UV Energy Cure for Formable Hard-Coated Polymeric Film & Sheet

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Modern day manufacturer’s, OEM’s and ODM’s have a wide range of substrate Materials to choose from – ceramics, glass, metals, plants, plastics, wood and/or combinations there-of. Linked to the scope of Materials chosen are the Methods and Apparatus chosen to achieve a desire product, component and/or sub-component outcomes.

Each material chosen and/or combination of materials thereof, have features and benefits, advantages and/or limitations specific to the exact combination of Materials, Methods and Apparatus chosen to achieve a specification and/or desired outcome – cosmetic, functional, physical and/or processing properties.

Additional consideration is undertaken as to cost of goods, lead times, logistics, regulatory issues, processing limitations, sourcing, sustainability, time-to-market, volume capabilities and/or capacities for the outcomes desired.

Plastics, in general, have the unique ability to be cast, extruded, formed and/or molded into 2 or 3-dimensional objects with a broad choice as to cosmetics, features, performance and/or physical characteristics via specific combinations of Materials, Methods and Apparatus.

Natural rubber is the earliest recorded volume use of plastics – as demand for water-proofing woven cotton fibers and finished garments in the late 18th century. Vulcanizing or cross-linking of rubber by adding sulfur or other compounds by Thomas Hancock in Great Britain and Charles Goodyear in the USA both in 1844, launched new industries based on rubber plastics objects being cast, extruded, formed or molded as 2 and 3-dimensional physical objects.

Celluloid class compounds, introduced in the late 19th century, were very first successful plastic incorporated into consumer and industrial products.

In the early 20th century, chemist Leo Hendrik Baekeland combined phenol and formaldehyde – which were available at depressed prices due to lack of demand, under heat and pressure combined into a dense synthetic polymer – Bakelite, which is still widely use to this day, found in all commercial aircraft, motor vehicles and nearly all electric motors.

As a boy, the presenter had Lionel® “O Gauge” electric train sets and Lionel® ZW transformer cases were made from molded Bakelite.

Coco Chanel had a highly successful line of Bakelite jewelry products in the mid-1920’s.

Bakelite is found in fabulous but exceedingly rare Art Deco design jewelry of the early to mid-20th century. Should an attendee be fortunate enough to inherit or own original Bakelite Art Deco pieces of this time period – their values may far exceed their weights in gold or platinum.

Prior to World War II, cellophane, cellulose acetate butyrate, nylon, polychloroprene – Neoprene™, polyethylene, polystyrene, polyethylene terephthalate, Polytetrafluoroethylene – Teflon™ and vinyl all
were invented, commercially manufactured and broadcast into the industrial and consumer products retail marketplace.

The Post-World War II period found the first photo polymer UV and EB+ photon excitation chemistry work, as well as the inventions and successful commercialization of polypropylene, polycarbonates, foamed polystyrene – Styrofoam™ and aromatic polyamide material, via method and apparatus as a fabric into Kevlar™.

Within the last several decades, polyester film stock replaced cellulose acetate for photographic films, reel-to-reel computer storage, video and audio tape recording.

Bayer AG introduced Peek – polyether ether ketone, PPS – polyphenylene sulfide and PES - polyester sulphone, while GE Plastics (now SABIC) brought to market PEI™ – polyetherimide, BASF introduced polyacetylene while ICI introduced Biopol – the first biodegradable plastic produced on a commercial scale based on polyhydroxybutyrate or PHB.

Polymer Materials may be fabricated in 2 or 3-dimensional shapes by one or more of the following scope Methods and Apparatus, as in Table 1:

<table>
<thead>
<tr>
<th>Method</th>
<th>Apparatus</th>
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<tbody>
<tr>
<td>Blow molding</td>
<td>In-mold decoration</td>
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<tr>
<td>Cast</td>
<td>In-mold labeling</td>
</tr>
<tr>
<td>Clad</td>
<td>Insert molding</td>
</tr>
<tr>
<td>Co-extrusion</td>
<td>Lamination</td>
</tr>
<tr>
<td>Extrusion</td>
<td>Over-molding</td>
</tr>
<tr>
<td>Foam molding</td>
<td>Rotational molding</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Twin-shot molding</td>
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</tbody>
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Table 1.

Extruded plastics, of Method and Apparatus where one or a plurality of plastic Materials are melted and formed in a continuous profile through various forms of shaping dies. Once cooled below a plastic’s glass transition temperature – Tg, outcome yields a continuous 2- or 3-dimensional profile shape, creating entirely new scope of use outcome for plastics.

Plastic’s co-extrusion and extrusion various Methods & Apparatus are characterized by:

- Blown film – very thin polymer film for packaging or continuous web sheet outcome
- Coating – where a secondary heated resin is applied via pressure rollers onto moving extruded web outcome
- Co-extrusion – where a plurality of extruders feed a single die to create a multiple layer outcome
- Compound extrusion – where a plurality of polymers and/or additives produce a homogenous outcome
- Extrusion coating – where a thin polymer layer is added upon film, foil and/or paper web outcome
- Film extrusion – where polymer is a continuous 2-dimension extrusion of less than 0.030” (0.76 mm) thickness but greater thickness than that of blown film outcome
- Extrusion lamination – where hot extruded polymer resin acts as the bonding medium to a second web – sans adhesive-use outcome
- Sheet extrusion - where polymer is a continuous 2-dimensional extrusion greater than or equal to 0.030” (0.76 mm) thickness and a curved outcome
- Tubing extrusion – where Method and Apparatus allow for a continuous portal in the drawn direction outcome

Polymer film/sheet substrate Materials most commonly available are listed in Table 2:

<table>
<thead>
<tr>
<th>Material</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>ABS</td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td></td>
</tr>
<tr>
<td>Acrylic/PMMA</td>
<td></td>
</tr>
<tr>
<td>Blends</td>
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<tr>
<td>Cellulose acetate butyrate</td>
<td></td>
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<tr>
<td>Impact Modified Acrylic / PMMA*</td>
<td></td>
</tr>
<tr>
<td>PETG *</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate *</td>
<td></td>
</tr>
<tr>
<td>Polyester (Co-polyester) *</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl Chloride</td>
<td></td>
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<tr>
<td>Styrene</td>
<td></td>
</tr>
<tr>
<td>Vinyl</td>
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</tbody>
</table>

* - Preferred Scopes of Use

Table 2

Plastic that is cast, co-extruded and/or extruded as a polymer film/sheet Material may be manufactured by a variety of options for end use desired specifications and/or scope of use intention outcomes, such as:

- Clear
- Laminate
- Opaque
  - Pigmented / colorants
  - Effect pigments
- Translucent
- Transparent

In addition, cast, co-extruded and/or extruded polymer film/sheet chromatic and/or indicia Methods may be of:

- Conformal coating
- Embossing
- Lamination
- Physical Vapor Deposition - PVD
- Plating-on-Plastics - POP
- Printing
- Resin-based

In addition, cast, co-extruded and/or extruded polymer film/sheet Methods and Apparatus for various fabrication final geometries may be of:

- Flat – 2-dimensional
- Bendable – 3-dimensional simple
- Formable – 3-dimensional complex and/or deep draw
• Moldable – 3-dimensional complex

While polymer Materials may be fabricated by a plurality of Methods as in Table 1, fillers and/or additives may be added cosmetic and/or functional scope properties to enhance abrasion, chemical, hardness, scratch and/or mar resistance of 2- and/or 3-dimensional fabricated plastic outcomes. Fillers and/or additives such as but not limited to carbon (graphite) glass and/or talc of conventional and/or nano scopes may enhance functional and/or physical properties of a validation coupon, and generally have broad range negative effects of cosmetic and/or processing parameter outcomes when combination of Material, Method and Apparatus is taken into consideration – induced stress, tensile and/or compressive, resulting in compromising polymer component’s integrity resulting in polymer warping and/or fracture from any number of secondary processes – inserts, applied cosmetic and or functional coatings and/or adhesives of solvent and/or co-solvent’s relief or annealing of internal, surface or combined process and/or fabrication induced stresses. One size does not fit all.

Polymer film/sheet with or without 2nd surface applied chromatics and/or indicia require of the 1st witnessable surface, generally required an additional element of chemical, cosmetic and/or physical protection – especially in hostile scope of use environments.

Where the component, sub-component and or product scope is of a 2-dimensional flat and/or 3-dimensional simple bendable outcome geometry, 1st surface addition of conventional hard faced material coatings may generally be employed – conformal industrial coatings, lamination, physical vapor deposition – PVD and/or Plating on Plastics – POP, not with-standing possibilities of induced stress relief resulting in warping, curling and/ or fracture.

Scope of use for formable 3-dimensional complex and/or deep draw polymer film/sheet processing where 1st surfaces still require abrasion, chemical, scratch and/or mar resistance, traditional applied hard face coating technologies are wholly unsuitable for any 3-dimensional geometries as the applied coatings lack the ability to elongate and result catastrophic failure due to cracking, separation and/or delamination.

Of Materials, Methods & Apparatus for UV / EB+ remedy:

• Aqueous ¯ - dry
• Aqueous /alcohol ¯ - dry
• Solvent ¯ - dry
• 100% solids – UV Cure

*- mixed dry/cure systems available

Use of aqueous-base materials possible remedy generally will be unsuitable. Vinyl and or vinyl-acrylic combination monomers while being cross-linkable and/or have properties of elongation, vinyl lacks the physical and functional protection parameters, while acrylic will crack and fracture under load. An impact modified acrylic could have desirable possibilities. More importantly, water molecules trapped within the coating will not have a means of escaping from UV dense cross linking. While a water-bake off can be done over time, just like with polycarbonate and PC or PMMA, but UV cross-linking will hinder this mechanism and upon reaching 100C (212F) – trapped water molecules will violently turn into steam and attempt to escape - destroying the coating during entrapment release mechanism.
Use of aqueous/alcohol-base materials will essentially have the same outcome as aqueous-base materials with the added issue of the high likelihood of co-solvent attack or stress annealing of the plastic. Warping and/or curling is almost a guaranteed certainty – resulting in components and or sub-components turning into “potato chip” geometries and dimensional stability becomes impossible.

Use of solvent-base materials with near absolute certainty, will result in stress anneal fracture at worst and enormous dimensional instability at best – a “potato chip” on steroids and should not be considered for this scope.

100% solids materials under UV Energy Cure have none of the limitations inherent to aqueous, aqueous/alcohol or solvent-based Materials of this scope of use. The matter at hand is what UV Energy Cure formulations generally are most suitable.

UV Energy Cure of UV-B and UV-C wavelengths have sufficient excitation energy to be employed by all three major UV polymer cross-linking technologies:

- Anionic
- Cationic
- Free radical

Electron Beam or EB+ Energy Cure is of beta radiation – β, very high kinetic energy electrons, generated, accelerated and target focused via induction mechanisms to cross-link polymers. EB+ is also common of hospital, medical and/or pharmaceutical environs for the scope of pathogen sterilization due to the high kinetic energy, but is not addressed within this presentation scope.

Cross-linking polymerization should not be confused with chain polymerization, where polymerization is of monomer additions at the end(s) of growing polymer chains. Note that UV Energy Cure may also engage chain polymerization in conjunction with polymer cross-linking.

Anionic polymerization was engaged by the author as an organic chemistry PhD candidate using strong and highly unstable lithium metal ligand groups rather than conventional electron transfer mechanisms. It may be considered a living (on-going) polymerization process, continuing until impurities, increased viscosity, monomer concentrations and/or polymer cross-linking density essentially terminate the reaction mechanisms.

The author has not found sufficient anionic polymers specific to engage this scope on a practical or commercial basis in prior research, albeit this may have improved. Clearly, as a living polymerization process, bears possible merit for hard-face coating of polymer film/sheet. The one drawback of note is in the use of highly unstable metal ligand groups.

Cationic polymerization involves cycloaliphatic epoxies and/or a plurality of other cationic monomers, cross-linking through the mechanism of a weak Lewis acid generated by photo initiators and is also considered a living polymerization mechanism. Research has shown that both C=C carbene and C=O carbonyl groups are crucial of this scope.
The author has discovered formulations of cycloaliphatic epoxies and/or a plurality of other cationic monomer Materials under proper Methods and Apparatus that fulfill the required elements of this scope.

EB+ or electron beam may be engaged to decompose photo initiators in generating weak Lewis acids but the author has not yet explored this avenue for cationic polymerization.

Free radical polymerization involves generation of free radicals - C, through photo initiators reacting with carbon alkene double bond C=C monomers to polymerize. Unlike anionic and cationic polymerization, free radicals can only generated by photon excitation and immediately cease once the UV excitation energy source terminates. Of this fact, free radical polymerization is wholly unsuitable for the scope and would not be recommended.

EB+ or electron beam may also be employed in opening C=C bonds without photo initiators.

Research promulgates mixed systems combining free-radical and cationic polymerization but as yet are not yet validated by the author specific to this scope.

In conclusion, of anionic and/or cationic polymerization using UV Energy Cure, both cross-linking technologies have the ability to produce a hard formable chemical resistant surface upon formable polymers – with cationic polymerization being the preferred embodiment for the scope of this article for volume production operations and scope of use. Free radical polymerization is unable to fulfill this scope of use and is not recommended.