Using the solubility parameter to design polyvinylidene chloride copolymers for improved hot tack performance in coatings

C. S. Chang
Senior chemist, Morton International, Inc., 1275 Lake Avenue, Woodstock, Ill. 60098

ABSTRACT *Polyvinylidene chloride copolymers enjoy extensive use as coatings in the flexible packaging industry because of their high-barrier resistance to both oxygen and moisture, coupled with their excellent clarity. These polymers also must have hot tack. It is possible to optimize this particular aspect of a heat seal bond by selecting copolymers that have a solubility parameter value of approximately 12.3.*

KEYWORDS
Coatings
Hot tack
Packaging
Solubility parameter
Thermoplastics

Flexible packaging can involve the use of a coating deposited on a web to produce a composite with properties unattainable with the unmodified web. One type of coating commonly required is a heat-sealable product that is used to bond one flexible web to itself or to another with the application of heat. Copolymers prepared from the reaction of vinylidene chloride with a variety of other monomers have often found use as such heat-seal coatings.

Polyvinylidene chloride (PVDC) copolymers offer the advantage of providing a high barrier to both oxygen and moisture while also giving excellent optical properties. In addition, these copolymers are prepared as dispersions in water, so they can be used in the flexible packaging industry without concerns for emissions of volatile organic compounds into the atmosphere.

Despite these advantages, the polyvinylidene chloride copolymers may sometimes be deficient in providing hot tack. Hot tack is the strength of a heat seal made by bonding the coating to itself or to another surface with the use of heat while the seal is still in the hot state. This property is important in form-fill-seal packaging operations where the heat seal bonds may be stressed before they can cool.

Many researchers feel that cohesive strength is primarily responsible for hot tack. They presume that better hot tack properties will result from coatings that have greater cohesive strength. There is a definition for hot tack in an out-of-date test method that takes only cohesive strength into account (*1*). Lutzelschwab and Buhrer have stated that the adhesive strength of a heat seal coating on a substrate is as important as the cohesive strength and plays an important role for the bonded material in the actual packaging process (*2*). Here, we provide the first evidence that hot tack is the sum of the cohesive and adhesive strengths as based on a correlation of the solubility parameters with the hot tack values for various polyvinylidene chloride copolymers. In addition, the solubility parameter is also a tool for designing a copolymer with optimal hot tack.

Solubility parameter

By definition, the solubility parameter δ is the square root of the cohesive energy density. That means that it is the ratio of the energy of vaporization, E_v, to the molar volume, V_m, at a given temperature:

$$\delta = (E_v/V_m)^{1/2} \quad (1)$$

Scatchard developed the concept of solubility parameter (*3*), and Hildebrand extended it (*4*). Formulators have found it to be a useful guide in selecting a solvent for polymers (*5*). The concept has since gradually developed to some extent as a tool for new polymer designs. Small (*6*) and later Rheineck and Lin (*7*) showed that the contribution of each atomic grouping occurring in a molecular structure could be totalled to estimate the solubility parameter value for an entire molecule. Fedors has provided an extension of this by increasing the number of atomic groups available (*8*).

According to Fedors's method, the contribution of each atomic group to the molar energy of vaporization and to the molar volume is summed over the molecular structure, and the square root of the ratio is taken to give the solubility parameter value. As an

example, consider that portion of a polymer which results from the use of ethyl acrylate as a monomer, as shown in **Table I.**

In this table, each of the groups that composes the ethyl acrylate portion of the polymer has been listed with the number of times it occurs. Also listed are the energy of vaporization, the molar volume, the complete energy of vaporization, and the complete molecular volume, which are the individual values times the number of times the groups occur. All of the energies of vaporization are summed to obtain a total, as are all of the molar volumes. The square root of the total energies of vaporization divided by the total molar volume gives the solubility parameter of 10.2.

Table II presents the values for the energies of vaporization, the molar volumes for vinylidene chloride, and some of the acrylic monomers that are commonly used with it to form copolymers which are useful as heat seal coatings. These values are necessary for calculating the solubility parameters of the copolymers discussed here.

I. Calculation of the solubility parameter for the ethyl acrylate portion of the polymer

		Energy of vaporization		*Molar volume*	
Group	*Number*	*Each, cal/mol*	*Total, cal/mol*	*Each, cm^3/mol*	*Total, cm^3/mol*
CH_3	1	1125	1125	33.5	33.5
CH_2	2	1180	2360	16.1	32.2
CH	1	820	820	-1.0	-1.0
COO	1	4300	4300	18.0	18.0
Total			8605		82.7

$\delta = (8605/82.7)^{1/2} = 10.2$.

II. Energies of vaporization and molar volume for selected monomers

Monomer	*Energy of vaporization, calories/mole*	*Molar volume, cm^3/mol*
Vinylidene chloride	7,050	44.9
Methyl acrylate	7,425	66.6
Ethyl acrylate	8,605	82.7
2-hydroxyethyl acrylate	15,780	75.3
2-hydroxyethyl methacrylate	16,435	90.6
Methyl methacrylate	8,080	81.9
Acrylic acid	8,600	43.6

Solubility parameter calculation for copolymers

To design a polyvinylidene chloride copolymer with a suitable solubility parameter value, it is necessary to examine the entire molecular structure of the system. Since each monomer contributes its fraction to the copolymer, the solubility parameter of the copolymer becomes a function of the sum of the energies of vaporization and the molar volumes of each individual monomer multiplied by the mole fraction of that monomer. **Table III** provides an example of this calculation for a copolymer whose molar composition is 83.3% vinylidene chloride, 14.0% ethyl acrylate, and 2.7% acrylic acid.

In Table III, each monomer makes a contribution to the energy of vaporization and to the molar volume according to its percentage in the total monomer system. Thus, the energy of vaporization and the molar volume for each individual monomer is multiplied by the respective percentages to obtain that portion of that overall energy of vaporization and the molar volume.

Experimental procedure

To minimize all factors that might contribute to errors in this study, all of the copolymers were prepared under the same reaction conditions, including temperature and the amount and type of surfactant and catalyst. Thus, each copolymer was prepared as an emulsion at 40°C using a persulfate-sulfite redox system in the presence of an anionic surfactant. The copolymers all used vinylidene chloride and contained various amounts of the other monomers, which are listed in Table II.

Each copolymer was coated onto a polypropylene film that was corona treated to a level of 42 dynes/cm at a coating weight of 2 dry lb/3000 ft^2. A 12-$in.^2$ piece of this coated film was then wrapped around a Teflon®-coated template 12 in. by 4 7/8 in. by 1/8 in., with the coated side facing the Teflon coating. An impulse heat sealer was used to bond the overlapped portion together to form an air-tight seal. To prepare samples for testing, the film "cylinder" is removed from the Teflon plate and is cut into four small pieces, each 3 in. wide.

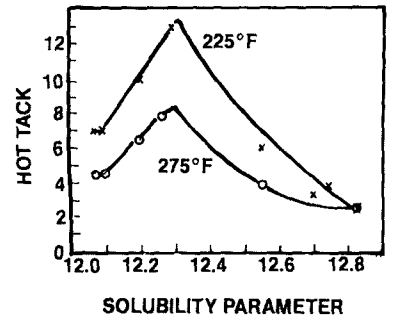
The copolymer coatings we used were sealed at temperatures of 225°F (107°C) and 275°F (135°C) using a dwell time of 1 s at a pressure of 20 psi. The 3-in.-wide cylinder film is partially slid onto a sample horn, as shown in **Fig. 1**, and is wrapped tightly with adhesive tape to let 2 1/2 in. of the film cylinder hang freely. This free portion

III. Calculation of the solubility parameter for the copolymer

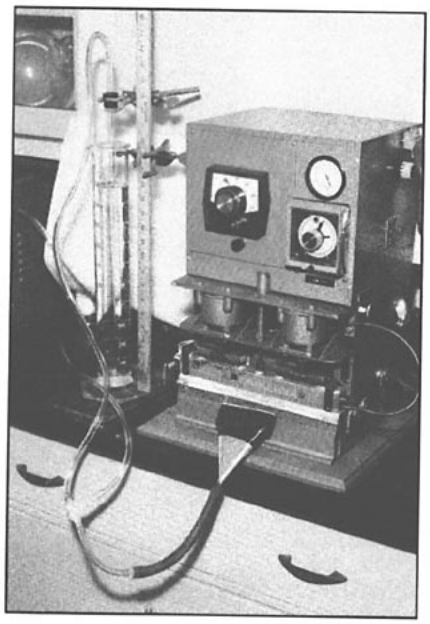
Group	Mole fraction	Energy of vaporization: Each, cal/mol	Energy of vaporization: Total, cal/mol	Molar volume, cm^3/mol	Contribution to molar volume, cm^3/mol
Vinyl chloride	0.833	7050	5872.65	44.9	37.402
Ethyl acrylate	0.140	8605	1204.70	82.9	11.578
Acrylic acid	0.027	8600	232.20	43.6	1.177
Total			7309.55		50.157

$\delta = (7309.55/50.157)^{1/2} = 12.07.$

2. Hot tack is sensitive to the solubility parameter, with a maximum value at about 12.3.



1. Apparatus used to measure hot tack values



IV. Composition of polymers designated as A through H

A	Vinylidene chloride, ethyl acrylate, 2-hydroxyethyl acrylate, acrylic acid
B	Vinylidene chloride, ethyl acrylate, 2-hydroxyethyl acrylate, acrylic acid, methyl methacrylate
C	Vinylidene chloride, acrylic acid, methyl methacrylate, methyl acrylate
D	Vinylidene chloride, ethyl acrylate, 2-hydroxyethyl acrylate
E	Vinylidene chloride, ethyl acrylate, acrylic acid
F	Vinylidene chloride, acrylic acid, methyl acrylate
G	Vinylidene chloride, ethyl acrylate, 2-hydroxyethyl methacrylate, acrylic acid
H	Vinylidene chloride, methyl acrylate, 2-hydroxyethyl acrylate

V. Solubility parameters and hot tack values for experimental copolymers in Table IV

	Solubility parameter	225°F, in.	275°F, in.
A	12.82	3	3
B	12.56	6	4
C	12.10	7	4.5
D	12.70	3.5	...
E	12.07	7	4.5
F	12.27	13	8
G	12.20	10	6.5
H	12.75	4	...

is sealed face-to-face on an impulse sealer to a depth of 1 in., leaving a 1 1/2 in. "bag."

An air pressure setting is selected by adjusting the depth of the glass tube in the water-filled cylinder. This pressure acts on the heat seal bond immediately upon the release of the jaws of the impulse heat sealer. Hot tack values are measured by the depth of the glass tube in the water where the bag has survived the pressure but failed the pressure at the next 1/2 in. lower level. A failure consists of separation of 1/8 in. or more in the seal area. Figure 1 is a photograph of this apparatus. Each coating is tested four times to obtain an average value.

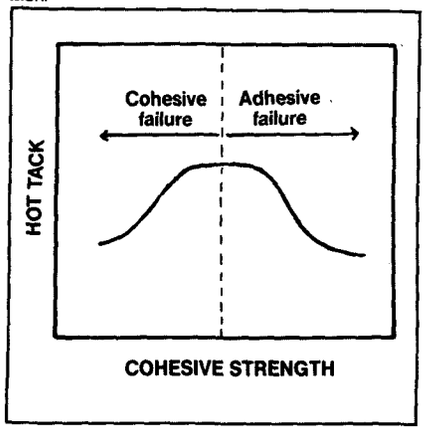
Test results

The copolymers we prepared are listed in **Table IV**. The calculated solubility values are indicated in **Table V** with the measured hot tack values at the two heat seal temperatures. These copolymers all have enough barrier to both oxygen and moisture to be practical for heat seal coatings. Thus, the calculated solubility parameters of the chosen copolymers fall within the rather narrow range of 12.00–12.90. In spite of this, the hot tack of the polyvinylidene chloride copolymers is extremely sensitive in this particular region and shows marked differences when the hot tack values and the solubility parameters are plotted as shown in Fig. 2.

Figure 3 illustrates the relationship between hot tack and cohesive strength. For any heat seal coating, the hot tack will increase as the cohesive strength increases until a maximum value is attained. The failure of the bond up to this point will be a failure of cohesion. Even though the cohesive strength continues to increase, the hot tack values now decrease because of failure of adhesion.

If the cohesive strength were solely responsible for hot tack, an increase of the solubility parameter should result in greater hot tack because of the greater cohesive strength. There should be a straight line relationship with a positive slope. This is not the

3. Cohesive or adhesive failure causes low hot tack.



case, however. As the solubility parameter increases, the hot tack value decreases. Further examination of the mode of failure indicates that the bond fails by adhesion failure. The downward concavity in Fig. 2 suggests that both the cohesive and the adhesive strength contribute to the hot tack. Thus, as shown in Fig. 3, either cohesive or adhesive failure can cause a low hot tack value. Furthermore, there is a maximum hot tack value. Before reaching it, the failure of the bond is cohesive; after reaching it, the failure of the bond is adhesive.

The unsymmetrical curve in Fig. 2, where the maximum hot tack occurs in the region of the lower solubility parameter, also shows that the adhesive strength does in fact play a more important role on hot tack than cohesive strength.

To achieve optimum hot tack values, the balance between the cohesive strength and the adhesive strength of a copolymer is important. In the polyvinylidene chloride copolymers of this study, a solubility parameter between 12.2 and 12.4 resulted in the highest hot tack value. Although the copolymers evaluated at the higher heat seal temperature of 275°F gave lower hot tack values, the relationship between hot tack and the solubility parameter remains the same.

One way to increase cohesive strength is to provide a degree of cross-linking in a copolymer by using a multifunctional monomer. Although an increase in molecular weight also will enhance the cohesive strength, above a certain point there will be an adverse effect on the adhesive strength, and failure will arise from a poor adhesive bond between the adhesive and the substrate. The polarity of a copolymer can affect its adhesion to a specific surface, but highly polar copolymers tend to adhere only to polar substrates (that is, having a high surface energy) by virtue of dipole–dipole interaction and hydrogen bonding. Conversely, nonpolar polymers will adhere well to nonpolar substrates with low surface energy.

Summary

Using the method of the atomic contribution, it is possible to synthesize polyvinylidene chloride copolymers with specific solubility parameter values. The relationship between hot tack and solubility parameter values is such that both cohesive strength and adhesive strength contribute to the bond. Thus, the solubility parameter is a concept that is useful in designing a copolymer with improved hot tack values.□

Literature cited

1. Proposed New Method T 683, TAPPI PRESS, Atlanta, 1972.
2. Lutzelschwab, L. and Buhrer, H. G., Modern Packaging 48(5): 31(1975).
3. Scatchard, G., Chemical Revues 8(2): 321(1931).
4. Hildebrand, J. H. and Scott, R. L., The Solubility of Nonelectrolytes, Rheinhold Publishing Corp., New York, 1950.
5. Gardon, J. L., J. of Physical Chemistry 67: 1935(1963).
6. Small, P. S., J. Applied Chemistry and Biotechnology 3: 75(1953).
7. Rheineck, A. E. and Lin, K. F., J. of Paint Technology 40(527): 611(1968).
8. Fedors, R. F., Polymer Engineering & Science 14(2): 147(1974).

Received for review Aug. 1, 1989.
Accepted Oct. 26, 1989.