

# Crystallinity of *Based on Polyvinylidene*

**M**any thermoplastic polymers are semi-crystalline; that is, they consist of amorphous regions and crystalline regions. In the amorphous regions, the polymer chains exist in a random pattern; in the crystalline regions, the polymer chains are in a regular, periodic pattern. The degree of crystallinity, and the size and physical arrangement of the crystallites, have a significant effect on the physical and mechanical properties of the polymer – and on organic coatings based on these polymers. Polyvinylidene fluoride (PVDF) is a thermoplastic, semi-crystalline polymer. Therefore, the properties of coatings based on PVDF, such as HYLAR® 5000, are affected by the degree of crystallinity.

## Basics of Polymer Crystallinity

It is well known that polymer molecules possess the ability to crystallize; that is, the polymer chains arrange themselves in a periodic pattern. The extent to which crystallization occurs depends on the type of polymer, its molecular microstructure and its thermal history. Most polymers that are thermodynamically predisposed to crystallize do not totally crystallize, but only partially crystallize. These are referred to as semi-crystalline polymers. The remaining non-crystalline segment of the polymer is termed amorphous, which refers to a random configuration of the polymer chains. An analogy is to imagine a bowl of cooked spaghetti as the polymer chains in the amorphous state. Conversely, the uncooked, rigid strands of spaghetti, as contained in the package, can be thought of as the crystalline form of the polymer chains. Mixing the cooked and uncooked strands of spaghetti is a reasonable representation of a semi-crystalline polymer.

The degree of crystallinity of a semi-crystalline polymer and the size and physical arrangement of the crystallites have a significant effect on the physical and mechanical properties of the polymer. There are many factors that can affect the rate and degree to which crystallization occurs in a particular polymer. These factors include: (a) polymer processing variables such as cooling rate from the molten state,

orientation of the polymer chains in the molten state, and melt temperature; (b) tacticity of the polymer (i.e., location of the specific chemical species along the carbon chain backbone; for example, location of hydrogen atoms along the carbon chain of polyethylene); (c) amount of chain branching; and (d) presence of additives such as nucleating agents.

Crystallization of polymers is a thermodynamic process. In most industrial processes, polymers are often cooled very rapidly from the molten state to improve productivity of the process. This is the case when coatings based on PVDF are quenched in water after baking on a coil coating line. In this rapidly cooled, quenched scenario, crystallization is controlled by kinetics – meaning that the rate at which crystals nucleate and grow becomes important. With many polymers that are prone to crystallization, it is possible to cool the melt so rapidly that the crystals are extremely small, or are completely absent and the material is amorphous. These rapidly quenched structures are meta-stable (i.e., not in their preferred thermodynamic crystalline state), and crystals can grow over time.

## Crystallization of PVDF

The literature reports that the crystallinity of pure PVDF can range from about 35 to 70%, depending on the method of production and thermo-mechanical history.<sup>1</sup> There is a difference in density of crystalline PVDF and amorphous PVDF<sup>2</sup>, as noted below:

Crystalline PVDF = 1.801 to 1.925 g/cc (dependent on if the crystal structure is monoclinic or orthorhombic)

Amorphous PVDF = 1.68 g/cc

The density of pure PVDF used in most commercial applications is typically 1.75 – 1.78 g/cc, which indicates a crystallinity of about 40%.<sup>3</sup>

The common types of crystals present in PVDF are spherulites. Figure 1 is a photomicrograph of a typical spherulite – a polystyrene spherulite taken with an optical microscope using polarized light. The spherulite structure shown in Figure 1 is typical

# Coatings

## Fluoride



of the spherulites observed in PVDF and shows the typical maltese cross pattern (i.e., a cross having four equal arms resembling arrowheads joined at the center points). Spherulites form by nucleation at different points in the polymer, and grow as spherical entities. The growth of the spherulites stops when they impinge on adjacent spherulites. Spherulite radii are of the order of one to several hundred microns.<sup>4</sup>

### Why Crystallinity is Important to PVDF-Based Coatings

The degree of crystallinity, and the size of the crystallites, can have a significant effect on the properties of coatings based on PVDF, as discussed below.

#### Effects of Quenching versus Air Cooling on Crystallite Growth

When coatings based on PVDF are coated on a coil-coating line, they are quenched in water after exiting the bake oven. The quenching is done to cool the painted surface prior to recoiling to prevent sticking of the coated surface to adjacent laps of the coil. The rapid cooling from the quenching prevents the growth of crystallites. However, this quenched state is thermodynamically unstable, and the crystals will have a tendency to grow larger over time to achieve their

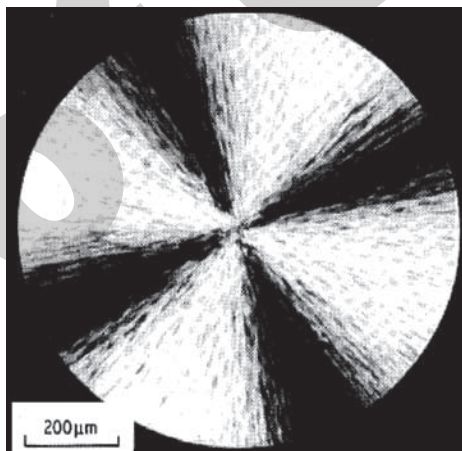
more thermodynamically preferred, natural state. In this quenched state, the coating has excellent flexibility, excellent surface smoothness and uniformity, high gloss, and overall outstanding properties. However, as the coating ages, crystallites will grow larger, which may have an adverse effect on the coating properties.

A classic example of this is the loss of coating flexibility that may occur if a coated coil is stored in a hot environment (e.g., a warehouse in a hot climate) for several months. In this case, the coating may craze at bends during the fabrication (e.g., roll-forming) into its final shape, such as a building panel. Also, the gloss and appearance

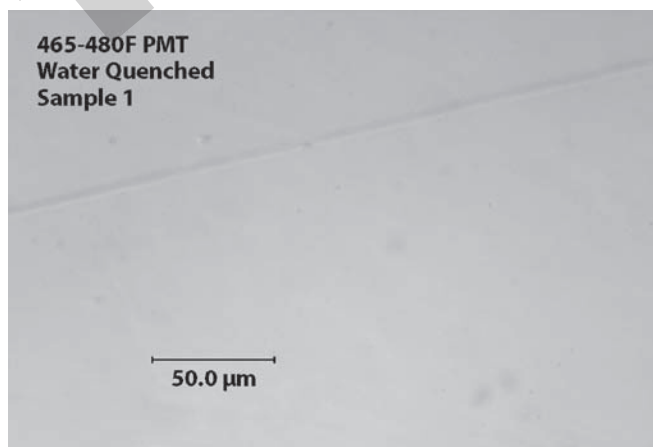
of the coating may be compromised. It must be stressed, however, that the deterioration of coating properties described in this example only occurs under circumstances of extreme aging of the coated coil.

When coatings based on PVDF are sprayed onto an extrusion or curtain wall, they are air cooled, not quenched. This slow cooling allows the crystallites to form in a thermodynamically preferred, natural manner. Therefore, the crystallites will change very little upon aging. However, the crystallites will grow larger if the coating is exposed to extreme temperatures (over about 200 °F) for long periods of time.

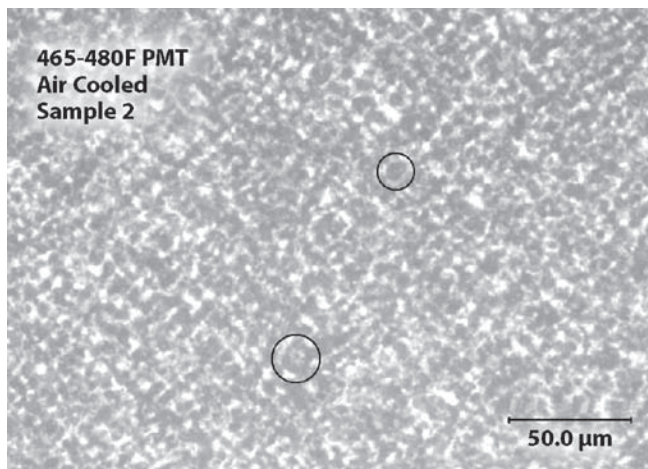
**FIGURE 1** | A single spherulite observed in polystyrene (optical micrograph taken in polarized light).<sup>5</sup>

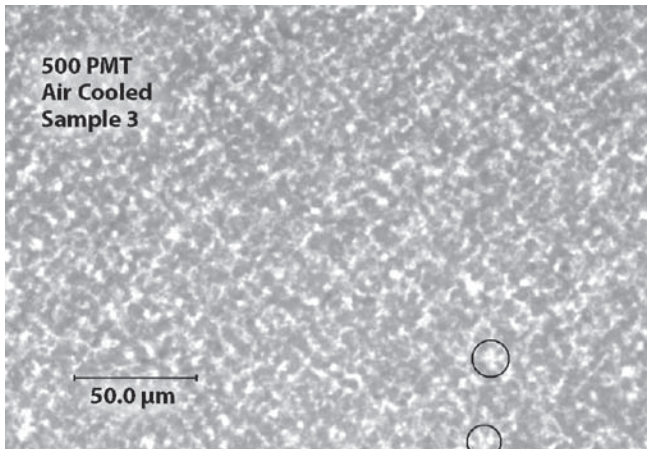


**FIGURE 2** | Film baked at the normal PVDF PMT of 465-480 °F and then quenched with water.



**FIGURE 3** | Film baked at 465-480 °F and air cooled after baking.



**FIGURE 4** | Film baked at a higher PMT (500 °F) and air cooled.**TABLE 1** | Coatings tests.

| Test                       | Air Cooled                        | Quenched                      |
|----------------------------|-----------------------------------|-------------------------------|
| Gloss <sup>1</sup>         | 51.6 (std dev = 0.5)              | 54.4 (std dev = 0.4)          |
| Flexibility <sup>2</sup>   | 0 T – no pickoff (slight crazing) | 0 T – no pickoff (no crazing) |
| Hardness <sup>3</sup>      | 78.1 (std dev = 4.0)              | 65.6 (std dev = 1.1)          |
| Sand Abrasion <sup>4</sup> | Pass (40 liters/mil)              | Pass (40 liters/mil)          |

Notes: 1. ASTM D 523 (60°) – average of 3 panels

2. NCCA 4.2.8

3. ASTM D 2240 – Shore Durometer A – average of 5 panels

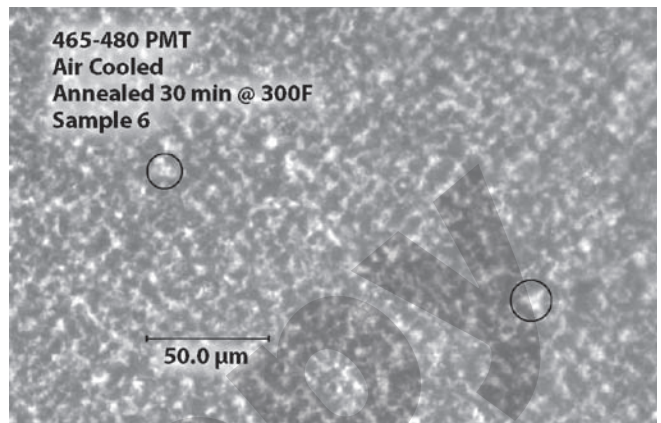
4. ASTM D 968

**TABLE 2** | Percent crystallinity.

| Sample # | Thermal Input                                | Percent Crystallinity (Measured by WAXD) |
|----------|----------------------------------------------|------------------------------------------|
| 1        | 465 – 480 °F PMT – quenched                  | 18.2                                     |
| 2        | 465 – 480 °F PMT – air cooled                | 23.1                                     |
| 3        | 500 °F PMT – air cooled                      | 21.0                                     |
| 6        | 465 – 480 °F PMT – annealed 30 min. @ 300 °F | 25.0                                     |
| 11       | 600 °F PMT – air cool                        | 28.8                                     |
| 12       | 600 °F PMT – cooled in oven for ~1 hour      | 31.4                                     |

Figures 2 – 5 show photomicrographs of quenched and air-cooled HYLAR 5000 films. The films were produced by applying a HYLAR 5000 clear coat (70 wt% PVDF/30 wt% acrylic) onto a polished metal plate by drawdown bar. The coatings were baked to achieve the desired peak metal temperature (PMT), and then either quenched in water, or allowed to cool in air or in an oven. The films were then peeled from the metal plate, resulting in a thin (~25 micron) film to analyze. Photomicrographs of the films were taken at 400X magnification using an optical microscope under polarized light.

Figure 2 shows the film that was baked at the normal PVDF PMT of 465-480 °F, and then quenched in water. There is no visual evidence of crystallites in the photomicrograph; it is featureless. The line that runs approximately 30°

**FIGURE 5** | Film baked at 465-480 °F, air cooled after baking, then annealed at 300 °F for 30 minutes.

from the horizontal is a crease in the film. The film was optically clear when observed with the naked eye. Wide angle x-ray diffraction (WAXD) analysis showed that this film is 18.2% crystalline. However, the crystallites are smaller than the wavelength of visible light (400-760 nm) and do not diffract light, resulting in clarity of the film.

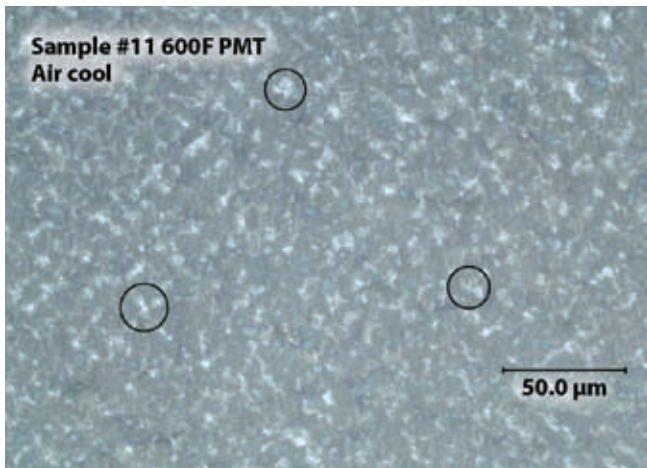
Figure 3 shows a film that was baked at the same PMT (465-480 °F) as the quenched film, but was air-cooled after baking. This micrograph shows a significant amount of crystallites, which are the white areas. The two circled areas in Figure 3 are highlighted because they are starting to show the maltese structure characteristic of spherulites. This film had a hazy, milky appearance when observed with the naked eye. The haziness is evidence of crystallites, which diffract light transmission through the film.

Figure 4 shows a film that was baked at a higher PMT (500 °F) than the previous two samples, and air cooled. The crystallites are more defined than in previous micrographs, particularly those that are circled. This film also had a hazy, milky appearance when observed with the naked eye.

Figure 5 shows a film that was baked at 465-480 °F PMT, air cooled after baking, then annealed at 300 °F for 30 minutes. This micrograph shows the most defined maltese spherulitic structure, particularly the one circled in the left side of the photo. As with Figures 3 and 4, this film also had a hazy, milky appearance when observed with the naked eye.

In addition to the experiments discussed above, PVDF films were prepared using extreme thermal conditions. Specific conditions were: (a) 600 °F PMT and air cooled (Figure 6); and (b) 600 °F PMT, but cooled in an oven for about 60 minutes (i.e., the heat was turned off in the oven, and the film was allowed to cool in the oven until it reached room temperature) (Figure 7). Figure 6 shows crystallites, but they are similar in size to those films that were baked at the normal bake temperature of 465-480 °F. However, Figure 7 shows very large crystallites (~50–75 microns diameter), which demonstrates that extended time at elevated temperature is more conducive to crystal growth than the bake peak metal temperature.

**FIGURE 6** | Film baked at 600 °F and air cooled.

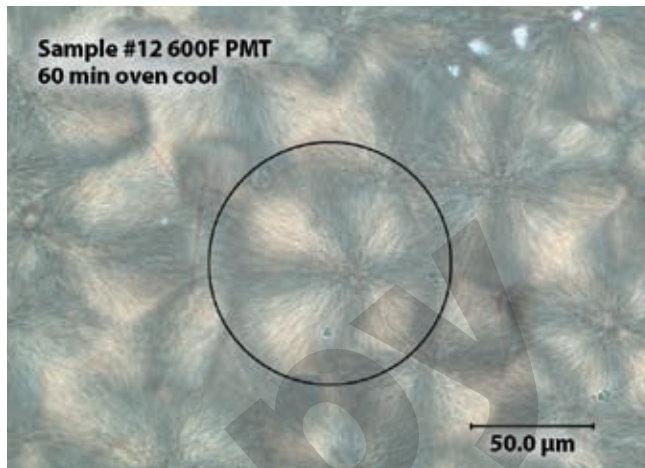


The photomicrographs in Figures 2-7 clearly show the effects of quenching versus air cooling on crystallite growth, and that higher thermal processing (particularly extended time at elevated temperature) increases spherulite size.

#### *Crystallinity and Coating Properties*

Several coating properties are affected by the crystallinity.

**FIGURE 7** | Film baked at 600 °F and cooled in an oven for 60 minutes.



For example, the difference in density between the PVDF crystalline and amorphous phases causes internal stresses in the coating. These factors can affect the overall surface appearance of the coating, and may lead to crazing of the coating, lower coating toughness, breaking of the interfacial bonds between the PVDF topcoat and primer, and reduction of gloss.

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To illustrate this phenomenon, a white PVDF-based coating was prepared, applied to aluminum panels, and then baked at the normal peak metal temperature of 465-480 °F. Panels were either quenched in water or air cooled. Test results are shown in Table 1; the air-cooled samples had lower gloss, more coating crazing and higher hardness than the quenched panels. These results are consistent with expectations of a coating with large crystals (air-cooled sample) compared to extremely small crystals (quenched sample).

In cases of extremely large crystallites, although an uncommon occurrence, the crystallites can affect the surface appearance of the coating (i.e., a rough, non-uniform surface that can lower gloss and be unsightly).

A PVDF film with extremely small crystals will be optically clear. A PVDF film with large crystals will have a hazy, milky appearance. This is an important issue for clear coats, which are often applied over PVDF color coats to provide additional protection and enhanced aesthetics.

### Crystallinity Measurements

The percent crystallinity of the described samples was measured using WAXD. The results (Table 2) show that the percent crystallinity generally increased with higher thermal input. Crystallinity of the 465-480 °F PMT/quenched sample was 18.2%. This result confirms that the quenched sample has a significant level of crystallinity, even though the crystallites are not visible at 400X and the film is optically clear. Crystallinity of the highest thermal energy input sample (600 °F PMT/cooled in oven for ~one hour) was 31.4%. These results also confirm that the crystals grow as the amount of thermal input to the film increases (i.e., higher bake temperature and/or extended time at elevated temperature).

These percent crystallinity values are lower than the estimated 40% crystallinity of pure PVDF, as discussed previously, because the films

used for the WAXD analyses were 70 wt% PVDF/30 wt% acrylic.

### Conclusions

Polyvinylidene fluoride (PVDF) is a thermoplastic, semi-crystalline polymer. Therefore, the properties of coatings based on PVDF, such as HYLAR

5000, are affected by the degree of crystallinity and crystal size. If PVDF-based coatings are quenched after baking, such as when the coating is applied on a coil coating line, the crystallinity is suppressed to the degree that the crystallites are so small they are not visible at 400X, and are smaller than

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the wavelength of visible light (400 – 760 nm). This state of suppressed crystallinity is meta-stable, and the crystallites will become larger when aged at elevated temperatures and/or extended lengths of time. If PVDF-based coatings are air cooled after baking, such as coatings sprayed onto

extrusions or curtain walls, then large crystallites are prevalent.

The thermal history (i.e., bake temperature, and particularly extended time at elevated temperature) of coatings based on PVDF also affects crystal size. The levels of crystallinity, and crystal size, have an effect on final

coating properties such as: flexibility, hardness, impact resistance, gloss, adhesion, clarity of clear coats and the overall appearance of the coating. The degree of crystallinity and crystal size of coatings based on semi-crystalline polymers such as PVDF can be controlled by controlling the thermal history of the coating, and the cooling rate after baking. ■

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