

# Specific adhesion model for bonding hot-melt polyamides to vinyl<sup>☆</sup>

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## Abstract

Hot-melt polyamides are an important market for the dimer acid made from the tall oil fatty acids liberated during the Kraft pulping process. These polyamides bond well to many substrates, but not to polyvinyl chloride (PVC), commonly called vinyl. Dimer-based polyamides made from secondary amines such as piperazine bond well to vinyl. No model for this unique adhesion has been proposed even though many commercial adhesives and other patents have utilized this feature of dimer-based polyamides. This paper examines the validity of models based on mechanical interlock, rheological properties, solubility parameters, and acid–base interactions. Available data are consistent with the acid–base model, which depends on the availability of tertiary amides made from secondary amine to bond to the vinyl hydrogen in contrast to the strong internal polyamide hydrogen bonding of secondary amides made from primary amines. Poly(ester-amides) with a similar proton acceptor ability also bond to vinyl.

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## 1. Background

One of the highest value products from trees is the dimer-based polyamide. To make this product, the fatty acid is liberated as a salt during the pulping of trees, especially pines from the Southeastern United States. The fatty salt is collected in soap skimmings during recycling of pulping chemicals in the Kraft process. These skimmings are acidified and distilled to yield a fatty acid fraction and a rosin acid fraction, both of which are utilized in adhesives. The fatty acid is heated with a clay catalyst to yield a "dimer acid" by reaction at the olefinic portion of the fatty acid. This dimer acid is then reacted with diamines to form dimer-based polyamide resins [1,2], which are used as binders in printing inks, epoxy-curing agents, and hot-melt adhesives. The market for hot-melt adhesives is mainly in the

manufacture of durable goods. Examples are shoe assembly, kitchen and bathroom cabinets, telecommunication cable repair sleeves, and window assembly [3].

The original polyamides were made using linear diamines [1,2]. A very novel patent was claimed for a specific type of polyamide that was made from cyclic diamines, such as piperazine [4]. Compared to other dimer-based polyamides, these resins were declared to give unique adhesion to polyvinyl chloride (PVC), termed vinyl in the remainder of this paper. Although more than 35 years have passed since this discovery [4], and there have been over 40 patents that involve piperazine-dimer acid polyamides, no model has been proposed to explain this specific adhesion to vinyl. In addition, the only polyamide hot-melt adhesives that have been reported to bond to vinyl were made from these secondary diamines. Although these polyamides bond well to plastics, some other dimer-based polyamides bond equally or better to plastics such as polyethylene and polypropylene.

## 2. Adhesion data for polyamides

Dimer-based polyamides are used to form strong bonds to a wide variety of materials. Original substrates

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Table 1  
Adhesion data from US patent 3,377,303

Acid component	Amine component	Vinyl adhesion <sup>a</sup> (N/cm)
Dimer acid, sebacic acid	Ethylenediamine, piperazine	36.5–64.2
Dimer acid, sebacic acid	Ethylenediamine, 1,3-di (4-piperidyl)propane	34.1–75.2
Dimer acid, sebacic acid	Ethylenediamine, 2,5-dimethyl-piperazine	18.6
Dimer acid, sebacic acid	Ethylenediamine, N-aminoethyl-piperazine	25.0
Dimer acid, sebacic acid	Ethylenediamine, dimerdiamine	1.4–4.0
Dimer acid, sebacic acid	Ethylenediamine, 1,4-bis(dminoethyl)benzene	0.9
Dimer acid, sebacic acid	Ethylenediamine, 1,5-cyclohexyl-bis(methylamine)	0.9

<sup>a</sup>Patina to standard cement liner in accordance with the Standard Cement Test Method for Elastomer Soles and Heels proscribed by Rubber Manufacturer's Association, Inc., adopted May 20, 1960. Values for vinyl adhesion are converted from pounds per square inch to newton per centimeter.

included wood, metal, and leather. For bonding to these substrates, most dimer-based polyamides give suitable adhesion. Their amorphous character, their ability to form hydrogen bonds in the amide region, and the presence of low-polarity domains in the fatty region play a definite role in good adhesion. Dimer-based polyamides have served well in the shoe industry, but the introduction of imitation leather made from vinyl led to the need for new polyamides since the dimer-based polyamides at that time did not bond well to vinyl. A patent by Peerman and Vertnik [4] provided examples of polyamides that do and do not bond well to vinyl. The data in this patent showed that piperazine-derived polyamides provide good bonds to vinyl, while those derived from dimer diamine, 1,4-(bisaminoethyl) benzene, and 1,4-cyclohexyl bismethylamine do not (Table 1). Dimer diamine is a primary diamine made from dimer acid by reaction with ammonia, followed by dehydration and reduction to the dimer diamine. In addition, polyamides that are derived from linear diamines such as ethylenediamine and hexamethylenediamine, do not bond to vinyl.

The Peerman and Vertnik patent [4] showed that polyamides made from cyclic disubstituted diamines provide the characteristic good bonding to vinyl. The two amines that were used extensively in this patent were piperazine and 1,3-di-(4-piperidyl)propane (dipip). Note that those polyamides derived from piperazine and dipip have much higher levels of linear codiacid, such as sebacic acid, azelaic acid, and terephthalic acid, than do most other dimer-based polyamides. With most dimer-based polyamides, the hydrogen bond between the amide groups makes the materials solid and gives them strength. When hydrogen bonds are absent, as in the case of piperazine- and diol-based homopolymers, the resulting polymers are liquid or semi-solid. Thus, for useful adhesives, piperazine-derived polymers need a significant amount of monosubstituted diamines and linear codiacids to give the product strength. In typical polyamides, with a dimer acid and linear diamine, the softening point is near 100°C, and the addition of

substantial quantities of linear codiacid raises the softening point too much for the polyamide to be useful as a hot-melt adhesive. Thus, one cannot make similar polymers with and without piperazine and expect to understand the effect on adhesion at the interface. Those polymers would have such different physical properties, such as softening point and strength, that the comparison would not be meaningful in an investigation of the nature of the adhesive interaction.

The original patent by Peerman and Vertnik [4] only described which polyamides gave good bonding to vinyl, but it did not propose any theory as to why these polyamides were unique in their performance. Some properties of piperazine-derived polyamides were described in a recent paper [5], but the unique bonding character of these polymers was not discussed. All the hot-melt polyamides described in the literature that bond well to vinyl are made from piperazine or similar type compounds (Fig. 1). Hot-melt poly(ester-amides) that bond to vinyl [6] will be discussed later in this paper.

### 3. Adhesion models

The standard adhesion models can be classified by mechanism as either mainly mechanical or chemical in nature. Mechanical interlock usually depends on the roughness of the surface. Chemical models depend on the type of interaction between the atoms present in both the substrate and adhesive. Both types of bonding depend on good wetting of the surface, which, in turn, requires that the surface energy of the adhesive be near or, preferably, less than that of the substrate. In addition, dynamic wetting is critical for mechanical interlock during the application of a hot-melt adhesive to a substrate.

Dynamic wetting involves viscosity as well as a surface energy term [7]. As expected, the lower the viscosity the better the wetting. Because the Peerman and Vertnik patent [4] does not show a correlation

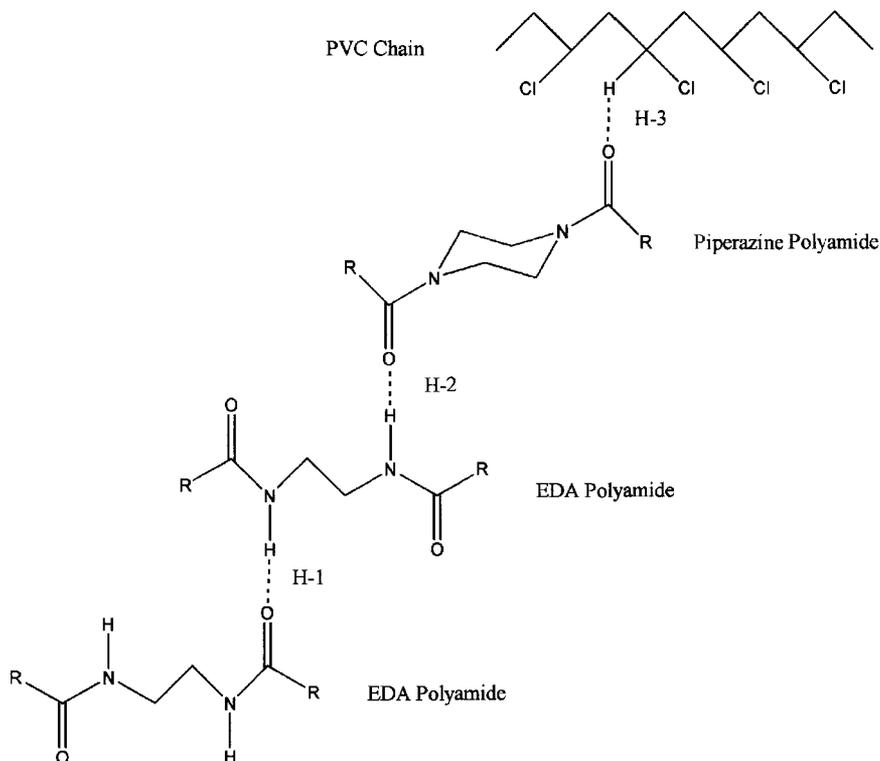


Fig. 1. Hydrogen bonding in polyamides and to vinyl

between adhesive strength to vinyl and viscosity of polyamides, we can assume that dynamic wetting is not likely the most important factor in these experiments. Moreover, polyamides bond to smooth as well as to rough vinyl substrates. Thus, because a mechanical interlocking model does not explain adhesion very well, we need to consider a chemical interaction model.

A number of models can be proposed to explain the specific adhesion related to the chemistry and physical properties of polyamides. These models are divided into three classes: rheology, solubility parameters, and acid-base interaction. Under rheology, the concepts involve the flow of the hot melt or its rate of setting to allow better wetting of the vinyl surface or adhesive with a modulus more similar to that of vinyl to better distribute the applied stress. The solubility parameter concept is that the polarity of vinyl-bonding polyamides is closer to that of vinyl than is the polarity of non-vinyl-bonding polyamides. The third model embraces an acid-base concept, which involves hydrogen bonding. The validity of each model is examined on the basis of the available information.

First, we need to better understand what makes up a typical hot-melt polyamide. Because of the commercial importance of these resins, most technology is in the patent literature. Thus, for many of these formulations, there is compositional information, but data on properties are limited. Most of the mass of a typical dimer-

based polyamide is based on the dimer fraction, which often constitutes 60% to 80% of the weight of the final product. The dimer acid is composed of a large number of components, whose structures include a multitude of branched acyclic, unsaturated cyclic, aromatic, and bicyclic species. Thus, the dimer portion contributes a very amorphous and non-polar character to the polymer. Moreover, dimer-based polyamides usually involve a 9- to 12-carbon diacid feed to raise the softening point and impart the strength of a more crystalline nylon. Polyamides are often made from two or more diamines to impart strength, flexibility, and sufficient open time. Linear aliphatic diamines, such as ethylenediamine and hexamethylenediamine, impart hardness and strength. Longer chain diamines, such as dimmer diamine, provide flexibility as a result of fewer amide groups in the resulting polyamide. Certain diamines, such as polyether diamines, can provide good low temperature properties. Where one diamine is piperazine or a similar diamine, the polyamide is softer as a result of fewer hydrogen bonds between the chains.

#### 4. Rheology

Rheological factors play a role in many stages of the bonding process. Since an adhesive needs to be liquid for application, its viscosity/temperature profile needs to be

proper for good wetting of the substrate. The proposals are that piperazine-derived polyamides give good specific adhesion by controlling the flow of the molten polymer or by giving the adhesive a modulus similar to that of vinyl for minimizing stress localization. For these explanations to be valid, non-vinyl bonding polyamides must not possess these properties.

The wetting starts as the molten adhesive is applied to the surface of the vinyl or as the adhesive film between two vinyl layers is melted by heating of the vinyl substrate. In wetting the substrate, it is important to fill the irregularities that occur on almost all surfaces [8]. A number of equations have been developed for filling the pores on the surface, but all of these contain both viscosity and surface tension parameters. The first parameter involves the viscosity of the molten adhesive. It is not surprising that the lower the viscosity, the greater the flow into the pores, especially as the cross-sectional area of the pore decreases. The data in the Peerman and Vertnik patent [4] do not show any correlation between vinyl bond strength and viscosity for polyamides that do and do not bond vinyl. In addition, many commercial polyamides have low viscosities but do not bond vinyl [9]. Surface tension is a bit harder to evaluate directly. However, surface tension is related to the solubility parameter. In the following section, the data show that solubility parameters do not relate well to vinyl-bonding ability. Thus, neither viscosity nor surface tension properties are different enough between vinyl- and non-vinyl-bonding polyamides to be a reasonable explanation for the difference in performance.

A second stage of wetting occurs as the molten adhesive is cooling into a solid. Since the initial temperature of the adhesive is high for only a short time, there is insufficient time for the adhesive to flow into all the pores as could be expected under equilibrium temperature conditions. It is known that not all dimer-based polyamides have the same open time, i.e., the time for the adhesive to become solid [7,10]. The longer the open time the more likely the polyamide is to wet the surface prior to solidification. The proposal is that the greater open time of piperazine-derived polyamides allows better wetting of the vinyl prior to setting. However, plastics are less sensitive to open time than are metals due to the lower rate of heat transfer in plastics [11]. Both piperazine- and non-piperazine-derived polyamides have good adhesion to metals, while only piperazine-derived polyamides have good adhesion to vinyl. In addition, the Peerman and Vertnik patent states that vinyl bonding occurs independent of whether the polyamide is applied as a molten liquid to unheated vinyl or as a film with both the adhesive and vinyl being heated to form a bond. The latter method should not be dependent on the open time of the adhesive since the substrate is not cooling the adhesive. Thus, the

available facts do not agree with the dynamic wetting hypothesis.

The other rheological factor is related to properties of the solid adhesive rather than the molten adhesive. Researchers have observed that bonds are often stronger if the modulus of the adhesive is similar to that of the substrate. The rationale is that less stress is concentrated at the interface if the adhesive and substrate are not highly different in modulus. A stiffer adhesive would cause greater stress at its interface with the substrate as the substrate is flexed, and the greater stress could exceed the bond strength of the adhesive to the substrate. Since piperazine incorporation reduces the internal hydrogen bonding of polyamides compared to the use of mono-substituted diamines, these polyamides generally have lower moduli. The hypothesis is that the lower moduli of piperazine-derived polyamides are closer to that of vinyl. Although most piperazine-derived polyamides have lower moduli than many other polyamides, some non-piperazine-derived polyamide formulations have lower moduli and do not bond to vinyl [9]. In fact, polyamides from dimer diamine have moduli and elongations similar to those of piperazine polyamides, but they show very low vinyl bond strength. In addition, flexibility (modulus) of vinyl is dependent on the amount of plasticizer added. The flexibility of vinyl does not influence which polyamides bond to vinyl and which do not. Thus, low stiffness of the polyamide does not appear to play a major role in this specific adhesion.

## 5. Solubility parameters

Solubility parameters have found wide use since they explain the solubility of the polymers and oligomers in solvents, polymer miscibility, and wetting of substrates for inks, coatings, and adhesives [12]. These parameters measure cohesive energy density and therefore are an indication of the interaction of a material with itself and other materials [13]. Solubility parameters have also been related to bond strength [14]. In this case, the solubility parameter model predicts that the lower polarity of piperazine-derived polyamides is closer to that of vinyl than is the polarity of non-piperazine-derived polyamides, which results in good bond strength.

Acetamide and *N,N*-dimethylacetamide could be model compounds for piperazine- and non-piperazine-derived polyamides. As shown in Table 2, the lower cohesive energy data for dimethylacetamide can be due to reduced hydrogen bonding, since dimethylacetamide is only a hydrogen bond acceptor and not both an acceptor and donor like acetamide, or to the more aliphatic character of dimethylacetamide. By using the data for *N*-ethylacetamide, we can sort out the

Table 2  
Solubility parameters for model acetamides

Compound	Hildebrand parameter <sup>a</sup> (MPa <sup>1/2</sup> )	Hydrogen bonding <sup>a</sup>	Parameter <sup>b</sup> (MPa <sup>1/2</sup> )			
			d <sub>T</sub>	d <sub>H</sub>	d <sub>P</sub>	d <sub>NP</sub>
Acetamide	34.2		30.2	20.6	16.4	14.7
<i>N</i> -Methylacetamide	29.9	Strong	26.4	16.5	13.7	15.4
<i>N,N</i> -Dimethylacetamide	22.1	Moderate	23.0	12.0	10.8	16.3
<i>N</i> -Ethylacetamide	25.2	Strong	24.7	14.5	12.5	15.6

<sup>a</sup>Hildebrand values from Chapter 8, Tables 1 and 6 of Ref. [12]

<sup>b</sup>Hoy solubility parameters calculated according to Ref. [15].

Table 3  
Calculated solubility parameters of polyamides

Source	Acid component	Amine component	Parameter <sup>a</sup> (MPa <sup>1/2</sup> )			
			d <sub>T</sub>	d <sub>H</sub>	d <sub>P</sub>	d <sub>NP</sub>
Vinyl	—	—	20.3	6.9	10.0	16.3
Commercial	Dimer + sebacic acids	Ethylenediamine	20.4	7.1	8.2	17.3
Commercial	Dimer + sebacic acids	Ethylenediamine, dimer diamine	19.8	6.1	7.4	17.4
Ex. I-(a) <sup>b</sup>	Dimer + sebacic acids	Ethylenediamine, dimer diamine	19.8	6.2	7.2	17.4
Commercial	Dimer + sebacic acids	Ethylenediamine, piperazine	20.2	6.7	7.6	17.5
Ex. I-1 <sup>b</sup>	Dimer + sebacic acids	Ethylenediamine, piperazine	20.5	9.2	7.7	16.6
Ex. I-7	Dimer + sebacic acids	Ethylenediamine, 1,3-di (4-piperidyl) propane	17.2	6.3	6.5	14.6
Ex. I-14 <sup>b</sup>	Dimer + sebacic acids	Ethylenediamine, <i>N</i> -aminoethyl-piperazine	20.4	7.5	8.1	17.1
Ex. 4 <sup>c</sup>	Dimer + azelaic acids	Ethylenediamine, 1,3-propanediamine, 1,4-cyclohexanedimethanol	20.7	7.3	8.6	17.3

<sup>a</sup>Hoy solubility parameters calculated according to Ref. [15].

<sup>b</sup>Example from US Patent 3,377,303.

<sup>c</sup>Example from US Patent 4,485,233.

contributions of both the aliphatic nature and hydrogen bonding. The less polar nature of dimethylacetamide compared to ethylacetamide shows that less hydrogen bonding lowers the Hildebrand and hydrogen bonding parameters. These data give credence to the solubility parameters as a reasonable model for better wetting of piperazine-derived polyamides.

The solubility parameter (6) for liquids can be measured directly by one of several methods. However, the main methods are indirect for solids. They consist of contact angles with a variety of liquids of different surface tensions, solubility data in different solvents, or the use of calculation methods. The calculation methods involve group contribution methods. One widely used method involves the factors derived by Hoy [15]. As shown in Table 2, these calculations indicate that the transition from *N*-ethylacetamide to *N,N*-dimethylacetamide lowers total (&), hydrogen bonding (&), and polar (d<sub>P</sub>) solubility parameters but has a smaller influence on the non-polar solubility parameter (d<sub>NP</sub>). This is in agreement with the measured data for these compounds, giving credence to the utility of solubility parameters for rationalizing the difference in adhesion of polyamides.

There are a number of difficulties in applying the group contribution methods to polyamides. The first is

that the dimer used to make polyamides consists of a large number of individual structures. For our calculations, we used the weight percentage of branched acyclic, unsaturated cyclic, aromatic, and bicyclic species as previously determined [16]. Although this assumption could throw off the absolute value, we used the values to compare on a relative basis the difference between piperazine- and non-piperazine-derived polyamides. Thus, we mainly looked for the difference in the contribution of the amide functional groups.

Differences in solubility data for several representative polyamides calculated by the Hoy method were generally small (Table 3). A main reason for the small difference between different polyamides is that the dimer is a dominant part of the molecule on a weight basis so that it dilutes the effect of the functional groups. Piperazine-derived polyamides are similar or in some cases actually more polar by these calculations than are polyamides made with dimer diamine and ethylenediamine or just ethylenediamine, because polyamides need more sebacic or azelaic acid to have good strength and creep resistance. The use of more of the shorter chain diacids with piperazine- or dipip-derived polyamides raises the number of amide groups and the solubility parameters. In addition, the solubility parameter of the

polyamide made from just ethylenediamine and dimer acid is close to that of vinyl. Thus, the solubility parameter data do not provide any support to the theory that piperazine-derived polyamides have solubility parameters closer to that of vinyl. Some of the polyamides not derived from piperazine bond low energy plastics, such as polyethylene and polypropylene, as well as—and sometimes better than—those made from piperazine.

Note that there are a number of different systems for breaking down total solubility into individual components. One of these alternative systems could explain specific interactions, but most do not contain all the functional groups necessary for doing this type of calculation. Our solubility study did not show any dramatic difference in the solubility of polyamides that bond to vinyl and those that do not [unpublished data]. The bulk of the data do not support the use of solubility parameters to explain specific adhesion results.

## 6. Acid–base and hydrogen bonding interaction

The third chemical model involves acid–base and hydrogen bond concepts. The use of acid–base concepts in relation to adhesion has been investigated [17]. Stronger interactions are expected if the substrate is an electron donor and the adhesive an electron acceptor or vice versa. In this case, adhesive attraction should be greater than cohesive attraction. However, if the polar groups are tied up in cohesive attraction when the adhesive is both an electron donor and acceptor, then the polar groups are less free to participate in adhesive attraction.

The properties of polyamides strongly depend on internal hydrogen bonding [18]. This is especially important for dimer-based polyamides since the large number of structures for the dimer portion lead to an amorphous polymer that should have little of the crystallinity that controls many properties of structural nylons. On the other hand, dimer-based polyamides have primary amide hydrogens and carbonyl groups that should be quite free for hydrogen bonding. The two fatty acids are tied together at about the 9–12 carbon atoms and have little or no branches or cyclic structures near the amide groups. Consequently, the amide groups are free for hydrogen bonding, but the branching and cyclic structures hinder the normal stacking of polyamide chains for forming crystallites.

On the other hand, polyamides that are made from piperazine amide groups can only be hydrogen bond acceptors since there is no proton for donation on the tertiary amides. If vinyl-bonding, piperazine-derived polyamides have many more moles of ethylenediamine than of piperazine, the piperazine amide can generally form hydrogen bonds with the ethylenediamine amide

(Fig. 1, H-2 hydrogen bond). However, at high enough levels of piperazine, the piperazine-derived amides will seek external hydrogen bond donors. In this case, the hydrogen next to the chloride in vinyl can be the donor [19], although there are other explanations for the interaction of carbonyls with polyvinyl chloride (PVC). The use of sufficient secondary amines leads to a polyamide that is seeking proton donors, and substrates, such as vinyl, can be the source of these donating groups, as in the H-3 hydrogen bond in Fig. 1. Thus, this model is consistent with the data showing that only certain polyamides bond to vinyl because of a specific chemical interaction.

The question can be raised as to why polyamides made from primary amines that form secondary amides with a proton do not participate in hydrogen bonds with vinyl. These polyamides probably do participate in hydrogen bonds with vinyl to a small degree, but the secondary amide would rather form strong bonds to other amide groups (see H-1 hydrogen bond in Fig. 1) than form weaker bonds to vinyl. Amides from primary amines can bond as well to the esters that are used as plasticizers for vinyl, which would not form a strong bond between polyamide and vinyl. On the other hand, amides from secondary amines can bond only to vinyl. As a result of the strong internal hydrogen bond, polyamides from primary amines are energetically unfavorable for forming a miscible phase with vinyl. On the other hand, tertiary polyamide chains from secondary amines do not have the strong internal hydrogen bonds; thus, they are more free to form a miscible phase with vinyl. Since polyamides made from greater piperazine contents bond to vinyl strongly, it is most likely that a greater number of the bonds bear the load during application of stress.

The definition of an adhesive is the ability of a material to hold two substrates together under some force. This ability is obviously dependent on the adhesive coming into close contact with the substrate. If the surfaces are held together by chemical attraction, then the strength and number of the individual chemical bonds will determine the overall strength at the interface. A normal polyamide forms few hydrogen bonds with vinyl because the amide tends to bond internally within the polyamide adhesive. On the other hand, if the polyamide has significant tertiary amide groups, a number of amides cannot bond internally and will therefore be involved in external chemical bonds with vinyl. A large number of these weaker hydrogen bonds can result in a strong bond overall. There is a limit to this approach for strengthening the bond. As the amount of internal hydrogen bonding in the polyamide decreases, stronger bonds may form to vinyl but the polyamide has less cohesive strength, so the failure mode changes from adhesive to cohesive.

Polyamides made from the less polar 2,5-dimethylpiperazine showed lower strength than polyamides from piperazine or dipip (Table 1). This supports the interaction of the amide with vinyl as being the site of adhesion. It would be expected that adding methyl groups would hinder the amide by weakening its bond to vinyl. The use of *N*-aminoethylpiperazine also reduced bond strength because some amide groups from secondary amines were replaced by those from primary amines. This is again consistent with the ratio of internal versus external hydrogen bonding for polyamides.

In summary, polyamides made from secondary diamines have several advantages over those from primary amines for bonding to vinyl. First, surface amide groups without hydrogen can bond only to vinyl. On the other hand, amides from primary amines can bond both to vinyl and to the ester plasticizer, with the latter mode not contributing to adhesive strength. Second, piperazine-derived polyamides have longer segments without hydrogen bonds than do ethylenediamine polyamides, which are free to interdiffuse with vinyl to form a type of mechanical interlock. Thus, this model is consistent with the available data.

## 7. Poly(ester-amides)

As discussed in the previous text, polyamides that bond to vinyl are made from secondary diamines, such as piperazine and dipip. In the literature, the only other vinyl-bonding, hot-melt, dimer acid-based polymers are poly(ester-amides). These polymers are made from diols and diamines reacted at the same time with the dimer acid and codacid. This generates polymers consisting of random ester groups and amide groups that may or may not contain a proton, depending on the diamine used. As discussed, for adhesion to vinyl, the most suitable model involves the bonding of the tertiary amide groups to the hydrogen alpha to chlorine on vinyl. The ester group can bond in a similar manner with the ester group, replacing the piperazine-derived portion of the polyamide. In the literature, the poly(ester-amides) derived from a primary diamine and a diol gave values of 4.6–24.2N/cm for peel strength to vinyl [6]. These data support our model for the relationship of vinyl bonding to groups that can form a significant hydrogen bond between the adhesive polymer and the vinyl polymer.

## 8. Conclusions

The theories of adhesive bonding can be grouped into mechanical and chemical. In mechanical theories, mechanical interlocking occurs on the macro scale and

interdiffusion occurs on the molecular level. Chemical theories depend on the atoms and functional groups that interact between adhesive and substrate. For all of these theories of adhesion the adhesive is assumed to have sufficient wetting properties to develop contact at the molecular level contact, at least in spots. Hot-melt polyamides made from primary diamines do not form strong bonds. The data do not fit for explanations involving mechanical bonding, rheology, and solubility parameters. The mechanical interlock mechanism is not likely on the bases that adhesion does not depend on the roughness of the vinyl surface and that hot-melt adhesives do not penetrate the roughness well because of their high molecular weight and fast solidification. Vinyl- and non-vinyl-bonding polyamides are not distinct based upon either their flow properties or their moduli, as would be required by two rheological models. Calculated solubility parameters are not able to distinguish polyamides on the basis of whether or not they bond to vinyl. However, a model based on acid–base interaction between the vinyl and adhesive fits with the available data. This model relies on the reduced internal bonding of the polyamide for the amides made from secondary diamines compared to those made from primary diamines. Those tertiary amide groups that are not tied up in internal bonds are free to be proton acceptor groups for bonding to the proton-donating vinyl resins. This model, in which free proton acceptors are required for bonding to vinyl, not only explains the adhesion of polyamides made from secondary diamines but also fits with the adhesion to vinyl for poly(ester-amides).

The acid–base interaction model explains the heretofore unexplained specific adhesion to vinyl of polyamides made from secondary diamines compared to the lack of adhesion of polyamides made from primary diamines. This is not meant to imply that rheological and cohesive energy density factors are not important for good adhesion. Rather, these factors are unsatisfactory explanations of the improved adhesion observed with polyamides that are made from piperazine.

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