Application Report

Optimizing Automotive Coatings

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Drop Shape Analyzer – DSA100

Force Tensiometer – K100

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Optimizing Automotive Coatings – the Balancing Act between Adhesion Energies, Interfacial Tensions, and Spreading Coefficients

Abstract

The optimization of any coating process involves controlling the bulk rheology of the coating, the surface chemistry aspects of the coating, and the surface energetics of the solid. Here we share some recent work on the surface chemistry aspects of solvent based coatings used to color the plastisol materials which make up much of the interior of most automobiles – dashboards, door interiors, arm rests, and the like. Without surface treatment (corona, flame, plasma, or other) plastisol is a fairly hydrophobic (low surface polarity) and moderately low overall surface energy material, onto which the coating needs to properly spread (wet) and then adhere. The goodness of adhesion needs to be considered in both, the short and the long term. The *spreading coefficient* of the coating on the substrate determines the uniformity of initial wetting. Coating/substrate *adhesion energy* (also known as work of adhesion) characterizes the short term bonding. And, coating/substrate *interfacial tension* – being that it represents the tension left in the formed bond (i.e. the bond's potential to break) – characterizes long term adhesion. Any alteration of either the substrate surface or the coating changes all three of these important parameters. The trick is to optimize all three properties at once. This note is an example case wherein we helped a customer improve one particular color coating, based on studying these parameters relative to those of another coating which was known to have many less adhesion issues.

Methods

The plastisol surfaces were characterized for surface energy with polar and dispersive components by the Fowkes method using diiodomethane and water as contact angle probe liquids. Contact angles were obtained using a KRÜSS Drop Shape Analyzer – DSA100. Coatings were measured for overall surface tension using the Wilhelmy plate method on a KRÜSS Force Tensiometer – K100. Their overall surface tensions were then partitioned into polar and dispersive components by testing the coatings for contact angle against polytetrafluoroethylene (PTFE) and again applying Fowkes' theory to solve for the dispersive component of the coating's surface tension. The Fowkes theory is described in mathematical detail elsewhere.[1]

Spreading coefficients for the coatings on the plastisol substrates are calculated as:

$$S = \sigma_S - \sigma_L - \sigma_{SL}$$

Adhesion energy is calculated as:

$$E_A = 2\,(\sigma_S^D\,\sigma_L^D)^{1/2} + 2\,(\sigma_S^P\,\sigma_L^P)^{1/2}$$

Interfacial tension between the coating and the plastisol is calculated as:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2\,(\sigma_S^D\,\sigma_L^D)^{1/2} - 2\,(\sigma_S^P\,\sigma_L^P)^{1/2}$$

wherein σ_S, σ_S^D, and σ_S^P is the overall, dispersive, and polar parts of the plastisol surface energy and σ_L, σ_L^D, and σ_L^P is the overall, dispersive, and polar parts of the coating surface tension respectively.

Experimental

Our customer initially had two types of color coatings for plastisol parts of car interiors to consider (pewter and taupe). The coatings had significant formulation differences beyond the pigments, mainly in terms of stabilization packages for the pigment, with some solvent system modifications as well. The primary solvent in each case was, however, Butanone (MEK, methyl-ethyl-ketone).

Fig. 1: Car interior

The pewter coating worked very well, in terms of initial spreading as well as short and long term adhesion. The taupe coating, however, had significant issues in terms of long term adhesion in particular. It tended to start flaking coming off the plastisol within 1 week of application.

The customer reported that they had been using a spreading coefficient based rule (which is commonly stated by coatings suppliers) of keeping the surface tension of the coating 10 mN/m below surface energy of the solid, and that they had measured the plastisol to have a surface energy (using dyne-pen approach) of about 36 mJ/m^2 and that both coatings had surface tensions is the range of 26 mN/m. Ignoring the interfacial tension between the coating and the substrate, this would give them about a 10 mN/m spreading coefficient for both coatings, which their coating supplier told them was adequate. However, they were obviously missing something, because the two coatings were behaving quite differently.

Using the methods described above we studied both coatings and the plastisol and determined the following properties to be characteristic of the systems.

Results

You will immediately note that we found nothing wrong with the customer's measurements, and concurred that the plastisol had a surface energy of 36 mJ/m^2 and that the coatings were similar in overall surface tension, with surface tensions in the 26 mN/m range.

	Substrate	**Coatings**	
	Plastisol	**Pewter**	**Taupe**
Overall Surface Energy (mJ/m^2)	36.04	26.74	26.53
Polar Component (mJ/m^2)	4.49	2.81	9.17
Dispersive Component (mJ/m^2)	31.55	23.93	17.36
Surface Polarity (%)	12.45	10.52	34.57
Adhesion Energy to Plastisol (mN/m)		62.06	59.64
Interfacial Tension (mN/m)		0.72	2.93
Spreading Coefficient (mN/m)		8.58	6.58

Table 1: Original Coating and Plastisol Properties

However, our more detailed analysis also revealed large differences in surface polarity between the two coatings (pewter = 10.52 %, taupe = 34.57 %) with the pewter coating obviously matching the surface polarity of the plastisol (12.45 %) much more closely. This leads to lower adhesion energy and spreading coefficient, and higher interfacial tension, for the taupe coating on the plastisol. The customer was fairly sure that the initial spreading and adhesion of the taupe coating during processing was tolerable. However, the long term adhesion was not – thus indicating that the higher interfacial tension versus the pewter coating was the least tolerable difference between the coatings.

Most typically for coatings customers report adhesion energies above 65 mN/m, spreading coefficients above about 8 mN/m, and interfacial tensions below 1 mN/m to 2 mN/m (depending on specific application) to meet their wet-out, short, and long term adhesion specs. So, you can see that we would, in theory, have concerns in all areas for the taupe coating. But, these are also general guidelines, and obviously the interfacial tension as related to the long term adhesion was of greatest concern.

Our initial approach was to add corona treatment to the plastisol line which runs with the taupe coating. Corona is ionized air created by discharging high frequency, high voltage, energy across an electrode. Corona treatment done in air oxidizes the surface of the film by dislodging electrons from the surface[2], thus causing it to bond chemically to available oxygen and ambient moisture in the air. This raises its surface energy and surface polarity[3,4]. Based on the voltages used one can, by trial and error, dial-in a level of treatment. The best we achieved, focusing on matching the surface polarity of the plastisol to that of the taupe coating was to get the plastisol surface polarity up to 31.25 %, which was accompanied by an increase in the overall surface energy of the plastisol to 41.05 mJ/m^2.

Using these values to calculate the adhesion energy, interfacial tension, and spreading coefficients for the taupe coating yielded the following values:

	Corona Treated Plastisol	**Taupe Coatings**
Overall Surface Energy (mJ/m^2)	41.05	26.53
Polar Component (mJ/m^2)	12.83	9.17
Dispersive Component (mJ/m^2)	28.22	17.36
Surface Polarity (%)	31.25	34.57
Adhesion Energy to Corona Treated Plastisol (mN/m)		65.97
Interfacial Tension (mN/m)		1.61
Spreading Coefficient (mN/m)		12.91

Table 2: Corona Treatment with Original Taupe Coating

The decrease in interfacial tension achieved by corona treating the plastisol did go a long way toward improving the long term adhesion of the taupe coating, and the adhesion energy improvement, while apparently not necessary, did not harm the process.

However, the customer experienced wet-out issues, wherein the coating was actually wetting out too well for their process – too much spreading from initial coating placement. This means the rise in spreading coefficient, which is mainly due to the corona treatment raising the overall surface energy of the plastisol too much (so that the gap in overall surface energy between the coating and substrate is too high) was not acceptable.

Eventually, by working with the coating manufacturer to alter the solvent composition in the coating, we were able to change to a reformulated taupe coating having the specifications shown below – most notably 20.06 % surface polarity, which is much closer to the 12.45 % of the original untreated plastisol.

The corona treatment on the plastisol could thereby be eliminated, which kept the plastisol pre-treatment consistent for both types of coatings (which was easier for the customer).

	Plastisol	**Reformulated Taupe**
Overall Surface Energy (mJ/m^2)	36.04	26.12
Polar Component (mJ/m^2)	4.49	5.24
Dispersive Component (mJ/m^2)	31.55	20.88
Surface Polarity (%)	12.45	20.06
Adhesion Energy to Plastisol (mN/m)		61.03
Interfacial Tension (mN/m)		1.13
Spreading Coefficient (mN/m)		8.79

Table 3: Taupe Coating Reformulation Solution

And, the new taupe coating turned out to be even better in terms of long term adhesion (as the interfacial tension data above also indicate), fine in terms of initial adhesion (which was never really a problem through the process), and to spread in a similar manner as the good pewter coating (as a spreading coefficient comparison would suggest).

Summary

This study was structured in a chronological way, to highlight the processes of considering spreading wetting, adhesion energy, and interfacial tension and the interplay between them. It is also a good example of a system for which overall surface tensions and overall surface energies (such as are measurable with a "dyne-pen" type approach) offer absolutely no guidance toward solving the problem. Without more sophisticated studies of polar and non-polar parts of the surface tensions and energies in this system, such as are possible with KRÜSS instruments, it would have been difficult to tune the corona treater, which was the intermediate solution in this work, and there would have been no foreshadowing of the improvement in the reformulated taupe coating – since the new formulation does not change in overall surface tension significantly from the original coating.

Additionally, this was a largely solvent based coating system, containing about 45 % MEK, for which it is often suggested that surface tension measurements and the like are of no use in solving problems. However, as in this case, we have found in several other coating systems that pigment, pigment stabilizers, and other additives can have a profound effect on the surface polarity of the coating despite minor changes in overall surface tension. Therefore, a more complete approach and considering all factors may not always, but often times can, lead to good understanding even in solvent based systems.

Literature

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