Functional variety

Effects and properties in surface-functional coating systems. Vladimir V. Verkholantsev.

An impressive number of different surface-functional coatings is used for various technical applications, their application fields are growing and widening. This article discusses the effects that are involved in such systems, the conditions to form self-organized polymer matrices and film structures, and the associated coatings properties and application technologies.

Organic coatings perform either decorative, protective, or special functions - mostly a combination of these. Typically, each property is affiliated with a specific part of the coating systems, as illustrated schematically in Figure 1. Among the special-function or special-application coatings, surface-functional coatings are a prolific group possessing particular surface properties and technical functions. Examples are various release coatings [1], easy-to-clean coatings (e.g. anti-graffiti, de-activation), water-repellent, or antistatic coatings (Table 1).

As Table 1 indicates, many specific surface functions are associated with low values of the surface energy. However, surface-functional coatings frequently have to meet additional requirements. For instance, cookware coatings must be heat-resistant, abrasion-resistant, and need specific mechanical properties (e.g. surface elasticity).

Intermolecular forces and cohesion energy

The chemical composition of the molecules, the molecular structure (backbone and pendant groups) and the associated molecular volume, flexibility, conformation, and interaction with neighboring molecules (polymer free volume) defines material properties. Organic molecules, and organic resins, their solutions and blends are usually non-electrolytes built from C, H, O, and N atoms, with high energy covalent (primary) bonds (60-700 kJ/mol). The presence of other elements, or of ionic and metallic intra-molecular bonds is not typical.

Significantly weaker (secondary) intermolecular forces (Van-der-Waals forces) in homogeneous condensed phases (cohesion forces) can be characterized quantitatively by the cohesion energy density (CED), or internal pressure (IP) (see Box). These intermolecular forces consist of four types: the London dispersion forces (0.2-20 kJ/mol), dipole-induced dipole interaction forces (1-2 kJ/mol), dipole/dipole (polar) forces (5-20 kJ/mol), and hydrogen bonds (7-30 kJ/mol). Near interfaces, non-compensated intermolecular forces are responsible for the free surface energy, the surface tension. Secondary interactions are also responsible for the solubility and compatibility of components and determine non-ordered or ordered subphase structures in multi-component systems. In multi-phase systems, such as dispersions, paints, and coatings, intermolecular forces also show up as particle-particle attraction forces (in dispersions, e.g. resin emulsions and pigment suspensions) and adhesion forces.

Surface energy of liquids and solids, contact angles

Several standard methods are in use to measure equilibrium and non-equilibrium values of the surface tension (e.g. Du Nuoy ring method, Wilhelmy plate method, sessile or pendant drop profile) and contact angles (e.g. direct goniometry, interfacial rise method, rate of penetration) [2]. The surface tension of solid surfaces is usually measured by one of three methods:

- the zisman technique, determining the critical surface tension (or wetting) of the solid with a series of test liquids with known surface tension [3],
- the Owens-Wendt method, which uses water as a polar and diiodomethane as a non-polar test liquid [4] - and the Wu method [5].

Table 3 [6] shows that the first two methods do not always provide consistent results, especially for extremely low free surface energy polymers. In this regime, the Wu method is more reliable. Results for some industrial substrates obtained by this technique are given in Table 4.

Non-polar, hydrophobic materials are characterized by relatively low values of their solubility parameters \( \delta \) and surface tensions \( \gamma \), because their cohesion and surface energies are governed mainly by dispersion forces. The following approach is useful to classify materials (resins, solvents, etc.) according to their energetic parameters:

- Polar: \( \delta_p > \delta_d \) and \( \gamma_p > \gamma_d \)
- Moderately-polar: \( \delta_p > \delta_d \) and \( \gamma_p > \gamma_d \)
- Non-polar: \( \delta_p \to 0 \) and \( \gamma_p \to 0 \)
- Extremely non-polar (and low surface energy): \( \delta_p \) and \( \gamma_d \) are very low, \( \delta_p \) and \( \gamma_d \) = 0

Polyolefins, silicones, and fluorocarbon polymers show low values of the surface tension and corresponding extremely low-energy surfaces, which are difficult to wet and coat. Ferrous metals and ceramics have high energy surfaces, and thus can readily painted if properly wettable. The majority of plastic polymers an non-ferrous metals occupy an intermediate position, being polar or moderately-polar non-electrolytes. Table 4 compares the equilibrium surface tensions of typical coating components and the critical surface tension for the wetting of the substrates.

Novel technologies, however, often require optimizing of interfacial processes involving solvents, surfactants, polymers, membranes, films, or porous materials. Then, knowledge of the dynamic characteristics is even more important than of equilibrium properties. In particular, dynamic values of the surface tension, contact angles, and adsorption are important for the design, fine-tuning and trouble-shooting of various processes in coatings technology.

Coatings composition and structure

The chemical nature (composition) of the coating components, the binder resin in particular, largely define the coatings properties. On the other hand, however, structural criteria are included in any relevant description of organic coatings. L.E. Scriven describes the coating as “thin and continuous and, often, uniform and smooth. Usually the final structure is important; often it is critical” [8].

Polymer and film structures (micro- and macro-structures)

In polymer materials, including organic coatings, several structural levels can be distinguished, with corresponding typical length scales (Figure 2):

- the molecular structure of the polymer
- the sub-phase (multi-molecular) and micro-heterophase structures of the matrix
- the phase structure due to the filling phases (pigments, extenders, fillers)
- the multi-coat structure (also known as macro-structure), comprising a few or many coats of the same or different paints, applied in a defined sequence.

Many valuable surface properties, e.g. gloss and dirt pick-up, are enhanced if the film surface is smooth (due to a homogeneous polymer structure). Alternatively, many coating properties, mechanical properties in particular, and
is to function as a binder for the base layer, behave as a stratifying component, the more polar polymer - Thermodynamic conditions: a polymer/polymer (cross-linking) reactions (or be only partially overlapped) stratification processes must precede the curing - Kinetic conditions: a fluid state (melt above the flow (mixtures) must occur - A phase separation in homogeneous polymer blends structures (Figure 3c). Spontaneous stratification of polymer formation of complex multi-layer or gradient coating

The self-stratifying coatings approach allows a one-step Gradient and self-stratifying structures corresponding base coat or primer. surface-functional) coatings need to be applied over a majority of industrial applications release (and other durable adhesion contacts difficult. For that reason, in the energy polymers, act on very short distances only, making dispersion intermolecular forces, typical for low surface materials adhere poorly to them [6], mainly because the surface composition free from migratory components hardness) - surface composition free from migratory components - inert, non-reactive, solvent-resistant surface Silicone liquids (oligomers) and polymers are typical release agents. They are generally difficult to wet and most materials adhere poorly to them [6], mainly because the dispersion intermolecular forces, typical for low surface energy polymers, act on very short distances only, making durable adhesion contacts difficult. For that reason, in the majority of industrial applications release (and other surface-functional) coatings need to be applied over a corresponding base coat or primer.

Gradient and self-stratifying structures The self-stratifying coatings approach allows a one-step formation of complex multi-layer or gradient coating structures (Figure 3c). Spontaneous stratification of polymer blends requires several conditions [9, 18]: - A phase separation in homogeneous polymer blends (mixtures) must occur - Kinetic conditions: a fluid state (melt above the flow temperature or polymer solution), phase separation and the stratification processes must precede the curing (cross-linking) reactions (or be only partially overlapped) - Thermodynamic conditions: a polymer/polymer incompatibility must exist. The less polar polymer is to behave as a stratifying component, the more polar polymer is to function as a binder for the base layer, - Surface energy balance; The spreading coefficient for the stratifying phase (see Box) must be positive, and the base polymer must wet the substrate properly. Thus, the self-stratification process can occur in a phase-separating liquid mixture containing a low surface energy stratifying resin and a substantially higher free surface energy base resin. For instance, silicone and fluoro-polymers self-stratify readily from their mixtures with epoxy resins [7]. Incompatibility with common coating resins is a remarkable feature of the low surface energy polymers. Therefore, the use of low surface energy polymers in self-stratifying coatings, and heterogeneous polymer compositions generally, seems to appear technically more efficient than conventional formulated compositions, with homogeneous mixtures prepared in the presence of "compatibilizers" such as solvents or resin modifiers. Bilateral self-stratification is registered in films formed from macro-homogeneous fluoro-polymer-containing mixtures [21], with thicknesses of the stratifying layer as low as 6 to 8 nm.

Automotive and coil coating There are special requirements for topcoats in complex, multi-layer coating types, mainly for industrial applications. Automotive coatings typically include (a) a substrate pre-treatment layer, (b) a primer, which enhances the overall adhesion performance, (c) an intercoat, providing the coatings body and its smoothing, (d) upper-coats, which can be a combination of pigmented (opaque) basecoat(s) and one or two layers of a clear (transparent) topcoat - which are the surface-functional coating, featuring a specific combination of surface-related properties.

Automotive topcoats, which normally are based on acrylic or polyurethane resins, combine outstanding appearance (gloss in particular) with scratch, weather (sunlight, humidity), and chemical resistance (e.g. against oxygen and acid rain). Incorporation of small amounts of long-chain perfluoralkyl containing methacrylate monomers into the polymer backbone allows the formation of a self-stratifying topcoat with additional release properties [22]. Presently, many industries are switching over from traditional coating processes to pre-coated metal, mainly coil-coated. Various surface-functional materials are also suitable for coil-coating, as separately applied topcoats, or in the form of self-stratifying compositions.

References
Surface tension: dependence on T and M

Surface tension due to London dispersion forces (which are present in all matter), p refers to polar forces (arising from all intermolecular interaction are considered for calculating the cohesion energy of non-electrolytes: dispersion (d), polar (p), and H-bonds (h):

\[ \gamma = \gamma_d + \gamma_p + \gamma_h \]

According to Hansen [24], three components of intermolecular interaction are considered for calculating the cohesion energy of non-electrolytes: dispersion (d), polar (p), and H-bonds (h):

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]

Surface tension

The classical Hildebrand-Wood equation [25] (applicable to liquids) holds that the surface tension \( \gamma \) is derived directly from the cohesion energy and, therefore, is governed by the secondary intermolecular forces: \( \delta = 4.1 (\gamma / \gamma_d )^{0.43} \)

According to Hansen [26], the Hildebrand-Wood formula can be split up using components of the surface tension, in analogy to the solubility parameters, reflecting the contribution of the corresponding intermolecular interactions:

\[ \gamma = 0.0175 V_c^{1/3} [\delta_d^2 + 0.632 (\delta_p^2 + \delta_h^2)] \]

Free surface energy and contact angles

The Owens-Wendt equation [4] provides a link between the surface tension (\( \gamma \)) of liquids and solid substrates, and the contact angle \( \theta \):

\[ \gamma = \gamma_d (1 + \cos \theta) / 2 + \gamma_p / 2 + \gamma_h^{1/2} \]

The subscript \( s \) refers to the contact angle test liquid, \( s \) to the solid surface; the superscript \( d \) refers to the component of surface tension due to London dispersion forces (which are present in all matter). \( p \) refers to polar forces (arising from all polar interactions including H-bonding). The total surface tension \( \gamma \) is the sum of two components:

\[ \gamma = \gamma_d + \gamma_p \]

According to the Harmonic mean method by Wu [5], the interfacial tension between liquids and solids \( \gamma_l \) is given by

\[ \gamma_l = \gamma_l^{1/3} - (4 \gamma_l^{1/3} / (\gamma_l^{1/3} + \gamma_l^{1/3}) (4 \gamma_l^{1/3} / (\gamma_l^{1/3} + \gamma_l^{1/3})) / (\gamma_l^{1/3} + \gamma_l^{1/3}) \]

Surface tension: dependence on T and M

The liquid surface tension is little affected by the vapor phase, and slowly decreases with increasing temperature. Empirically \( \gamma = \gamma_0 (1 - T / T_c)^n \)

where \( \gamma_0 \) is the surface tension at \( \theta = 0 \), \( T_c \) is the critical temperature of the material, and \( n \) is an empirical parameter (approx. 11/9 for organic liquids) [27].

The liquid polymer surface tension depends on the molecular weight according to the LeGrand and Gaines equation [28]:

\[ \gamma = \gamma_m - K M_n^{1/3} \]

\( \gamma_m \) is the surface tension at infinitely high molecular weight, \( M_n \) the number average molecular weight, \( K \) is a constant. Thus, the surface tension of polydimethyl siloxane is 15.7 mN/m at \( M_n = 162 \), and 18.8 mN/m at \( M_n = 1200 \) [29].

Work of adhesion and cohesion, spreading coefficient

The work of adhesion \( W_a \) (the work per unit of interface required to separate two phases reversibly) is related to the energetic characteristics of fluid and substrate phases (stratifying or base) through

\[ W_a = \gamma_{lv} + \gamma_{lv} - \gamma_{ls} (1 + \cos \theta) \]

where \( \gamma_{lv} \), \( \gamma_{lv} \), and \( \gamma_{ls} \) are the interfacial tensions associated with the substrate/vapor, liquid/vapor and substrate/liquid interfaces, respectively. \( W_a \) is maximized when the contact angle \( \theta = 0 \).

For the spreading process (spontaneous wetting) to occur, the \( W_a \) must be greater than the work of cohesion (\( W_c = 2 \gamma_{lv} \)), i.e. the spreading coefficient \( S \)

\[ S = \gamma_{lv} - (\gamma_{lv} + \gamma_{lv}) = W_a - W_c \]

must be positive.

The author:

-> Prof. Vladimir V. Verkhokolantsev was born in 1937 in St. Petersburg. He graduated in chemical engineering and started his career as a technologist in a paint factory. Upon receiving his PhD in 1965 and Dr. Sci. in chemical engineering in 1970 he became a senior research chemist and then associate professor at the Lensovet Chemical Technology Institute in St. Petersburg. Later, he was appointed full professor at the Building Engineering Institute, then professor and director of department at the Coating Research Institute in Moscow. He joined Tambour Ltd. in Israel in 1991 as head of the research group. At present he is a freelance consultant.
Figure 2: Structural elements in coating systems and their typical size.
Figure 3: (a) Complex coating with surface-functional topcoat, (b) base coat, surface treated (surface modified) with a surface-functional material, (c) self-stratifying coatings with gradient structure in the intercoat.
Table 1: Typical surface-functional coatings and associated properties

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Low surface energy</th>
<th>Surface hardness</th>
<th>Surface elasticity</th>
<th>Chemical resistance</th>
<th>High surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anti-slip (anti-skid)</td>
<td></td>
<td>+</td>
<td></td>
<td>+</td>
<td></td>
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<tr>
<td>Self-healing (super scratch resistance)</td>
<td></td>
<td>+</td>
<td></td>
<td>+</td>
<td></td>
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<tr>
<td>Abrasion resistant</td>
<td></td>
<td>+</td>
<td></td>
<td>+</td>
<td></td>
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<tr>
<td>Low friction (non-stick)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Anti-Grafitti (anti-mar)</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
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<tr>
<td>Release coatings</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>(low soiling, anti-deposition)</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
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<tr>
<td>Ice-release</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Cookware release</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slip (self-lubricating)</td>
<td>+</td>
<td></td>
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<td></td>
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<tr>
<td>De-activation</td>
<td>+</td>
<td>+</td>
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<td>+</td>
<td></td>
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<tr>
<td>Hygienic Coatings</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Maintenance-free and easy-care</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
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<tr>
<td>Water-repellent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Foulant-release</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td></td>
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<tr>
<td>Soft-feel</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
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</tbody>
</table>
Table 2: Free surface energies of several polymers typical for release coatings [6]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Owens-Wendt mN/m</th>
<th>Zisman mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethyl siloxane</td>
<td>19.3</td>
<td>22.6</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>19.1</td>
<td>18.3</td>
</tr>
<tr>
<td>Polyfluoro-siloxane (1)</td>
<td>13.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Polyfluoro-siloxane (2)</td>
<td>7.0</td>
<td>14.9</td>
</tr>
<tr>
<td>Substrate</td>
<td>(\theta_{\text{H}_2\text{O}})</td>
<td>(\theta_{\text{MI}})</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Uncleaned steel</td>
<td>90</td>
<td>37</td>
</tr>
<tr>
<td>Acetone cleaned steel</td>
<td>85</td>
<td>42</td>
</tr>
<tr>
<td>Abraded steel</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Aluminium foil</td>
<td>47</td>
<td>33</td>
</tr>
</tbody>
</table>
Table 4: The surface tensions of selected coating components and the critical surface tension of wetting for selected substrates at 25°C (mN/m)

<table>
<thead>
<tr>
<th>Solvents</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.7</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48.4</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>30.0</td>
</tr>
<tr>
<td>Mineral spirits</td>
<td>24.0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Binder resins</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine resin</td>
<td>57 - 58</td>
</tr>
<tr>
<td>Epoxy resins</td>
<td>43-47</td>
</tr>
<tr>
<td>65% Soya Alkyd</td>
<td>38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrates</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare steel</td>
<td>38 - 43</td>
</tr>
<tr>
<td>Pre-treated steel</td>
<td>40 - 48</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>43</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>41</td>
</tr>
</tbody>
</table>
Phrase thesaurus through replacing words with similar meaning of Functional and Variety. FV stands for "Functional Variety". Variety replaced. functional form. functional change. functional type. functional race. functional species.

In sociolinguistics, language variety or lect is any distinctive form of a language or linguistic expression, including dialect, register, and jargon. Richard Nordquist is a freelance writer and former professor of English and Rhetoric who wrote college-level Grammar and Composition textbooks. FUNCTIONAL VARIETY OF LANGUAGE The study of language variation is an important part of sociolinguistics, to the extent that it requires reference to social factors. Languages vary from one place to another, from one social group to another, and from one situation to another. The term variety is the label given to the form of a language used by any group of speakers or used in a particular field. A variety is characterized by the basic lexicon, phonology, syntax shared by members of the group.