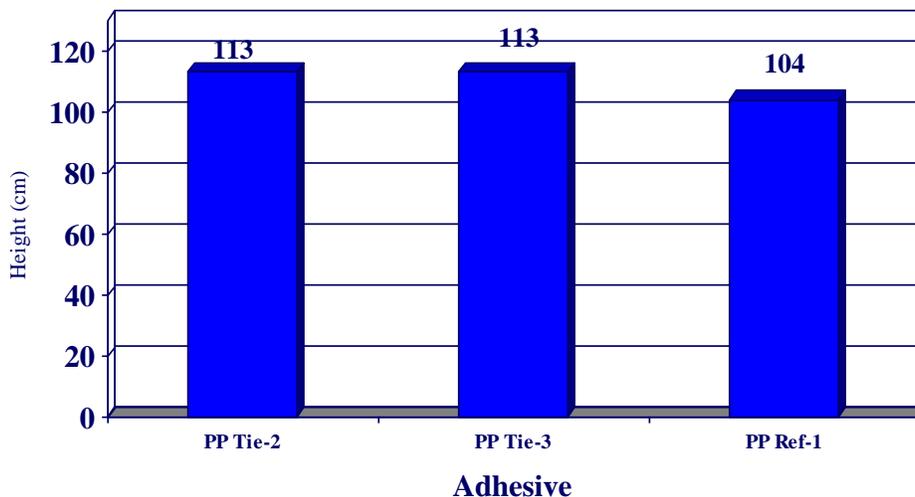
Figure 12: Complex Viscosity versus Frequency for PP- Based Tie Layer Blends with EVOH

Complex Viscosity Comparison at 230C
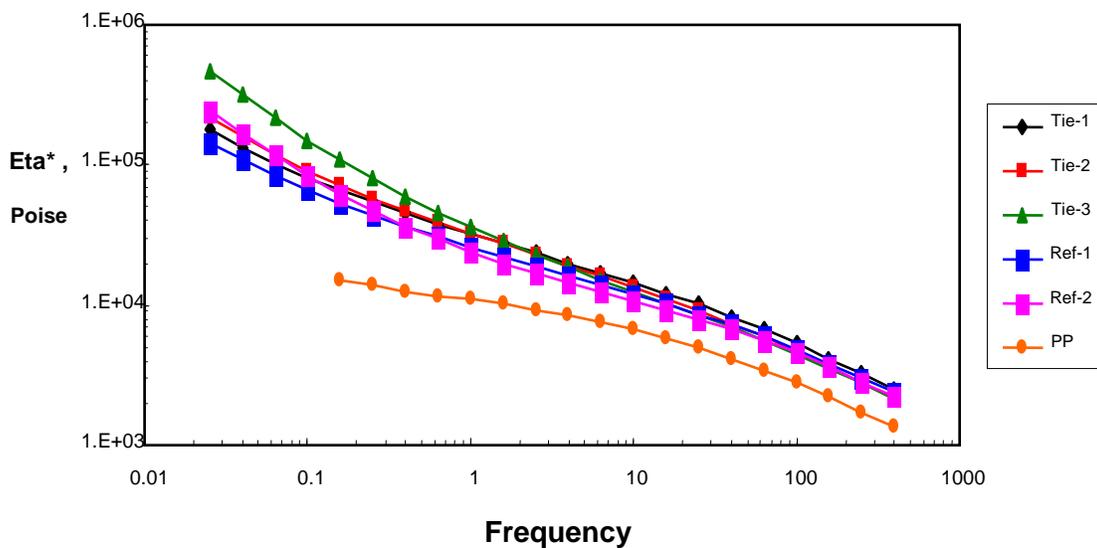
Figure 13: G' versus Frequency for PP-Based Tie Layer Blends with EVOH
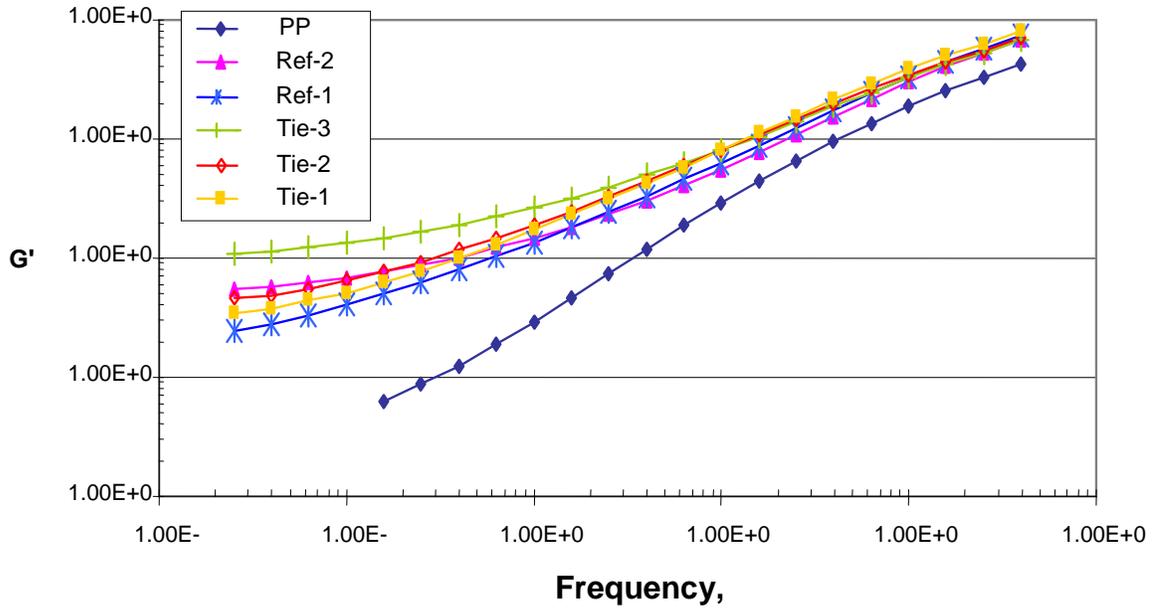
G' Versus

Figure 14: G" versus Frequency for PP-Based Tie Layer Blends with EVOH
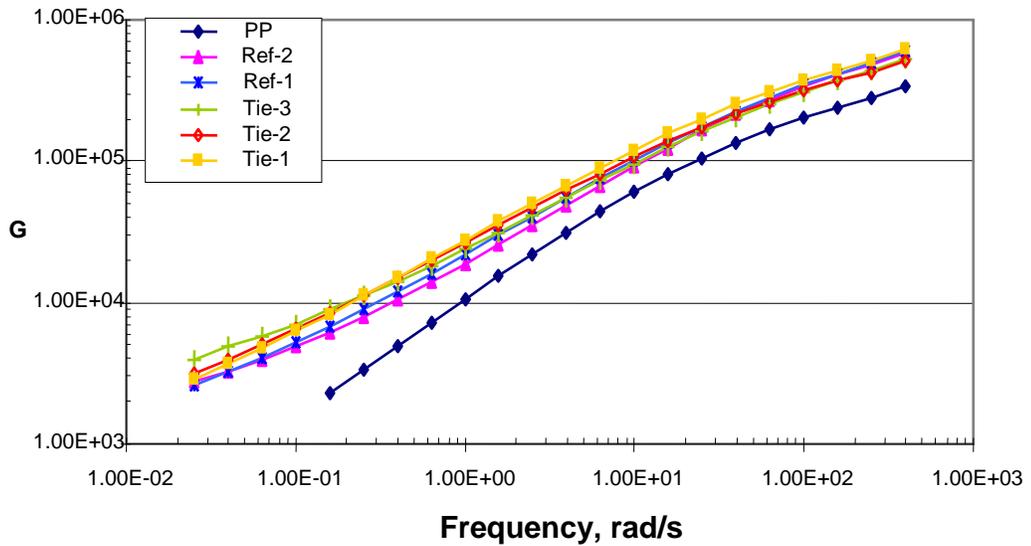
G" Versus

Figure 15: G'/G" versus Frequency for PP-Based Tie Layer Blends with EVOH

Effect of Tie-Layer Performance on G' / G"
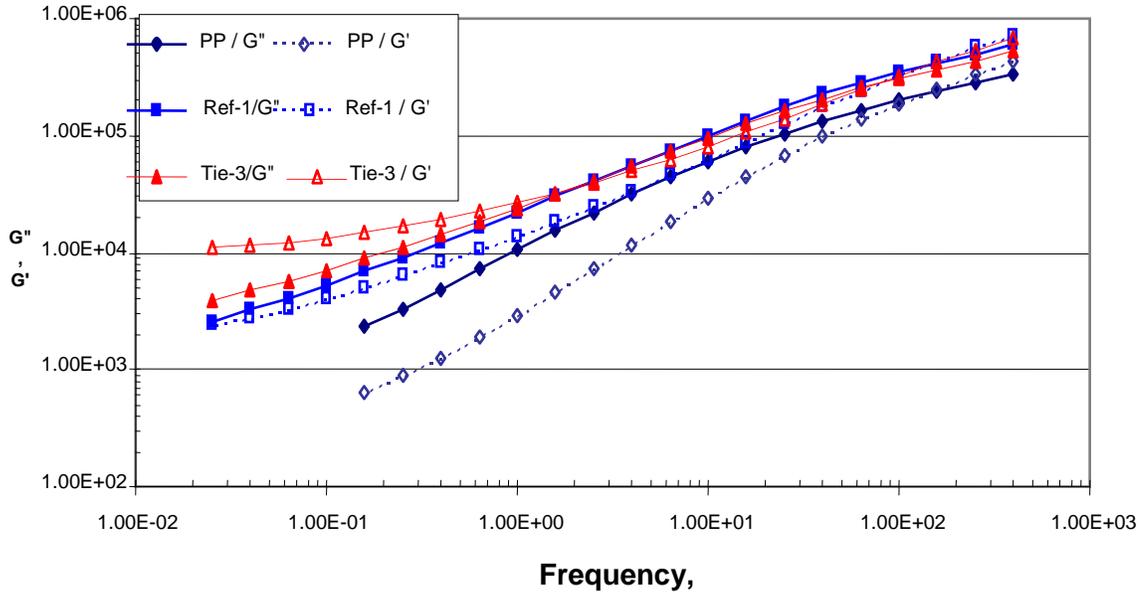
Figure 16: Thickness Normalization of FTIR Spectra for PP Tie and PP Blends with EVOH
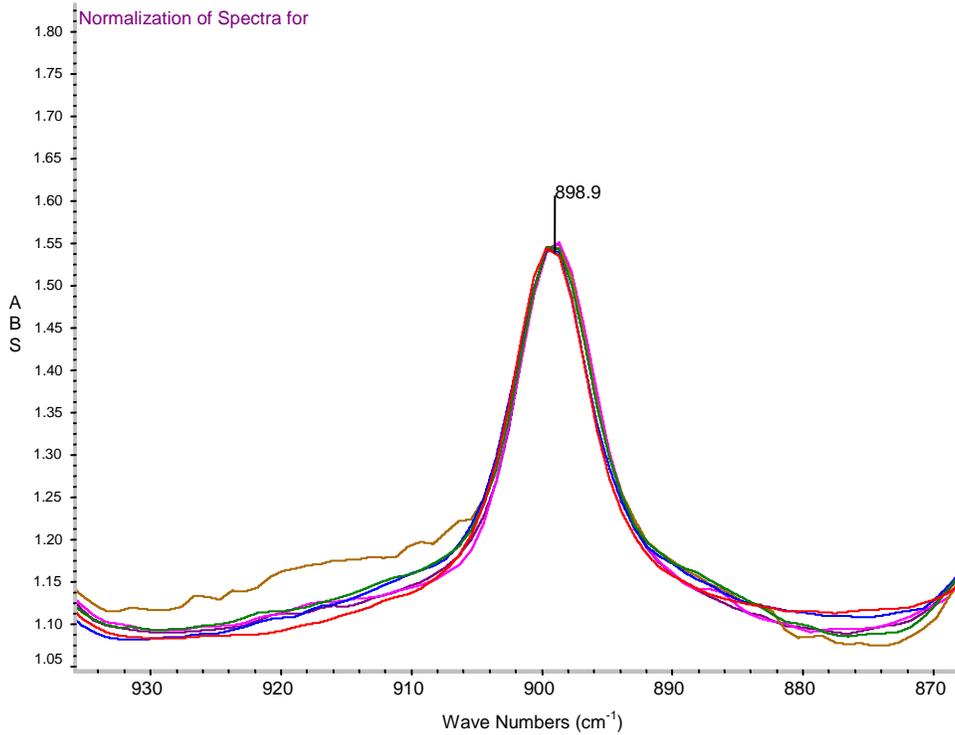
Figure 17: FTIR Spectra for PP Tie and PP Blends with EVOH
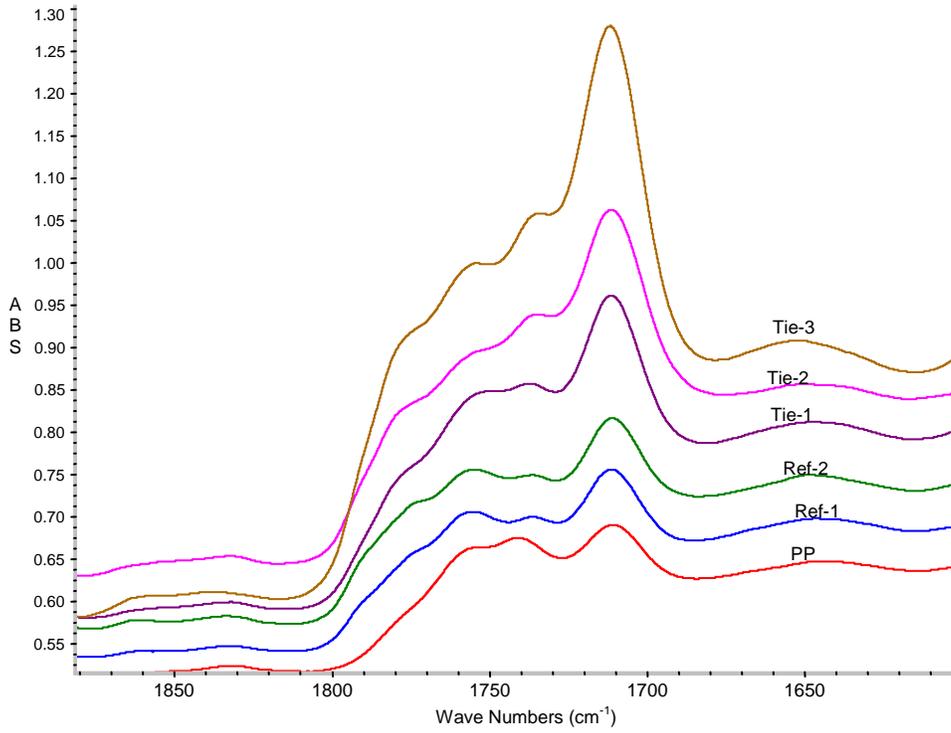
Figure 18:   Correlation between Adhesion and Ester Formation in PP Tie / EVOH Structures
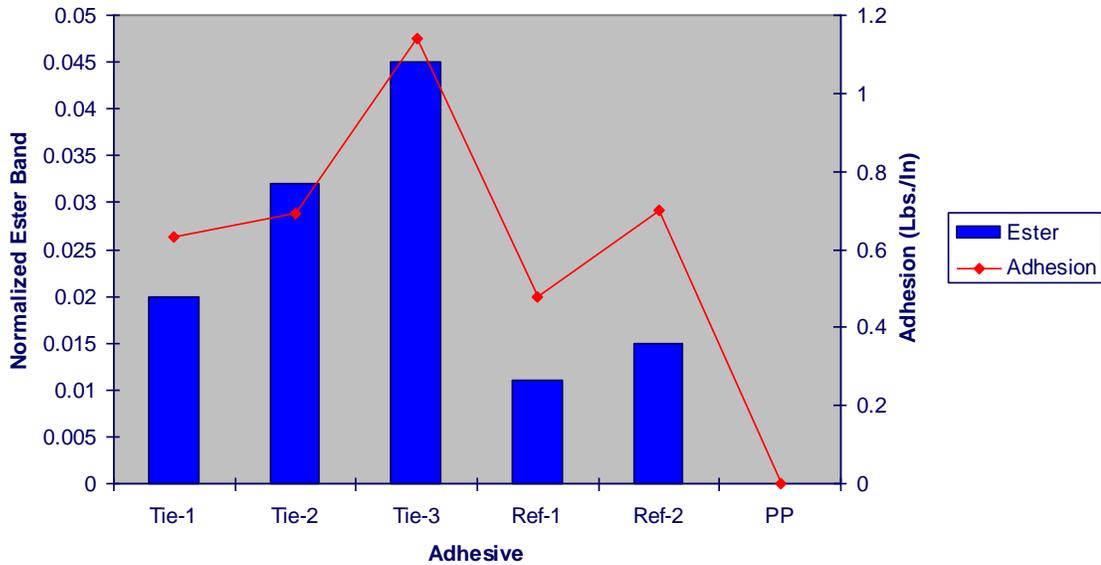
Figure 19: Correlation between Adhesion and Acid Formation in PP Tie / EVOH Structures

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