JOINING OF MEDICAL PLASTICS USING ATMOSPHERIC DISCHARGE PRETREATMENTS OF ADHERENTS PRIOR TO ADHESIVE BONDING

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Abstract

Joining of medical plastics for devices are becoming more complex and more sophisticated, both in performance specifications and structural complexity. Whether used in the form of instrumentation or surgical tools, for diagnostic monitoring or therapeutic purposes, medical devices typically consist of components and materials that must be joined in some way. Joining processes, such as adhesive bonding, can provide technical and economic advantages when preceded by surface preparation treatments such as air, flame and chemical plasma discharges. This paper explores the use of discharge surface treatments in the production of medical devices and reviews specific treatment applications in the medical device manufacturing industry.

Introduction

Plastics usage in the healthcare field encompasses several distinct markets, and predominantly involving applications for medical devices and for packaging. Plastics usage in medical devices have sustained an average annual growth rates far in excess of the Gross Domestic Product (GDP). Specifically, US demand for medical plastics will increase nearly 3% per year to 3.6 billion pounds in 2008, valued at $5.0 billion.

The aging of the U.S. population, continuing cost reduction pressures in the healthcare field, advances in polymer performance, introduction of new and often life-saving devices, and the ever-present environmental / disposable / non-disposable medical device triad have driven plastic usage.

The strongest advances in plastics usage are expected for engineered resins such as polycarbonate and thermoplastic elastomers, which have favorable cost-performance benefits. Polypropylene, polyethylene, polyurethane and polyvinyl chloride and will retain leading positions in non-invasive medical products and standard medical packaging due to their low cost and amenability to radiation sterilization.

Polypropylene, like polyethylene, is a crystalline thermoplastic which has excellent thermal and chemical resistance properties and high moisture resistance. Polypropylenes are specifically often selected for their good mechanical properties, but they are a difficult-to-bond substrate since they feature no surface functional sites or inherent surface roughness to which an adhesive can secure itself. Polypropylenes are also characterized by either linear or branched carbon chain polymers, low surface energies, low porosity, and non-polar surfaces. Polyethylene, and particularly low density polyethylene, is a semi-crystalline thermoplastic produced by way of a free-radical-polymerization reaction. Although this polyolefin typically has lower strength and hardness properties, it offers numerous benefits including flexibility, clarity, and enhanced impact and stress cracking resistance. High-density polyethylene is similar to low-density polypropylene in the polymerization process used to obtain the resin. However, the density of the polyethylene increases, resulting in higher strengths, increased hardness, and enhanced chemical and abrasion resistance.

Hard-to-bond plastics such as polyolefins are most often assembled using adhesives. While adhesives are the most versatile assembly method for plastics, only a few industrial adhesives offer suitable bond strengths on hard-to-bond plastics. Cyanoacrylate, light-curing cyanoacrylate, hot-melt and light-curing acrylic adhesives have typically been used with typical difficult-to-bond plastics. Acrylic adhesives are also being introduced for use with hard-to-bond plastics.

Cyanoacrylate adhesives are polar, linear molecules that undergo an anionic polymerization reaction. A weak base, such as moisture, triggers the reaction causing the linear chains to form. Many cyanoacrylate formulations are available with varying viscosities, cure times, strength properties and temperature resistance. Cyanoacrylates form thermoplastic resins when cured. Standard unfilled ethyl monomer based cyanoacrylates typically exhibit low impact and peel strengths, low to moderate solvent resistance, and maximum operating temperatures of 160-180 degrees F. They will fixture in as little as three seconds. Rubber-modified cyanoacrylate formulations offer improved peel and impact strengths over standard cyanoacrylates. The compounded rubber added to ethyl formulations slightly increases fixture time to 30 seconds to two minutes. Thermally resistant ethyl cyanoacrylates can withstand continuous exposure to test temperatures up to 250 degrees F. Light-curing acrylics cure by way of a free radical reaction to form thermoset resins when exposed to light of the...
appropriate wavelength and intensity. Light-curing cyanoacrylates are ethyl-based products that have photoinitiators added to the formulation, allowing them to fixture rapidly on exposure to low-intensity light, and to cure in shadowed areas. Physical performance characteristics of these adhesives are similar to those of traditional cyanoacrylates. Polyolefin hot melts provide good resistance to moisture as well as excellent resistance to polar solvents, acids, bases and alcohols, offering superior adhesion to polypropylene when compared to other types of hot melts. Reactive urethane hot melts perform well on hard-to-bond plastics, processing at temperatures of approximately 250 degrees F which is as much as 200 degrees F cooler than EVA, polyamide, and polyolefin hot melts.1

**Descriptions of Equipment & Processes**

Release agents and other contaminations on molded and formed medical parts, however, can impede the performance of these adhesives dramatically if they are not addressed with surface pretreatments such as air plasma, flame plasma or atmospheric chemical plasma.

An air plasma treating system consists of two major components, a power supply and treatment station. The power supply accepts standard utility electrical power and converts it into single phase, higher frequency power that is supplied to the treating device. The treating device applies this power to the surface of medical plastics through an air gap, via an electrode design. When air is exposed to different voltages, an electrical discharge develops. When this occurs, neutral molecules and electrically charged molecules collide. These collisions cause neutral molecules to become electrically charged, resulting in filamentary discharges or "streamers". Such filamentary discharges create a cloud of ionized air - or an "air plasma". When a medical plastic surface is placed under an air plasma discharge, electrons bombard the treatment surface with energies two to three times that necessary to break the molecular bonds on the surface of most substrates. The resulting free radicals react rapidly with other free radicals on the same or different molecular chain, resulting in cross-linking. Oxidative affects on treated surfaces increases surface energy as a result of polar groups being created on the surface, primarily in the form of hydroxyl groups, carbonyl groups, amide groups and carboxylic acid. Electron and ion bombardment will also create a cleaning effect on surfaces of medical plastics. Since exposures of treated surfaces to high levels of ambient humidity and temperature accelerates polymer side chain mobility and treatment degradation, it is recommended that down-stream plastic decoration take place directly following treatment.

Flame plasma systems are comprised of a combustion/electrical station and a burner assembly, manufactured with two primary burner configurations – *ribbon* and *enhanced velocity*. A flame plasma is formed when a flammable gas and atmospheric air are combined and combusted to form an intense blue flame. The surface of medical plastics are made polar as species in the flame plasma affect the electron distribution and density on the surface. Polar functional groups such as ether, ester, carbonyl, carboxyl, and hydroxyl are contained in a flame plasma; these are incorporated into the surface and affect the electron density of the polymer material.2 This polarization and functionalization is made through reactive oxidation of a surface. ESCA analysis shows that oxidation depth through flame treatment is 5-10nm. This is generally less in depth than air plasma treatment, where oxidation depth is believed to be over 10nm. However, flame plasma treatment’s extensive oxidation, due to reactions with OH radicals in the flame, results in a cleaned and highly wettable surface which is relatively stable upon aging3.

An atmospheric chemical plasma system is also composed of a power supply and treatment station whereby the system generates an electrically charged atmosphere similar to air plasma, but uses chemical atmospheres in place of air to introduce a wide range of reactive species for low temperature material processing. The chemical plasma process can involve surface preparation via the breakdown of low molecular weight organic materials (LMWOM) and surface decontamination, fine etching of the surface to create new topographies, grafting of new functional groups or chemical species on the surface, and the deposition of coatings on the surface. The treatment process is designed to allow the interchange of gas chemistries relative to the application requirements. In the case of medical plastic parts, loose surface oligomers and other residues are repetitively cleaved and degraded until they are removed largely by a combination of bombardment by ions and electrons. These organic residues are converted into water vapor, carbon dioxide, and other nontoxic gases or volatilized materials. A noble carrier gas such as argon is typically used to initiate the breakdown of LMWOM and create surface etching for greater adhesion of adhesives. The gas species which is ionized, along with the composition and structure of the polymer itself, are the key factors that determine the degree of etching. To maximize adhesion of adhesives on plastics (particularly thermoplastic olefins), the deposition of polar functional groups from the use of oxygen and acetylene reactive gases with the carrier gas can be particularly effective.4 Atmospheric chemical plasma treatment systems are typically non-thermal, atmospheric-pressure, glow-discharge plasma.
systems which generate uniform and homogenous treatments. The level of surface tension and longevity of treatment are both typically greater than air plasma treatment effects, and similar in treatment effect to flame plasmas. The medical plastic is optimally treated by atmospheric chemical plasma when it is positioned several millimeters downstream from the source. Line speed, power level, chemistry, chemistry mixtures and material composition primarily determine levels of etching and functionalization which can be achieved.

Application of Equipment and Processes

It was theorized the application of air plasma and flame plasma surface pretreatment would sufficiently clean the surface of polypropylene, polyethylene and polyurethane -based medical plastic parts of LMWOM following molding and forming processes. If accomplished, this surface improvement would be identified through surface tension testing using ethyl cellosolve / formamide (dyne) solutions, and subsequently through adhesive adhesion testing. As such, an air plasma device (Figure 1) was employed with an internal air blower to discharge a blown arc at 480W. The performance of this device was compared with a flame plasma device (Figure 2) with compressed air and methane inputs. The stoichiometric ratio air/gas ratio was maintained at 10:1 to create a thermal discharge of 11,282 BTUs/hr.

Medical device manufacturers provided common plastic part assemblies for conveyance beneath each of the treatment devices at industry-standard discharge gaps between treatment device head and substrate to achieve optimum electron bombardments.

Presentation of Data & Results

Trial pretreatment conditions and results are shown in Figure 3. Results presented indicate a final dyne, or surface tension, at which minimum adhesive adhesion was achieved relative to assembly requirements specified by the medical device manufacturers supplying these materials.

Relative to conditions, it is noted that the airflow of the air plasma device optimized treatment at approximately twice the airflow of the flame treatment device, and the dwell time of air plasma treatment was ten times that of flame plasma. Although this is the case, the high velocity and thermal output of the flame plasma device created the necessity to distribute this output at a higher (optimized) speed so as not to affect the surface morphology of the trial materials. This optimized speed met all medical device manufacturer’s process requirements.

Interpretation of Data

It is evident from the trial data that flame plasma effected a higher level of cleaning and surface tension compared to air plasma through higher electron bombardment, increased surface electron density, and high surface oxidation.

The primary effect of the enhanced velocity discharge burner relative to the flame plasma device is interpreted to be related to 1) increased treatment (bombardment) efficiency, 2) greater power density transfer, and 3) a more homogeneous discharge profile.

Conclusions

The use of low polarity polyolefins in the manufacturing of medical device assemblies such as catheters, syringes, tubings and other components may be more suitably cleaned of molding and forming organic contaminations and functionalized using flame plasmas as opposed to air plasmas for improved adhesive adhesion. It is noteworthy that the assembly profiles used in this study had sufficient wall thickness so as to show no thermal pretreatment effects under the flame plasma trial conditions cited. Air plasma technologies may be just as applicable in achieving cleaning, functionalizing, and adhesion objectives if required processing speeds are low and if part wall thicknesses are thin.

References

Illustrations

Figure 1. Air Plasma discharge

Figure 2. Flame Plasma Discharge (enhanced velocity burner type)

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Figure 3. Trial Treatment Chart