Surface Functionalization of Polymer Films

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ABSTRACT

The surface of polymer films is often functionalized to facilitate additional operations that range from printing and laminating to vacuum metallizing. Surface modification can be implemented by various processes such as surface treatment, polymer coatings and co-extruded "polymer skins". This paper reviews state of the art functionalization methods that include flame and plasma treatment, polymer coatings applied in ambient pressure by conventional coating techniques and radiation cured polymer coatings deposited in a vacuum environment. The modified surface characteristics address a variety of application specific properties that include wet-ability, adhesion, release, seal-ability, printability, gas and moisture barrier, and optical, electrical, and abrasion resistance. The feasibility of using such operations in wide polymer webs is discussed along with characterization data of modified polymer film surfaces.

PLASMA TREATMENT

Plasma is an ionized form of gas and can be obtained using AC or DC power input and ionizing a gas medium. A plasma, commonly referred to as the fourth state of matter, is an ensemble of randomly moving charged particles with a sufficient particle density to remain, on average, electrically neutral. Plasmas are used in a very diverse range of processing applications ranging from manufacturing integrated circuits used in the microelectronics industry to treating polymer films and for the destruction of toxic waste [1-3]. Plasma processes can be grouped into two classes, low and high density, and are often displayed in an electron temperature versus density phase-space plot. Low-density direct-current and radio-frequency glow discharges are usually nonequilibrium, i.e. the electron and heavy particle (ions, neutral) temperatures are not equal. Low-density plasmas have hot electrons (T_e>10^4 K) with cold ions and neutrals. Energetic electrons collide with and dissociate and ionize low-temperature neutrals, creating highly reactive free radicals and ions. These reactive species enable many chemical processes to occur with low-temperature feed stock and substrates. Low density plasmas are usually associated with low material-throughput processes such as surface modification. In high-density, thermal plasmas such as atmospheric-pressure arcs and torches, electron temperature is equal to heavy particle temperature, and this provides an effective source of concentrated enthalpy which can be used in areas such as melting and vaporization of materials.

Low density (or glow discharge) plasmas are used in a variety of processes such as: surface treatment, physical sputtering, plasma etching, reactive ion etching, sputter deposition, plasma-enhanced chemical vapor deposition, ashing, ion plating, reactive sputter deposition, and a range of ion beam-based techniques, which all rely on the formation and properties of plasmas. The types of plasmas encountered in surface treatment processing techniques and systems are typically formed by partially ionizing a gas at a pressure well below atmosphere. For the most part, these plasmas are weakly ionized, with an ionization fraction of 10^{-5} to 10^{-1}. Electron cyclotron resonance (ECR) plasmas can have higher ionization at high powers [4]. Low density plasmas can be established by AC or DC power input and these systems can have many different type of geometries depending upon the application.

Plasma treatment of polymer films on a moving web removes the contaminants from the surface and functionalizes the polymer surface by introducing functional groups such as: hydroxyl (-OH), carbonyl (-C=O), carboxyl group (-COOH), or amino groups (NH_x). This functionalization leads to better wettability, and improved adhesion or bondability between polymer surfaces and other materials deposited on these surfaces. Numerous researchers have discussed various aspects of plasma treatment of polymer substrates [5-7]. The main parameters for plasma treatment are as follows:

- Input power
- Plasma density
- Pressure
- Gas composition and flow rate
- System geometry

One type* of plasma treater combines hollow cathode and magnets. The hollow cathodes are positioned on one side of the moving web, while the magnets are placed on the other side of the moving web. By doing so, a high intensity plasma is generated in the immediate vicinity of the web to be treated. In this configuration, during the negative part of the cycle, the hollow cathode creates intense plasma zones that are directed towards the film surface. During the positive cycle, the web

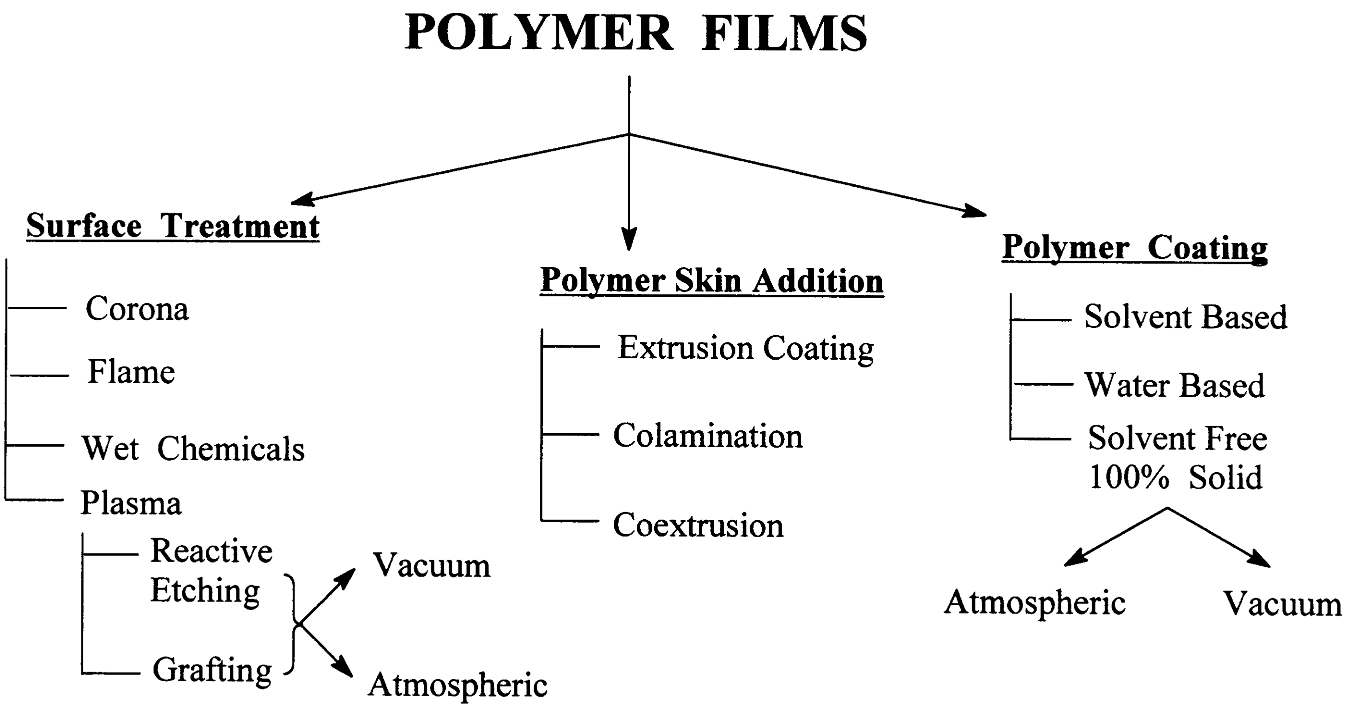

Figure 1. Various types of treatment for polymer films.

becomes part of the sputtering cathode, and in addition to the treatment it is actually sputtered by the bombardment of the reactive and/or with inert positive ions. This configuration provides a superior level of surface treatment.

ATMOSPHERIC PLASMA TREATMENT PROCESS

Sigma Technologies has developed a new atmospheric plasma treatment system (patent pending) for functionalizing polymer films. The newly developed atmospheric plasma treatment (APT) system has unique advantages over the presently used technologies of corona and flame treatment. The APT system allows to create a uniform and homogenous high density plasma at atmospheric pressure and at low temperatures using a broad range of inert and reactive gases and can be used for treating and modifying the surface properties of organic and inorganic materials. APT process treats and functionlizes films in such a manner similar to the vacuum plasma treatment process. Production equipment testing has been successfully performed for the treatment/functionalization of various polymer films including polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), and polyethylene teraphthalate (PET) films on moving webs. The surface energies of the treated films increased substantially (without any backside treatment) thereby enhancing the wettability, printability and the adhesion properties of these films.

ACRYLATE COATINGS

Acrylate coating techniques, including solvent based, water based and solvent free vacuum or atmospheric coatings, have shown a broad range of applications. This versatile and economically viable technology can be used to enhance the properties of a variety of polymer films and to create composite films with new and unique properties. Sigma has developed acrylate based formulations with chromophoric properties to deposit color polymer films in a vacuum environment. High dielectric constant acrylate materials have been molecularly synthesized for capacitor applications. Acrylate formulations with combinations of hydro and oleophilic and phobic properties have been used to coat polymer and fabric webs.

Photonic Coatings

Flash evaporation vacuum deposition technique was applied to a variety of materials which produce molecularly doped, radiation cured, photonic polymer films. Sigma has produced fullerene (C_{60})-based photoconductive polymer composite coatings via a solvent-free, high speed, vacuum flash evaporation and radiation curing techniques. This advanced processing technique led to photoconductive films with less defects and higher performance than those produced by the conventional solvent-based spin coating process. The high control over the film thickness, homogeneity and reproducibility guaranteed the high quality of the produced photonic coatings. A variety of acrylate-based photonic formulations have been designed, produced and processed at Sigma. Different chemistries were used to produce various photo-electric responses. Some of the produced photonic materials showed photocurrent pulses at a very low, or even without, applied field.

These photonic coatings may have great applications in xerographic and photo sensors areas. In addition to the photoconductivity, the cured polymer composite coatings showed the other characteristics common for crosslinked acrylate coatings: High thermal stability, abrasion resistance and flexibility make these photoconductive coatings superior to the existing photoconductive materials.

Hydrophobic/Oleophobic Coatings

A variety of acrylate based formulations with fluorine content ranging between 40 to 65% have been developed. These low refractive index, Teflon-like, fluorinated coatings are required for various applications, such as eye glasses coating. A polyester, PET, film coated with an acrylate based fluorinated formulation showed surface energy less than 26 dynes/cm and contact angle with water of 110 .

Hydrophilic Coatings

A highly functionalized acrylate based formulation was used to coat polytetrafluoroethylene film. About 0.3 micron of the coating was vacuum deposited and electron beam cured. The coated PTFE film showed surface energy of 58-60 dynes/cm and contact angle of 26-24 . For a similar application, functionalized coatings have been developed in order to enhance the adhesion of water-based inks (environmental safer) to polypropylene (OPP) films.

High Dielectric Coatings

High energy density polymer coatings were developed for capacitor applications. Formulated dielectric polymers prepared from commercial monomers show dielectric of $K = 2.2\text{-}6.0$. Molecularly synthesized dielectric monomers have been produced for capacitor applications. Sigma specialty monomers produced polymer of higher dielectric, $K = 10$ to 15.

For integrated fuel systems, perchlorate functionalized radiation curable acrylate-based formulations were prepared and processed via the flash evaporation vacuum deposition technique.

Metal Chelating Membranes

Acrylate-based films functionalized with selective chelating molecules were deposited in vacuum and cured with electron beam. These membranes can be used for separation and recovery of heavy metals such as Pb, Cu, Ca, Ni.

Optical Limiting Coatings

Molecularly doped optical limiting coatings, for eyes and equipment protection from laser and other harmful radiations, were manufactured.

Infra Red Transmitting Coatings

Both clear and colored (blue, grey orang and green) IR transmitting coatings with more than 85% transmission at wave length ranging between 3.3 to 15 microns were prepared in vacuum.

Adhesion Promoters

Acid-base, chelation, sulfide, and silane chemistries were combined in radiation curable acrylate based formulations in order to achieve excellent adhesion to gold, silicon, chromium, stainless steel, aluminum, and plastic substrates. These specialty formulations are processable via both vacuum and atmospheric systems and curable with UV or EB irradiation. These coatings passed the adhesion, crosshatch, ASTM D-3359-83, 3M 610 tape test with less than 1% peeling off.

POLYMER SKIN ADDITION

An alternative method of film functionalization is the direct surface addition of polymers to the film surface, which contain the desired surface chemistry. There are two primary technologies available for use today, polymer coating and the direct addition of polymers as solid or molten layers during the manufacturing process for biaxially orienting films[8]. The primary purpose for the direct addition of polymer surfaces are to increase or decrease the surface free energy of the film(impact wetability), to directly control chemical species on the film surface for metallized film barrier control[9] , to improve bonding in secondary steps(coating , printing, lamination, or metallization), to improve gas and chemical(flavour and aroma) barrier of the film[10] or to add low melting surfaces for sealing. Surfaces which are currently added commercially to polypropylene films today are : Acrylic polymers, polyvinylidene chloride(PVdC), polyvinyl alcohol (PVOH), polyethylene vinyl alcohol (EVOH) , polyethylene vinyl acetate (EVA), high density polyethylene (HDPE), low density polyethylene (LDPE) linear low density polyethylene (LLDPE), polybutylene (PB), polypropylene (PP) ,ethylene propylene copolymers (EP copolymer), ethylene, butylene , propylene terpolymers (EBP terpolymer), polyethylene terephthlate (PET), Nylon, polyurethane (PU) and silicone polymers. Typical product designs are shown in figures 2 through 7.

Polymer Solution Coating

In this process[8] polymers are dissolved or dispersed into liquid carriers and deposited on the film surface and dried. During the drying process the polymers form a continuos polymer layer on the film surface Fig 1 and 2). Not all polymers are suitable for this method of addition due to the availability of solvent systems, polymer emulsions or the ability to form a continuos film on drying. Adhesion and wetting of the polymer can be controlled by prior surface treatment, coextrusion of polymer skins or by priming of the treated surface with another polymer such as polyethyleneimine (PEI) , polyurethane or epoxy based polymers. Polymer coatings are used when the polymer being used is difficult to melt process such as (PVdC) , acrylic polymers or PVOH. In current practice with oriented polypropylene (OPP) the coatings are applied from aqueous solution and dried in hot air ovens. The polymers chosen for coating supply improved machinability, printing, sealability , chemical barrier (flavour and aroma) or oxygen gas barrier or a combination of these functions for modern packaging films. In some instances silicone based polymers are used without solvent and are cured with heat or e-beams to effect chemical crosslinking of the polymer layer. This is done to supply a low surface free energy film for easy release of adhesives in tape or label applications. Because the coating step is a secondary process performed after orientation of the film , it adds an additional processing cost to the film increasing the cost of the product. Because of this few companies add coated surfaces to OPP films and they are value added products valued for the properties which the coating polymers add to the basic film properties.

COLAMINATION

In this process a solid polymer layer is thermally adhered to the underlying polymer film during the manufacturing process[8]. This method of skin addition is seldom used in manufacturing because, many polymers are easily added by extrusion coating or coextrusion. However there are instances when the polymer skin would not survive the normal OPP manufacturing sequence, specifically the hot roll stretching step due to the polymers melting point. In these instances the polymer is contacted with the hot, stretched film before it enters into the second stretching step which occurs in a hot air oven between diverging rail system(tenter frame) [8]. The polymer melts and adheres to the underlying film base as it is stretched in the tenter frame becoming an integral layer of the film product. Typically polymers which melt below 140^0 C and are used as sealents can be added by this method.

EXTRUSION COATING

This process is similar in concept to the colamination process in the addition of low melting or difficult to stretch polymers between the first and second stretching steps of a modern tenter frame orienter. Instead of a solid polymer layer the polymer is first melted in an extruder and is dropped as a molten sheet from a slit die directly on to the moving film web. Typically the molten sheet is pressed against the moving polymer web between a chilled steel roll using a nip roll. This adheres the polymer melt to the base layer and prevents the melting of the base layer. The composite structure then enters the tenter frame where it is reheated and stretched. The polymer surface may remelt in the tenter frame or may be oriented with the base layer of the film. Polymers added by this process are either low melting or strongly adherent to hot metal surfaces, which would prevent their addition by coextrusion. In addition polymers which will under go uniaxial but not biaxial orientation may be used in the orientation process.

COEXTRUSION

This is the most widely used manufacturing method for the direct addition of polymer skin materials in modern film manufacturing[8]. In this process polymers are melted in separate extruders and then combined as molten streams in an extrusion die using feed block and single cavity die or in a multi-manifold die technology. This process allows the direct layering of polymers together and today is used commercially in three, four and five layer film products (Fig 3 to 6). Typically the polymer layers are chosen for their inherent inter-layer adhesion which is usually controlled by copolymerization. For instance homopolymer propylene (PP) is combined with ethylene, propylene copolymers (EP copolymer) and ethylene, butylene , propylene terpolymers (EBP terpolymer) to add low melting surfaces to the PP film. In addition these surfaces may be further improved for subsequent conversion, such as printing, by the various surface treatment methods described above. In some instances the desired polymer surface will not adhere directly to the PP core layer because of the incompatibility between the polymer layers. In this case an intermediate layer with improved compatibility with both core and skin polymers may be selected and layered between them. These polymers are readily available commercially for many polymer combinations and are called tie layers. The tie resins are usually chemically modified homopolymers of PP or polyethylene (PE) with polar groups such as unsaturated anhydrides which yield acid side chains or polymer end groups. These new functional groups interact effectively with the unmodified core layer and the skin resin significantly improving the interfacial adhesion of both polymers. Thus the perform the same function in coextrusion as the primer layer in the coating process described above. Polymers, which are readily coextruded with OPP cores are EP copolymers, EBP terpolymers, HDPE, MDPE, PETG, amorphous Nylon, and EVOH.

CONCLUSIONS

There currently exists many techniques for the effective functionalization of polymer film surfaces. Typical polymer films, such as OPP, must be surface modified in some fashion due to the inherent nature of the polymer surface and the commercial requirements for the manufacture of useful products from polymer films. Typical manufacturing process which are applied to polymer film products, such as printing, laminating, metallizing, bonding to metal, sealing to other polymers or releasing from other polymers all require that the polymer surface take on properties different from the bulk polymer used to manufacture the film. The many approaches presented here are all competing with each other to be the most economical approach to solve any particular applications need. Which approach represents the “best” method will depend upon the polymer film being modified, the needs of the application and the availability of surface modification technology from suppliers to the film producer or converter. In the past the principle modification technologies required large capital expenditures to layer new polymers onto the existing single layer films then available. Today many new approaches are possible due to the increased complexity of available film substrates, new film modification technologies and due to a more complete understanding of the surface chemical requirements of specific applications. With this enhanced product and process understanding, it is now possible to combine techniques to modify base film surfaces with inexpensive polymers to substitute for more expensive alternative polymer surfaces, to apply extremely thin polymer layers and to combine several process steps into a single manufacturing process. This should allow for a bright future for polymer films which due to modern surface functionalization technologies can continue to expand into new application areas.

Figure 2. Typical Acrylic Coated OPP Product Design

Sealable Acrylic coating layer
Bonding Layer

Homopolymer Core

Bonding Layer

Sealable Acrylic coating layer

Figure 3. Typical PVdC/Acrylic Coated OPP Product Design

Sealable PVdC coating layer
Bonding Layer

Homopolymer Core

Bonding Layer

Sealable Acrylic coating layer

Figure 4. Typical sealable OPP Product Design

functional polymer surface

Homopolymer PP Core

EBP-Terpolymer sealant

Figure 5. Typical Broad Seal Range (BSR) Coextruded OPP Product Design

Treated EBP-Terpolymer sealant surface

Homopolymer PP Core

EBP-Terpolymer sealant

Figure 6. US Patent 5,153,074 Type Metallized OPP Product Design

Aluminium layer
HDPE[11] ,Nylon, APET, EVOH[12] Metallizable surface

Tie layer

Homopolymer Core

Terpolymer sealant

Figure 7. Coated/Metallized OPP Product Design

Aluminium layer
Treated EP-Copolymer surface[13]

Homopolymer PP Core

Bonding Layer
Sealable Acrylic Coating

NOTE

* Sigma Technologies International patented design.

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