Physical Properties of Cured Coatings

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Introduction

Usually a cured coating is a thin film, which can be separated from a support. Formation of this film is the culmination of the whole work of preparing of a formulation and it's UV–cure (or cure by other radiation). In this paper we will talk only about cured coatings (films). The study of physical/mechanical properties of films is the subject of material science. We look for coatings with useful properties, such as high elongation to break, abrasion resistance, hardness, etc. The *enhanced* or *improved properties* of a cured coating should be explained in every case: one customer needs soft elastomers, another customer needs hard coatings with low elongation to break, one needs hydrophilicity (good wetting by water), another needs hydrophobicity (water repellency), etc. Coatings have different properties: electric conductivity or lack thereof, transmission of radio waves or not, shiny or matte, there are different modern smart coatings. The traditional role of coatings and paints is the protection of substrates. We will briefly consider only some basic physical properties in this memo.

Typical Stress–Strain Behavior

A natural impulse when first handed a piece of a coating is to stretch the film by hand. In order to elongate a film, one needs to apply force (F, measured in newtons or N). Evidently, the thicker and wider is the film, the larger should be the force. That is why instead of F, polymer chemists use stress, which is force divided area of cross–section S, P= F/S, measured in pascals or Pa. 1 Pa = 1 N/m^2. Thus, stress is measured in the units of pressure.

$$1 \text{ MPa} = 145 \text{ psi}^{1}$$

Megapascal is 10^6 Pa; psi is pound of force per square inch.

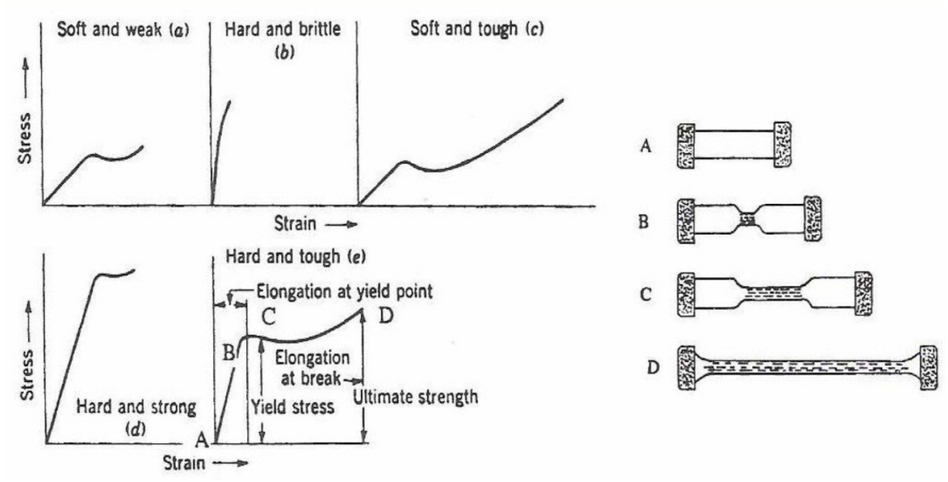
Imagine also not a film but a rod: one can apply pressure and compress a rod. Now we need to consider strain, a relative change in shape or size on an object due to externally–applied forces. Usually coatings chemists are interested only in elongation of films. Strain of 1.67 or 67% means that under a certain stress a film elongated up to 67% of it original length. Let us introduce the Young's modulus:

$$\text{Young's modulus} = \text{Stress/Strain}$$

Young's modulus is measured in Pa because strain is dimensionless. Quite similar or identical values are tensile modulus, elastic modulus and storage modulus. (The latter is always denoted as E'.) Figure 1 demonstrates the typical stress–strain curves for coatings:

Many synthetic organic polymers have tensile modulus in the range of ~10^4 MPa or ~10^6 psi. It is evident from the data of Figure 1, that it is an oversimplification to ascribe a coating one tensile modulus because modulus depends upon stress.

Figure 1. Typical stress–strain curves for coatings. Please study the Figure. (From a polymer textbook.)



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[1] The growth of Asian, Indian and Eastern European markets will lead to necessity to use metric or SI or IUPAC system. It is the hope of the author that the US Customary Unit System will disappear, or will be used simultaneously with its metric system equivalent.

Apparently reported tensile moduli in product data sheets are some kind of average values, or they are the initial slopes. In coatings for optical fibers a formulator is interested in so called 3 secant modulus, which is a modulus at a strain of only 2.5%, and the rest of a stress–strain curve is of no interest. Strictly speaking, it should be explained how modulus was defined in each case.

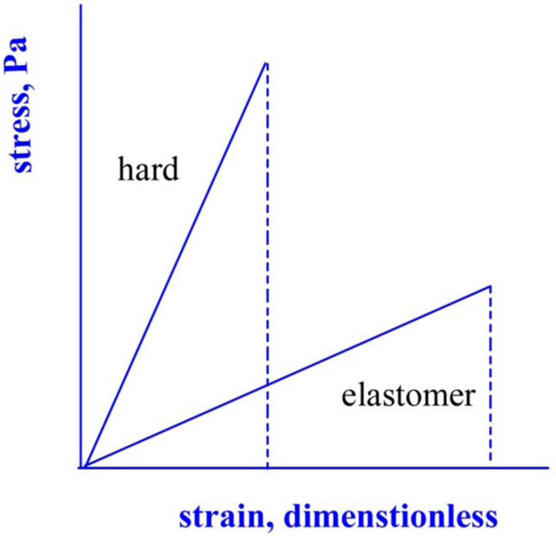
Elongation–at–break is another important characteristic of a coating. Elastomers (rubbers) can be extended at least 7–10 times prior to break. For example, a cured formulation based mainly on Bomar® oligomer BR–3641AA has an elongation at break of 5300%, which means that a strain of the film at break is 54. BR–301, which gives hard and strong films, has elongation at break of 3%, or a strain of 1.03. Numerical values of modulus and elongation at break depend upon the rate of stretching of a film. Evidently, all of the data depend upon temperature. Product data sheets often report a tensile strength or tensile–at–break, which is a measure of stress (Pa) at break.

Stress–strain curves frequently have a maximum called yield, cf. Figure 1. Sometimes stress–at–yield can be even *higher* than tensile–at–break. (Figure 1d, e presents stress at yield only slightly *lower* than a tensile stress.)

Take a strip of polyethylene cut from a household polyethylene bag. Start to stretch the film slowly with two hands. You will notice that at a certain strain you have to apply larger force than the force at the last moment when film breaks.

The plot of stress vs. strain (Figure 1) gives additional valuable piece of information. If we measure the area underneath the stress–strain curve, the number we get is called toughness. Toughness (energy/ volume; J/m^3) is a scientific term, and it is a measure of energy a sample can absorb before it breaks. Toughness is called also work–to–break. Figure 2 below presents examples of hard and soft coatings which have exactly the same toughness. Usually coatings with high toughness are valuable.

Figure 2. Stress–strain curves for two coatings. One is hard, possibly crosslinked, the second is soft and is an elastomer.



Glass Transition Temperature T_g

Tg is a very important characteristic of coating. We skip strict definitions of T_g [2] and will mention that the polymer above Tg is usually flexible and polymer below T_g is usually vitrified and brittle. Polymer chain segments can't move freely below Tg. This transition is less pronounced and less obvious than melting point (m.p.) Tm. Sometimes polymers melt as common liquids. $T_m > T_g$ for all polymers. Tg should be kept in mind during coatings application. Say, we want to be coating to be elastic at room temperature; thus we need a coating with T_g below room temperature.

[2] T_g is properly defined as the temperature at which there is an increase in the thermal expansion coefficient.

Interestingly, polymer, contrary to the crystalline and amorphous solid low MW compounds, is partially crystallized. There are thermal analysis methods for calculating the degree of crystallinity of a polymer. Somewhat similar, polymers demonstrate *both* elastic and viscous flow response upon the energy imparted by an applied strain. Storage modulus E' (cf. Section 1) measures the recoverable portion of energy. Loss modulus E" measures the viscous response. Viscous response is the loss of energy imparted by the applied strain. Viscous flow leads to dissipation (loss) of energy as heat. Ideal elastomer has certain E" ≠ 0 and E' = 0. Common Newtonian liquid has E' = 0 and a certain E" ≠ 0, which is the liquid viscosity. Usually, polymers possess non–zero E' and E". In order to determine E' and E", a stress–strain analysis is run dynamically using instruments like dynamic mechanical analyzer (DMA). That instrument applies oscillating strain with a specific frequency. So called *loss tangent* (tan delta) is identified as:

$$E''/E' = \tan \delta$$

E', E" and tan δ depend upon temperature, cf. Figure 3 on the next page.

It is common to assign the peak of tan delta curve as the T_g:

$$(\tan \delta)_{max} = T_g$$

Some researchers assign a peak of the loss modulus E" as the T_g or the inflection point of E' curve as the T_g. Tg can be measured by other methods, say differential scanning calorimeter. Thus, it is important to report the way Tg was measured. Once more, the most common is the T_g measure as a max of tan δ.

Even in this case, a value of T_g depends upon frequency of stress–strain oscillations and the rate of heating a sample. (Coating chemists report conditions of viscosity measurement (temperature, spindle, rotational speed or rpm.) T_g is less obvious notion than dynamic viscosity, and details of T_g measurement should be presented.)

Coatings can have more than one maximum on tan δ – T curve, or more that one T_g. For example, polyurethanes with their "soft" ("long" polyol) and "hard" (hydrogen–bonded urethane or carbamate links) segments may have a relatively low Tg originating from freezing/allowing movements of polyol "soft" segments and a higher T_g originating from freezing/allowing movements of "hard" carbamate segments. Please cf. conclusions on the last page.

Conclusions

1. We have learned about different types of moduli and what elongation at break and toughness are. These are important characteristics of films. There are several types of different stress–strain curves for different types of coatings.
2. Coatings with high toughness are valuable.
3. Another important characteristic is T_g. Simply speaking, coating above Tg is soft and coating below T_g is hard. Tg is usually measure by DMA, and T_g is ascribed to the temperature at which the maximum on the curve tan δ vs. T is observed.
4. The following correlation exists: the higher T_g, the harder is the coating.
5. It is desirable when presenting the physical properties of coatings to specify the conditions of measurement. It is always desirable to follow proper ASTM methods.

Figure 3. Dynamic properties of a highly–crosslinked acrylic coating. (From a coatings textbook.)