



Autohesion of polymers

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ABSTRACT

Autohesion (direct-bonding or self-bonding) is the formation of bonds between two surfaces of an identical polymer at elevated temperature (usually just above T_g). It is an emerging technique that has the potential to cleanly and precisely join/bond polymers without the need for adhesives. Autohesion is particularly useful for applications that require hermetic and precise polymer bonding, such as in microfluidics, MEMS, and in the encapsulation of active medical implants. This article discusses the latest debate on the main mechanisms proposed to explain autohesion of polymers such as diffusion, crystalline growth, thermodynamic and chemical bonding. Surface activation techniques that are used to facilitate autohesion such as plasma treatment, chemicals, UV and ozone treatments are explored. In addition, topics such as molecular characteristics of polymers that influence autohesion, limits to bonding strength and hermetic bonding are critically discussed. Methods for evaluating autohesion strength of polymers are also described. Comparisons between prediction models from different research groups with experimental values for autohesive bonding strength are shown. Finally, conclusions and suggestions for further research are presented.

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1. Introduction to autohesion (direct-bonding or self-bonding)

Autohesion is a technique that has the potential to provide strong bonding between two polymer surfaces without the shortcomings of other joining techniques such as mechanical fastening and fusion bonding. Autohesion is a process in which two surfaces of the same material are joined together without the assistance of adhesives. It utilizes chain inter-diffusion [1–5], chain bridging and crystal growth over the interface [6–11].

Autohesion of polymers occurs when two polymer surfaces of the same material are brought into contact at a temperature above the glass transition temperature T_g and below the melting temperature T_m [12]. Autohesion leads to the formation of strong bonds at amorphous polymer interfaces through interdiffusion and subsequent entanglement of polymer chains across the interface [13]. However, the autohesive bond strength developed at semi-crystalline polymer interfaces is rather weak due to limited chain mobility associated with the presence of crystals.

Autohesion of polymers is strongly influenced by surface properties of polymers that include surface energy and polarity [14], morphology [15], topography [16] and surface chemistry [17]. Polymers are generally hydrophobic and have low surface energy, which are not favourable for forming strong bonds [18]. Thus, surface properties of polymers need to be altered in order to improve bonding of polymers. Surface modification techniques such as ultraviolet (UV) irradiation, corona discharge and plasma treatment have been used to treat polymer surfaces for improved bonding [17,19–22].

Plasma treatments enhance surface properties of polymers to facilitate autohesion without affecting their favourable bulk properties [23,24]. Low-temperature plasma processes offer a number of unique advantages, including the following [25–28]: (1) they are dry and environmentally friendly; (2) they can be easily controlled by variation of process gases and operating parameters including plasma power, treatment time and operating pressure, yielding greater consistency and reproducibility; (3) they are conformal and allow uniform surface treatment of complex shaped objects such as microfluidic chips and medical implants. Plasma-based approaches such as plasma activation, plasma polymerization and plasma immersion ion implantation/deposition (PIII&D) have been widely employed to tailor surface properties of polymers for biomedical applications [29–34]. Plasma treatments using gases such as Ar, N₂

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and O₂ activate polymer surfaces mainly through incorporation of chemically reactive functionality onto polymer substrates [35–37]. Plasma polymerization allows a uniform deposition of ultrathin films with unique physical, chemical and biological characteristics [38,39]. PIII&D process combines the advantages of conventional plasma and ion beam technology, providing deeper modification depth than conventional plasma treatment [40].

2. Bonding of polymers

There are many methods used to bond polymers. Mechanical fastening, fusion bonding, laser welding, and chemical (adhesive and solvent) bonding have been used successfully [41–45]. However, the use of these methods in MEMS or biomedical applications has strong disadvantages. For example, mechanical fastening induces stress concentrations [46]. Fusion bonding requires high energy and must occur close or at the polymer melting range which for most MEMS or biomedical applications is too excessive, especially for polymers used for implant encapsulation. The high temperature might induce damage to the encapsulated components and/or deformation [47]. Hence, autohesion techniques that do not use excessive heat (temperatures just above T_g of the polymer), force or solvents are desired for polymer bonding.

Adhesive bonding is not ideal for some applications because of deterioration of the joint over time, especially in wet environments [41], and potential release of toxic agents from the adhesive. These toxins may lead to complications in food and medical applications, especially when used for an extended period of time. Many studies report on the toxicity effect of adhesives and bonding primers [48,49]. Vajrabhaya et al. [49] reported different cell survival rates when different bonding primers were used in an in-vitro with the study case of 3-D cell culture of Bovine pulp-derived cells transfected with Simian virus 40 Large T antigens under perfusion conditions. In the biomedical field, implantable devices that require encapsulation of active components or that require components that need to be joined are frequently fabricated using metals, because of the lack of suitable bonding technologies for polymers. If a bonding technology for polymers equivalent to the welding of metals would be available, many implantable devices could be fabricated from polymers. Polymers such as polyether ether ketone (PEEK, polytetrafluoroethylene (PTFE), polyether sulfone (PES), poly(alkyl methacrylates) (PAMAs), polyphenylene sulfide (PPS), polyurethane and polydimethylsiloxane (PDMS) are used successfully in various biomedical applications [50–55]. PEEK and PES have been identified recently as suitable by many researchers for in-vivo implants due to their long-lasting stability in an in-vivo environment in addition to their excellent thermal and mechanical properties [54–56].

The development of bonding technologies for these polymers has lagged behind the development of the polymers themselves; this is partly a consequence of the polymers that have been developed, since they are not readily amenable to conventional bonding technologies, such as welding, friction stir and ultrasonic joining techniques. For a polymer joining technology to be considered for use in the biomedical field it must be biocompatible with no release of toxic by-products, and it must maintain strength and hermeticity over long periods in a wet, aggressive, and corrosive environment such as the human body.

The field of microfluidics has led to a new incentive for autohesion. Microfluidics is concerned with the direction, control and measurement of fluid flowing in small channels. Applications include medical diagnostics and biosensing. Polymers are ideal materials in which to form microfluidic channels [57–59]. A common fabrication strategy is to form channels in a bulk polymer and use autohesion to seal the channels against an opposing polymer

surface [60]. Autohesion is preferred over adhesive bonding to prevent the unwanted intrusion of adhesive into the microfluidic channels.

3. Autohesion mechanisms

3.1. Molecular bonding mechanism

Chemical bonds formed at the polymer/polymer interface can greatly enhance the bonding strength of polymers. Fig. 1 shows the schematic representations of chemical bonding mechanisms at polymer–polymer interfaces for polyethylene short molecule as an example. Chemical bonds are generally primary covalent bonds which are formed by chemical reaction of functional groups between the two polymer surfaces to be joined. In comparison with secondary interactions, such as van der Waals interaction, covalent bonds have a much higher bond energy, of about 60–700 kJ/mol, whereas those of van der Waals interactions and hydrogen bonds are less than 50 kJ/mol [61]. Therefore, chemical bonding is much stronger and resistant to disruption than secondary bonding.

Fakirov [62] studied the autohesion of PET and explained that the chemical bonds formed by chemical reactions between neighboring chains at the highly crystalline PET/PET interface mainly contribute to strength development. He proposed chemical reactions between molecular chains at the interface to be the mechanism for the healing process of semi-crystalline linear condensation polymers (such as polyesters, polyamides and polycarbonates). Another study by Fakirov and Avramova [63] also demonstrated that a chemical reaction between macromolecules located at the interface was mainly responsible for bonding of crosslinked polyamides.

Chemical bonding mechanism may be promoted by the presence of reactive polar functional groups which enable the formation of strong chemical bonds between two contacting polymer surfaces and result in an increase in bond strength. Energetic surface treatments such as plasma treatment [64] and ion beam irradiation [65], may be used to introduce functional groups to the polymer surfaces.

Awaja et al. [7,8] showed for a variety of plasma treatment systems that the bond strength is strongly correlated with the free radical density in the material. They develop a theory based on free radicals activated molecular bonding as the driver for autohesion. The autohesion free radicals theory has a strong predictive power for the strength of an autohesive bond [8].

The autohesion free radical theory utilizes the concept of the creation of unpaired electrons in polymers when radiation or ion bombardments disrupts the molecular structure at the surface by excitation of the electrons or by displacement of the atoms. In a system that represents a plasma treatment of PEEK surface, Awaja et al. [7,8] measured the number of unpaired electrons using electron spin resonance (ESR). They reported a small background concentration of unpaired electrons in PEEK, however, the concentration of unpaired electrons dramatically increase, by a factor of approximately 1000, when PEEK is subjected to plasma immersion ion implantation, a modified form of plasma treatment. The concentration of electrons increases as the bias voltage increases (Fig. 2). They described that the plasma generated electrons are likely to be mobile owing to their ability to tunnel from one localized wave function to another.

When two polymer surfaces are brought together, physical attractive forces such as van der Waals forces act. However, these are short range interactions that are only relevant under ideal conditions, such as those that occur when perfectly smooth, flat surfaces are brought together [48]. For polymers, these conditions are extremely difficult to achieve and hence this method is usually

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