SVC Topics

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PVD Processes: Polymers As Substrate Materials

Most polymers encountered in PVD processing are based on hydrogen and carbon (carbon-based). Other polymers can be silicon-based, boron-based or other. The polymers can be in the form of very thin sheets (webs); thicker material, such as blowmolded containers; or very thick forms, such as molded structural parts. They can also be in the form of coatings applied to other surfaces, such as the basecoats used in the decorative coating industry.

A polymer is a large molecule built up by the repetition of small, simple chemical units called repeat units. The repeat units come from the reaction of monomer species with each other. The monomer of polyethylene (PE), for example, is ($CH_2=CH_2$) and the repeat unit in the polyethylene polymer is ($—CH_2CH_2—$). In some cases, the repetition is in separate linear chains, while in others the chains are branched and interlocked to form a three-dimensional network.

Table 1 shows some of the repeat units commonly encountered in materials used in PVD processing. The hexagonal structures are benzene rings. Table 2 gives some typical bond lengths and dissociation energies. Generally, the main chain ("backbone") of the polymer contains only carbon and hydrogen, while other atoms, such as O, Cl, N and sometimes metals, are contained in side-groups. In some cases, the hydrogen can be partially or totally replaced by chlorine, or by fluorine, such as in polytetrafluoroethylene (PTFE) ($—CF_2CF_2—$).

The presence of oxygen in the polymer has an important bearing on the adhesion of PVD films to polymers. If the polymer contains oxygen, the oxygen can bond to oxygen-active film materials, such as aluminum,

Table 1
Repeat Units for Some Commercial Polymers

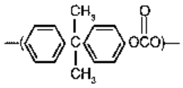
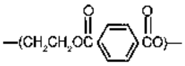
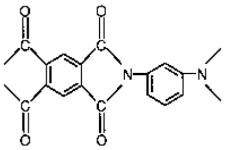
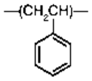
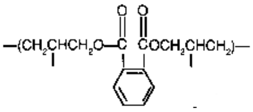
Polypropylene (PP) →	$—(CH_2\underset{CH_3}{\underset{\mid}{CH}})—$	**Polychloroprene (neoprene)** →	$—(CH_2\underset{Cl}{\underset{\mid}{C}}=CHCH_2)—$
High-density polyethylene (PE) →	$—(CH_2CH_2)—$	**Polytetrafluoroethylene (PTFE)** →	$—(CF_2CF_2)—$
Silicone →	$—(\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{Si}}}}—O)—$	**Polymethyl methacrylate (PMMA)** →	$—(CH_2\overset{CH_3}{\overset{\mid}{\underset{O=COCH_3}{\underset{\mid}{C}}}})—$
Polycarbonate →		**Poly(ethylene terephthalate) (PET)** →	
Polyvinyl chloride (PVC) →	$—(CH_2\underset{Cl}{\underset{\mid}{CH}})—$	**Polyamide (Nylon 12)** →	$—[(CH_2)_{11}\overset{O}{\overset{\|}{C}}—\overset{H}{\overset{\mid}{N}}]—$
Polyimide →		**Polystyrene** →	
		Diallyl phthalate →	

Table 2
Typical Bond Lengths
& Dissociation Energies in Polymers*

Bond	Bond length (Å)	Dissociation energy (kcal/mole)
C–C	1.54	83
C=C	1.34	146
C–H	1.10	99
C–N	1.47	73
C–O	1.46	86
C=O (carbonyl group)	1.21	179
C–F	1.32	123
C–Cl	1.77	81
N–H	1.01	93
O–H (hydroxyl group)	0.96	111
O–O	1.32	35

chromium and titanium. If the oxygen is not present in the polymer structure, oxygen, in the form of carbonyl (C=O) groups, may be "grafted" to the polymer surface by flame, corona or oxygen-plasma treatments prior to film deposition. Excessive reaction of the surface with oxygen can result in weakening the polymer surface before the film is deposited, giving poor film adhesion. Nitrogen can also be grafted onto the polymer surface to form an amide or imide group.

Polymerization generally occurs by one of two mechanisms. Condensation (or step reaction) polymerization occurs when one unit at a time is added to the chain, often with the elimination of a small molecule (usually water). This makes the repeating unit lack some atoms present in the monomer. Examples of condensation polymers are polyesters, polyamide, polysiloxane and polyimides.

Addition (or chain) polymerizaton is promoted by active centers, such as cations, anions and free radicals, and the reaction is initiated by some factor, such as ultraviolet radiation. One initiation event can lead to the polymerization of thousands of monomer molecules. The repeat units contain all the atoms of the monomer. Examples of the addition polymers are polyethylene, polypropylene, polyvinyl chloride, polytetrafluoroethylene and polymethyl methacrylate.

In plasma polymerization, the monomer is injected into a plasma where it is "activated" by dissociation and bond scission. This allows reaction between the molecules, which can take place in the gas phase or on a surface. Depending on the plasma conditions, plasma polymerization can result in a polymeric material in which the original monomer is recognizable or not recognizable. The plasma-polymerized materials may have properties significantly different from a polymer formed by other means from the same monomer. A polymer formed by plasma polymerization of a polysiloxane, for example, can either be hydrophobic or hydrophilic, depending on the plasma conditions. The newly deposited plasma-deposited polymer may have a significant number of unsatisfied bonds, which makes the surface very reactive. Other gases and vapors, such as oxygen, can be mixed with the monomer to change the composition of the deposited plasma.

Often during fabrication of a polymeric material, the molecules attain some degree of preferential orientation. In sheets and films, the orientation is obtained by stressing the film, and the orientation is in the plane of the material. The orientation can be in one direction (uniaxial orientation), such as in oriented polypropylene (OPP) web material, or in several directions, such as biaxially oriented polypropylene (BOPP) web material.

Plasticizers are low-molecular-weight polymers that are added to polymers to increase their fluidity during processing, to increase the flexibility of the formed part (then called flexibilizers) or change other properties. The plasticizer may constitute up to 40 percent of the polymer material. The plasticizer can continually exude to the surface of the polymer, where it can remain as a fluid-like surface contaminant or volatilize, particularly if heated.

Stabilizers are added to polymers to increase their resistance to degradation by ultraviolet radiation or heat. Carbon black is one of the best UV stabilizers. Lead, cadmium and tin compounds are used as thermal

Table 3
Some Polymers & Their Applications

Polymer	Application
Polyethylene	High-density (HD-PE), molded structures, piping Low-density (LD-PE), packaging film, waterproof sheeting, extruded coatings
Polypropylene (PP)	Packaging film, fibers
Polychloroprene (neoprene)	Elastomer seals, encapsulation
Polystyrene	Molded & thermoformed structures, used in co-polymers
Polyvinyl chloride, unplasticized (uPVC)	Rigid tubing, molded structures, blow-molded containers, thermoforming sheets
Polyvinyl chloride, plasticized (PVC)	Packaging film, flexible tubing, cloth-like applications, inflatable goods
Polytetrafluoroethylene (PTFE)	Chemical-resistant structures, low-friction surfaces
Polymethyl methacrylate (PMMA)	Windows, molded lenses
Polycarbonate	Impact-resistant windows, optical lenses, molded structures, compact discs
Polyethylene terephthalate (PET)	Packaging films, base for recording tape, blow-molded containers
Diallyl phthalate	Molded precision structures, such as housings & gears
Polyamides	Molded structures, fibers, packaging films
Polyimides	High-temperature encapsulation, electrical insulation
Silicones	Elastomers, encapsulation, medical tubulation

stabilizers in polyvinyl chloride. Other materials, such as fibers or fillers, can also be added to the polymer. Typically, these additives do not migrate in the polymer.

Lubricants, such as waxes or oil, may be added to the polymer to reduce friction of the surfaces. These lubricants continually exude to the surface, presenting problems in metallizing these materials. Ionic materials may be present on the surface of polymers as antistatic agents to prevent electrical (static) charge buildup. These materials may be coated on the surface of the finished product or may be incorporated into the bulk polymer and continually exuded to the surface. At the surface, they combine with moisture to form an electrically conducting electrolyte. This material may present a problem in metallization—particularly if chloride ions are present—because it can cause corrosion.

Water and solvents may be incorporated into the polymer, either as a leftover from the polymerization process or from absorption from the environment. For example, Kapton™ polyimide (condensation polymer) can have two percent or more water in its structure from the processing, and Nylon™ polyamide can absorb up to 10 percent water from the ambient. Water in the polymer can outgas during vacuum processing and can cause interfacial corrosion after a metallization film has been deposited on the surface.

In some cases, several polymer materials may be mixed to form copolymers. The resulting material may have a random structure or may have a periodic structure (block or graft copolymers), which has large regions of one material or the other. Many commercial polymeric materials are copolymers. Examples are butadiene/styrene copolymer rubber for tires and styrene/acrylonitrile copolymers for impact-resistant molded parts.

Polymer web materials can be obtained as a “metallization-grade” material. This material does not exude low-molecular-weight polymers from the bulk, but it may have appreciable water or solvent content, depending on how it has been stored. The metalization-grade material also has fewer surface features that can cause pinholes or optical blemishes in the deposited thin film.

Metallization of polymers that contain low-molecular-weight species that can exude to the surface, may require the surface to be sealed with a basecoat polymer material. This material forms a barrier to prevent diffusion of these species to the surface. Some work has been done in flow-coating and electron-beam curing of the very thin polymer basecoats on web materials in a vacuum system to decrease the number of surface blemishes. P&SF

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* Fred W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd ed., Wiley-Interscience (1971).