

Thermal bonding of PMMA: effect of polymer molecular weight

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Abstract Microfluidics devices have attracted increasing interest over the last decade. Glass was initially the materials of choice for these devices but polymers such as polymethylmethacrylate (PMMA) have a great potential to be used for these devices because of their low cost, ease of fabrication and chemical properties. A key step in fabrication of these microfluidic devices is the enclosing of microchannels by cover plate, i.e., layer to layer bonding. This investigation focused on the thermal bonding of PMMA layers of different molecular weights. The bond strength and the effect of temperature and pressure on bond strength between various PMMA pairs of different molecular weights were studied. Thermal bonding was realized using a hot embossing system. PMMA strips made from predefined parameters were prepared and a customized CNC machine mold was used to determine the optimized parameters of the thermal bonding. The PMMA pairs investigated are of molecular weights 96.7, 120, 350 and 996 kDa using Instron machine; the shear strength of the thermally bonded specimens was determined. For the

PMMA pairs investigated, the greatest shear strength of 1.589 ± 0.286 MPa was observed between molecular weights of 350 and 996 kDa.

1 Introduction

During last decade, field of microfluidics has emerged into one of the most dynamic field in analytical chemistry (McDonald et al. 2000; Boone et al. 2002; Soper et al. 2000). It has the potential benefits of reduced size, disposability, improved performance, low cost, reduced sample and reagent volume, and reduced power consumption. However, the choice of materials and fabrication procedure are critical aspects of commercial microfluidic devices. Polymer materials have become the most promising materials for microfluidics devices due to the advantages of low cost, ease of fabrication, biocompatibility and higher flexibility over their traditional counterpart like glass and silicon. Different polymer materials like poly(dimethylsiloxane) (PDMS), poly(methyl methacrylate) (PMMA) or polycarbonate (PC) have become the most promising materials. PMMA, owing to the advantage of low cost, high transparency and excellent dielectric as well as mechanical properties, has become one of the dominant materials for fabrication of microfluidic devices.

Due to growing interest in disposable microfluidic devices, several plastic-chip manufacturing processes have been developed in recent years, including X-ray photolithography, hot embossing or imprinting, laser ablation, injection molding, etc. With all these methods, the fabricated microchannels are sealed on the top with a cover plate of the same plastic material to form enclosed microstructure.

Thus the key step in the fabrication of these microfluidic devices is the enclosing of microchannel by cover plate.

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This layer to layer bonding is a very important procedure and challenging issue in the design and fabrication of polymer based microfluidic devices. Several methods for sealing of polymeric substrates have been demonstrated, including thermal bonding in convention oven or in hot embossing machine (Kelly and Woolley 2003; Fiorini and Jeffries 2003) gluing such as SU-8 resist, PDMS films (Han et al. 2003), laser lamination (Robert et al. 1997) and surface modification associated with other bonding methods (Lee et al. 2003; Zhu et al. 2004). Of these methods, thermal bonding approaches are especially desirable since they allow the formation of a uniform channel surface comprised entirely of the same polymeric material. Other sealing approaches unavoidably introduce multiple materials to form the microchannels which cause inhomogeneities in the ζ -potential along the channels and cause undesired effects on the electrodynamics of the microsystem such as Taylor dispersion and reduced electrophoretic separation efficiencies (Kelly and Woolley 2003). However, conventional thermal bonding approaches still faces the sever challenges of microchannel deformation, low reproducibility and poor yield, which warrants continuing research to improve the thermal bonding methods. Recently Zhu et al. (2007) has investigated the traditional thermal bonding as well as the surface modification bonding with respect to temperature, surface modification, pressure and aging effect with PMMA.

This investigation focused on the thermal bonding of PMMA layers of different molecular weights. The bond strength and the effects of temperature and pressure on bond strength between various PMMA pairs of different molecular weights were studied.

2 Experimental

Polymethylmethacrylate of molecular weights 96.7, 120, 350 and 996 kDa were purchased from Sigma-Aldrich. The pellets were molded to sheets of 1 mm thickness by using a laboratory scale hydraulic hot press. The test specimens were cut into sizes. The samples were bonded in a lap shear joint geometry with contact area of 15 mm \times 11 mm \times 1 mm using the Carver Laboratory press. The PMMA substrates were put together and heated to the bonding temperature before bonding pressure were applied in the hot embossing system. After bonding for a given time, the samples were cooled to room temperature under pressure.

The methodology adopted is depicted in Fig. 1. The bonding pairings were selected with low T_g PMMA at the top and high T_g PMMA on the bottom and the bonding temperature selected were just above the T_g of the low T_g PMMA.

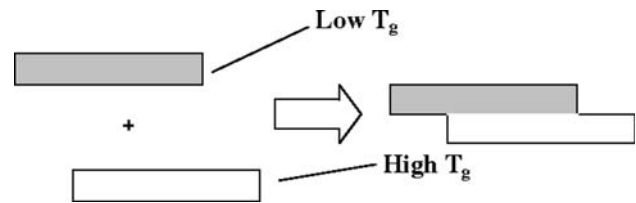


Fig. 1 Bonding methodology

The bond strength and its dependence on bonding temperature and pressure were measured by tensile testing in an Instron-5569 model. An experimental speed of 1 mm/min was used in this study. The maximum force was divided by the bonded area to calculate the bond strength before failure. For each measurement, five sample specimens were taken. Surface profile was analyzed using a JEOL JSM-5600LV scanning electron microscope.

3 Results and discussions

The types of different molecular weights of PMMA combinations and heating temperature, heating time, cooling time, cooling load, etc. used for this study are depicted in Tables 1 and 2, respectively.

Figure 2 shows a general plotting of the data of force against extension collected from the Instron machine. In all the cases show a linear increment of shear force with respect to the extension of the specimen. The specimen portrayed Hooke's law of elasticity by showing perfect elastic deformation before the fracture. The threshold force and the extension at which it occurred were obtained. Together with the dimensions of the bonded area measured before each testing, the shear strength was obtained. The results for bonding between 96.7 and 120 kDa, 96.7 and 350 kDa, 96.7 and 996 kDa, 120 with 996 kDa and 350 and 996 kDa are obtained. Using the calculated shear strength of each specimen for each bonding type, the mean shear strength was calculated. Table 3 shows the mean shear strength of different types of bonding tested. It is observed that the bond strength increases with increasing of molecular weight pairs for constant bonding load of 3

Table 1 Types of different molecular weight combinations

Lower T_g PMMA strip (M_w)	Higher T_g PMMA strip (M_w)	Thermal bonding type
96.7 kDa	120 kDa	96.7 kDa/120 kDa [A]
96.7 kDa	350 kDa	96.7 kDa/350 kDa [B]
96.7 kDa	996 kDa	96.7 kDa/996 kDa [C]
120 kDa	350 kDa	120 kDa/350 kDa [D]
120 kDa	996 kDa	120 kDa/996 kDa [E]
350 kDa	996 kDa	350 kDa/996 kDa [F]

Table 2 Parameters used for bonding

Upper PMMA strip (M_w)	Heating temperature ($^{\circ}\text{C}$)	Heating time (min)	Cooling time (min)	Heating load (kg)	Cooling load (kg)
96.7 kDa/120 kDa	95	5	20	3,000	3,000
96.7 kDa/350 kDa	95	5	20	3,000	3,000
96.7 kDa/996 kDa	95	5	20	3,000	3,000
120 kDa/350 kDa	105	5	20	3,000	3,000
120 kDa/996 kDa	105	5	20	3,000	3,000
350 kDa/996 kDa	125	5	20	3,000	3,000

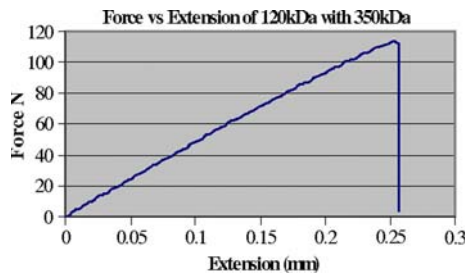


Fig. 2 Force versus extension of 120 with 350 kDa

Table 3 Mean shear strength of bonding for different combinations

Types of bonding	Lap shear strength (MPa)
96.7 kDa/120 kDa	0.112 ± 0.001
96.7 kDa/350 kDa	0.211 ± 0.003
96.7 kDa/996 kDa	0.342 ± 0.004
120 kDa/350 kDa	0.562 ± 0.005
120 kDa/996 kDa	0.852 ± 0.004
350 kDa/996 kDa	1.589 ± 0.005

metric ton and heating time of 5 min. It is observed that the bond strength increases with increasing of molecular weight pairs for constant bonding load of 3 metric ton and heating time of 5 min.

When two compatible polymer surfaces are brought into contact at elevated temperatures, adhesion occurs at the interface. A high strength is developed above the glass transition temperature (T_g) of amorphous polymers where the molecular mobility is high and the process is diffusion controlled (Kline and Wool 1988; Jud et al. 1981). That means that there is diffusion of segments of the macromolecular chains across the interface. It is observed that the mean shear strength of bonding between molecular weight 350 and 996 kDa is the maximum. This can be attributed to the interdiffusion of large number of macromolecular chain segments at the interface. We have concentrated our study for the effect of temperature and pressure for the pair of bonding between the molecular weights 350 and 996 kDa.

Figure 3 shows the effect of bonding temperature on bond strength at a bonding pressure of 1.225 MPa for the

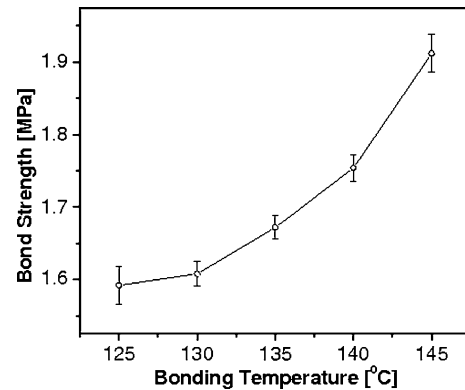


Fig. 3 Effect of bonding temperature on bond strength at constant pressure of 1.225 MPa

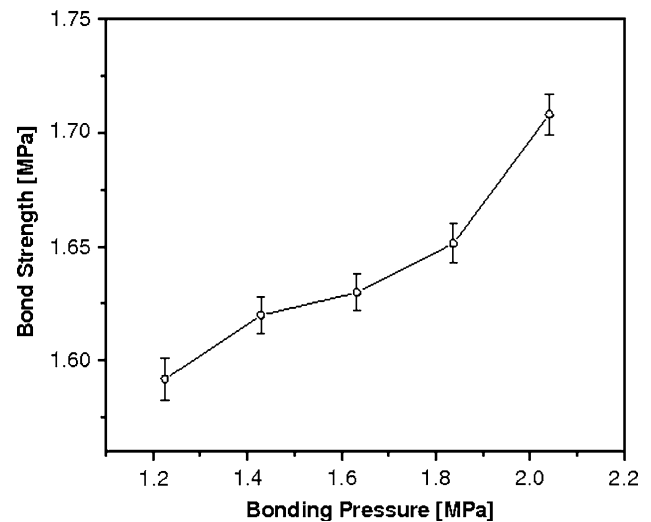


Fig. 4 Effect of bond strength on bonding pressure at bonding temperature of 125°C

bonding between 350 and 996 kDa pair. It is observed that the bond strength increases with increase of bonding temperature. Higher temperature will damage the specimen although it can heighten the bond strength. Beyond the temperature of 145°C, the specimen deformed and so the data were not taken into consideration.

Figure 4 shows the bonding pressure’s effect of bond strength of the bonding between 350 and 996 kDa PMMA.

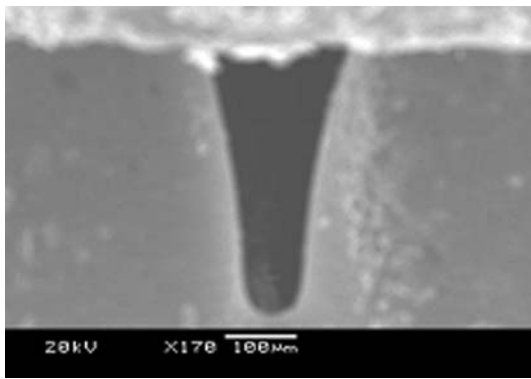


Fig. 5 Bonding between laser cut microchannel of 996 kDa PMMA and 350 kDa PMMA at bonding pressure of 1.225 MPa and temperature of 135°C

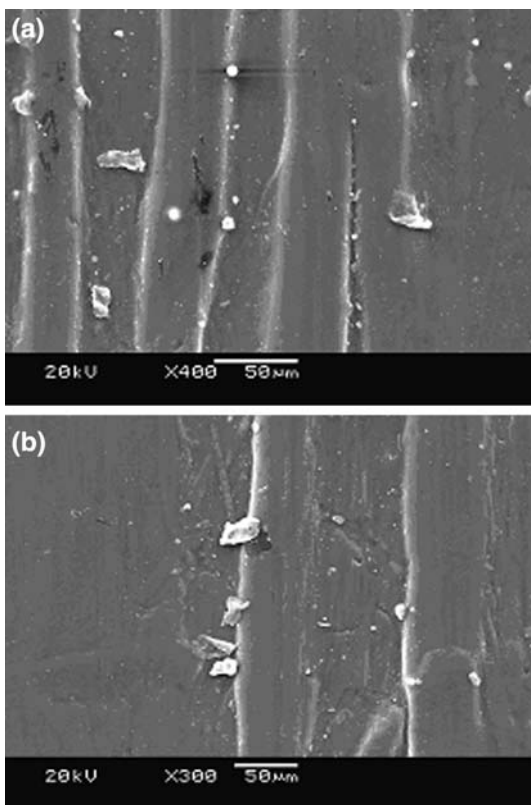


Fig. 6 a, b SEM micrographs of PMMA surfaces after bonding at different magnifications

Though the bond strength increases with increasing bonding pressure, the specimens get deformed beyond 2.225 MPa.

Figure 5 shows a laser cut microchannel of 996 kDa PMMA is covered with 350 kDa PMMA at bonding pressure of 1.225 MPa and temperature of 135°C having no deformation of the microchannel.

Figure 6a and b shows the surface morphology of the PMMA after fracture of the bonded pairs as observed by

scanning electron microscopy. It is seen that the fractured surface shows a specific morphology. This morphology (and rugosity) indicates that there is some molecular mobility at the PMMA/PMMA interfaces. When two amorphous polymer surfaces are brought into contact at elevated temperatures (above T_g) where the molecular mobility is high, adhesion occurs at the interface. The chain ends penetrate to the opposite side of the interface in the surface layer, leading to high strength. It has also been proposed that the polymer surface layer is more mobile than the chains in the bulk since very significant decrease of T_g have been observed in that layer of the polymer (Mayer 1994; Kajiyama et al. 1995).

These studies indicate that the conformational structure and molecular mobility at the polymer surface differ from those of the bulk; molecules and specially the chain ends are less entangled and more mobile. Therefore there is possibility of chain ends to penetrate to the opposite side of the interface in the surface layer leading to the interdiffusion at the surface of glassy polymer.

4 Conclusions

The bonding strength increases with increase in molecular weights of the PMMA. The bonding between the molecular weights 350 and 996 kDa has maximum strength. The bond strength increases with increase in bonding temperature and pressure. At bonding pressure of 1.225 MPa and temperature of 135°C, the bonding between 350 with 996 kDa shows bond strength of 1.91 MPa without any deformation of the specimen. SEM micrographs show the bonding is due to interdiffusion of polymer chains at the interfaces.

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