

Comparative Studies of Solvent Bonding and Adhesive Bonding for Fabrication of Transparent Polymers

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This investigation highlights rationale of solvent bonding and adhesive bonding for fabrication of a transparent polymer such as polycarbonate with a high-throughput process. Studies under ultra violet spectra and visible spectra reveal that in comparison with adhesive bonding of a polymer, solvent diffusion bonding is more transparent. Polycarbonate is hydrophilic in nature resulting in a low contact angle of water as well as the presence of polar functional groups on the polymer surface. It is observed that a lap shear tensile strength of a solvent bonding polymer is significantly higher than that of an acrylic adhesive bonded polycarbonate, and fabrication of polycarbonate by solvent bonding merely takes few seconds. Solvent bonding of a polymer results in a cohesive failure from polymer as analyzed under the scanning electron microscopy, this is why solvent bonding shows a significantly higher bond strength.

Keywords: adhesion, wetting, polycarbonate, solvent bonding, mechanical properties, industrial applications.

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1. INTRODUCTION

Amorphous-polymer-based microfluidic chips have generated significant interest in not only medical research due to some key advantages such as fast response time, low cost, easy disposal, excellent optical properties and suitability for mass production [1, 2]. Joining plastic composites in medical devices is becoming more complex and more sophisticated both in performance specifications and structural complexity [3, 4]. Most widely used methods for joining plastic in microfluidic devices are thermal bonding, adhesive bonding, and solvent bonding [5]. Chen et al [6] and Ogonczyk et al. [7] have emphasized that thermal bonding of a polymer at higher temperatures would result in the deformation and collapse of micro-channels. Micro-channels are most essential elements in microfluidic systems and, therefore, fabrication of polymeric channels is of great interest for biomedical application [8].

The ambient temperature bonding, such as adhesive bonding, is generally favoured for fabrication of polymeric microfluidic devices [9], however, this method introduces another material to the interface, which can cause compatibility problems with the fluid flowing through micro-channels [10]. Recent articles published on solvent bonding in terms of fabrication of a polymer show that solvent bonding is a more effective method for joining a transparent polymer [11]. Moreover, this method results in aesthetic and homogenous joints with low weight and relatively strong bonding without introducing a foreign adhesive material [12]. However, selection

of an appropriate solvent, optimization of various parameters of solvent bonding and durability of a solvent bonded transparent polymer under aggressive environment is yet to be established.

Based on these considerations, the objective of this work is to optimise performance of the solvent bonding of polycarbonate in comparison with the acrylic adhesive bonding of polycarbonate in respect of dimensional stability, manufacturing time, strength, and finally its durability under aggressive chemical environments.

1.1. Fundamental aspects of solvent bonding

Thermodynamically, a polymer can be dissolved in a liquid spontaneously subject to the free energy of mixing, i.e., when ΔG_{MIX} , is less than 0 [13]:

$$\Delta G_{MIX} = \Delta H_{MIX} - T\Delta S_{MIX}, \quad (1)$$

where ΔH_{MIX} is the heat of mixing, T is the absolute temperature, and ΔS_{MIX} is the entropy change in the mixing process. Hence, an increase in the temperature affects lowering of free energy of mixing; thereby promoting dissolution. Therefore, for effective solvent bonding, the solvent should have a solubility parameter very close to that of the polymer. The Hildebrand solubility parameter, δ , is the square root of the cohesive energy density (CED):

$$\delta = (\text{CED})^{1/2} = (\Delta E_V/V)^{1/2}, \quad (2)$$

where ΔE_V is the cohesive energy (or energy of vaporization) and V is the molar volume. The cohesive energy represents the energy required to break

all cohesive bonds to convert a liquid into a gas. The following relation also relates the cohesive energy to the absolute temperature:

$$\Delta E_{vap} = \Delta H_{vap} - RT, \quad (3)$$

where ΔH_{vap} is the molar heat of vaporization and R is the gas constant. Hence, an increase in the temperature leads to a decrease in the solubility parameter of liquids.

1.2. Fundamental aspects of adhesive bonding

Adhesion is a mechanism due to an action of molecular forces and can be attributed to thermodynamic work of adhesion (W_a). It is described by the Dupre equation as:

$$W_a = \Upsilon_1 + \Upsilon_2 - \Upsilon_{12}, \quad (4)$$

where Υ_1 and Υ_2 are the surface free energies of contacting materials and Υ_{12} is the interfacial free energy. The surface free energy is primarily based on wetting on the solid surfaces by liquids and is commonly defined as work of adhesion, which is calculated by the Dupre-Young equation as below:

$$W_a = \Upsilon_1 (1 + \cos\theta). \quad (5)$$

Ideal wetting, i.e., when θ is 0° , is the work of adhesion attained to maximum [14].

2. EXPERIMENTAL

2.1. Materials

The materials used were: bisphenol-A-based polycarbonate sheet (dimensions 125 mm x 25 mm x 2 mm); the solvent dichloromethane, and the transparent acrylic adhesive

2.2. Preparation of solvent bonding of polycarbonate

The solvent used in this experiment shows a solubility parameter near to the solubility parameter of polycarbonate ($\delta = 21$) [15], e.g., dichloromethane [$\delta = (20.2 \text{ MJ/m}^3)^{1/2}$]. Firstly, two-polymer sheets were dipped into 1 ml solvent to initiate the procedure of solvent bonding of polycarbonate, then the two sheets were pressed together under pressure. The bonding time varied from 4 to 10 seconds.

2.3. Preparation of acrylic adhesive bonding of polycarbonate

The acrylic adhesives are generally used in medical industry due to their fast curing and optical transparency. The two polycarbonate sheets were fabricated by using a calculated amount of adhesive in both sides and joined under pressure. The adhesively bonded polycarbonate was cured at room

temperature for 24hr according to the time mentioned by supplier.

2.4. Performance of solvent bonding and acrylic adhesive bonding in Ringer's solution

The performance of the adhesive bonding of polycarbonate and of the solvent bonding of polycarbonate were investigated by exposing the bonding under Ringer's solution. The experiment was performed at 40°C for 1 and 2 weeks without applying any pressure. The composition of aggressive Ringer's solution used in experiments is shown in Table 1.

Table 1. Composition of Ringer's solution

Name of Salts	Weight (in gm) of salt (in 1 lt. water)
Sodium Chloride	6.5
Potassium Chloride	0.14
Calcium Chloride	0.129
Sodium Bicarbonate	0.2
Dextrose	2

2.5. Measurement of contact angle

The contact angle was measured by a sessile drop technique using deionized water. The Modular "CAM 200-Optical contact angle and surface tension meter" was used to perform contact angle measurements. The dimensions of the test samples were 125 mm x 25 mm x 2 mm.

2.6. Measurement of adhesion strength

In order to find the adhesion strength of polycarbonate, the tests were carried out with the lap-shear tensile configuration. The lap-shear tensile test was performed according to the recommendations of the American Society for Testing Material (ASTM D5656-10) under a load cell of 5 kN at a test speed of 5 mm/min at room temperature. The test samples with dimensions of 125 mm x 25 mm x 2 mm were prepared for both the solvent bonding and the acrylic adhesive bonding of polycarbonate sheets. For each condition, five samples were tested and the mean value is reported in the Results.

2.7. Spectroscopic measurements of neat, solvent-bonded and acrylic-adhesive-bonded polycarbonates

A neat polycarbonate, a solvent-bonded polycarbonate, and an acrylic-adhesive-bonded polycarbonate were characterized by using the Fourier transform infrared spectra (FTIR), ultra violet (UV) and visible spectra.

2.8. Optical microscopic and scanning electron microscopic study of solvent-bonded and acrylic-adhesive-bonded polycarbonate

The morphology of a solvent-bonded polycarbonate was characterized by optical microscopy; a

fractographic analysis of a solvent-bonded polycarbonate and an acrylic-adhesive-bonded polycarbonate were carried out using JEOL JSM 7500F emission scanning electron microscope.

3. RESULTS

3.1. UV-visible spectroscopic study of solvent bonding and acrylic adhesive bonding of polycarbonate

UV-visible spectra of a neat polycarbonate, a solvent-bonded polycarbonate, and an acrylic-adhesive-bonded polycarbonate sheets are shown in Figure 1a and b. The UV-visible spectra revealed that the UV light does not pass through the neat polycarbonate sheet but visible light is transmitted through that sheet. The visible light is transmitted in 72% through the neat polycarbonate sheet whereas it is transmitted in 44% through the solvent-bonded polycarbonate sheet, and in 33% through the acrylic-adhesive-bonded polycarbonate sheet. Therefore, it is concluded that the solvent-bonded polycarbonate sheet shows more transparency than the acrylic-adhesive-bonded polycarbonate.

3.2. Optical microscopic studies of dichloromethane (DCM) solvent bonding of polycarbonate

Figure 2a and b shows the solvent molecules that appear to be entrapped into the matrix of the polycarbonate sheet. The images were taken in two different magnifications. The solvent molecules are uniformly distributed into the polycarbonate sheet, which is identified by the images shown below.

3.3. FTIR study of neat and dichloromethane (DCM)-solvent-adsorbed polycarbonate

The FTIR spectra of the polycarbonate is shown in Fig. 3 and listed in Table 2. The principal absorption bands are at 2926 cm^{-1} (ring C-H bending), 1765 cm^{-1} (C=O stretching), 1502 cm^{-1} (skeletal ring vibration), 1225 and 1152 cm^{-1} (C-O stretching). These absorption bands are almost identical in the case of the solvent bonding of polycarbonate as evident from Figure 3.

3.4. FTIR study of acrylic-adhesive-bonded polycarbonate

The data of the FTIR analysis of the acrylic-adhesive-bonded polycarbonate is shown in Fig. 4 and listed in Table 3. The principal absorption bands are at 2918 cm^{-1} (ring C-H bending), 1732 cm^{-1} (C=O stretching), 1371 , 1221 and 1121 cm^{-1} (C-O stretching). A new peak is observed at 3452 cm^{-1} . Thus, it may be concluded that there is a possibility of hydrogen bonding in between the acrylic adhesive and the polymer surface.

3.5. Studies on lap-shear tensile strength of solvent bonding of polycarbonate with bonding time

The lap-shear tensile strength of the DCM-solvent-bonded polycarbonate with bonding time intervals is shown in Figure 5. As is observed there, the lap-shear tensile strength is directly proportional to the bonding time. The lap-shear tensile strength of 13.65 MPa is obtained when the bonding time is 4 seconds and it increases with increasing the bonding time and reaches the maximum when the bonding time is 10 seconds.

3.6. Studies of lap-shear tensile test with dimensional stability of polycarbonate laminate by DCM solvent

Figure 6 shows that the dimensional stability of polycarbonate is directly proportional to the applied bonding pressure. It is evident there that due to the increase in the bonding pressure, the lap-shear tensile strength increases considerably, however, this happened with the sacrifice of the dimensional stability of the polycarbonate sheet. When the maximal pressing load of 4 N was applied, the lap-shear tensile strength went to 32 MPa, while the, thickness of overlap went down from 4 mm to 3.25 mm. Therefore, in conclusion, for specific applications for biomedical, it is essential to compromise the applied load in respect of its lap-shear tensile strength and the dimensional stability of polycarbonate.

3.7. Contact angle of water on polycarbonate surfaces

Contact angles of water on the polycarbonate surface are shown in Figure 7. Water is a polar solvent while polycarbonate is, up to a certain extent, hydrophilic in nature. It clearly indicates that the contact angle merely decreases from 82.97° to 82.92° with increase in time, but, the work of adhesion does not increase as such, however, this extent of the surface wetting strongly supports strong solvent bonding which may not be sufficient for an adhesive bonding. Contact angles vs. time and work of adhesion are shown in Table 4.

3.8. Studies of lap-shear tensile strength of acrylic-adhesive-bonded polycarbonate

The lap-shear tensile strength of an acrylic adhesive joint of a polycarbonate sheet is shown in Figure 8. The lap-shear tensile strength of polycarbonate depends on its wetting characteristics and quantity of acrylic adhesive dispersed on the polycarbonate surface. The findings show that the lap-shear tensile strength of the adhesive-bonded polycarbonate is significantly lower than that of the solvent-bonded polycarbonate. However, due to an

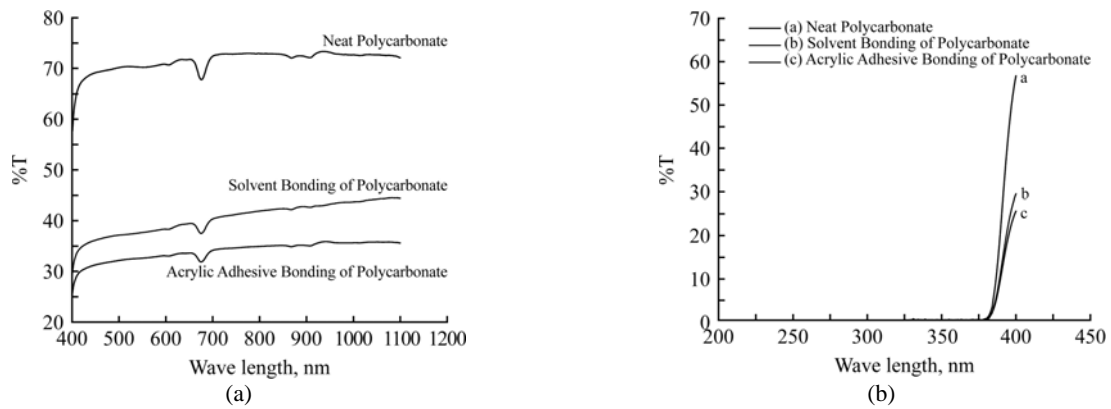


Fig. 1. Visible-spectra (a) and UV spectra (b) of neat polycarbonate, solvent-bonded polycarbonate, and acrylic-adhesive-bonded polycarbonate.



Fig. 2. Optical microscopy images of DCM solvent bonding of polycarbonate at (a) 10X and (b) 5X magnification.

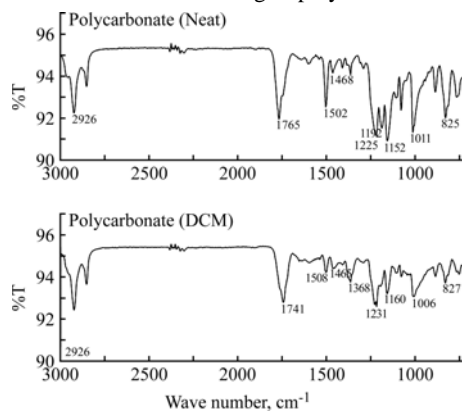


Fig. 3. FTIR spectra of neat polycarbonate and DCM-solvent-absorbed polycarbonate.

Table 2. FTIR data of neat and solvent-bonded polycarbonate sheets

	*Observed peak (cm ⁻¹)	Reference peaks (cm ⁻¹)	Present functional group
Neat polycarbonate	2926s	3000–2850	C-H stretch (alkane)
	1765s	1820–1670	C=O group (carbonyl)
	1502s	1600–1400	C=C group (aromatic)
	1468m	1480–1350	C-H bend (alkane)
	1225s	1320–1210	C-O stretch (carbonyl)
	1192m	1300–1000	C-O stretch (ester)
	1152s		
	1011s		
	2926s	3000–2850	C-H stretch (alkane)
	1741s	1820–1670	C=O group (carbonyl)

Polycarbonate in DCM solvent	1508m	1600–1400	C=C group (aromatic)
	1465w	1480–1350	C-H bend (alkane)
	1368m	1320–1210	C-O stretch (carbonyl)
	1231s		
	1160m	1300–1000	C-O stretch (ester)
1006m			

* Note: Peak intensity: br=broad, s=strong, m=medium, w=weak.

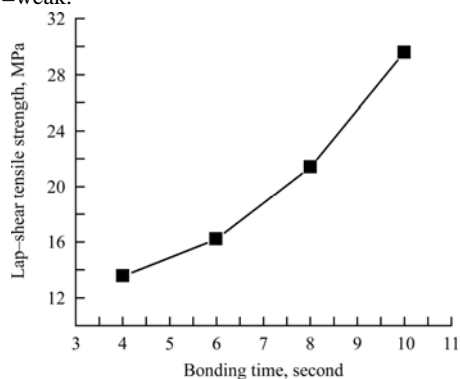
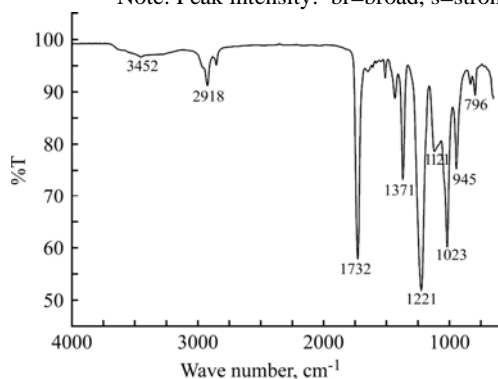


Fig. 4. FTIR spectra of acrylic-adhesive-bonded polycarbonate. **Fig. 5.** Lap-shear tensile strength of polycarbonate in DCM solvent vs. bonding time.

Table 3. FTIR data of acrylic adhesive bonded polycarbonate

*Observed peaks (cm ⁻¹)	Reference peaks (cm ⁻¹)	Present functional group
3452br	3600–3200	OH broad (for H-bonding)
2918m	3000–2850	CH stretch (alkane)
1732s	1725–1700	C=O group present (acid)
1371s, 1221s	1320–1210	C-O group present (acid)
1121w, 1023s	1150–1070	C-O group present (ether)

*Note: Peak intensity: br=broad, s=strong, m=medium, w=weak.

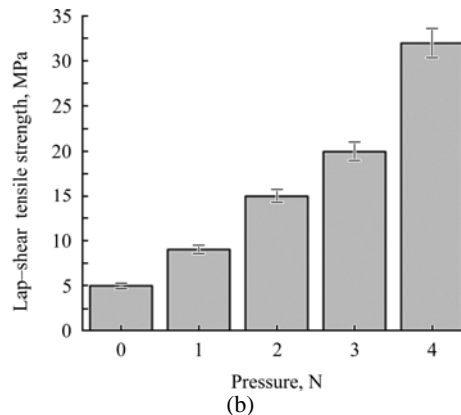
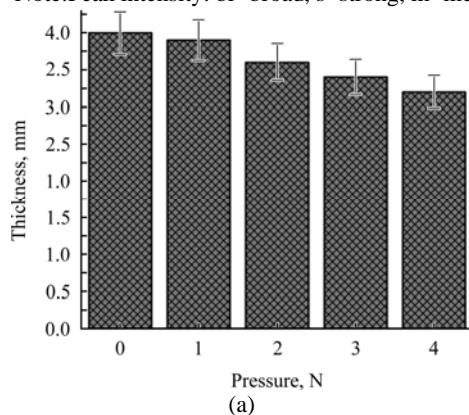


Fig. 6. Dimensional stability and lap-shear tensile strength of solvent-bonded polycarbonate vs. pressure.

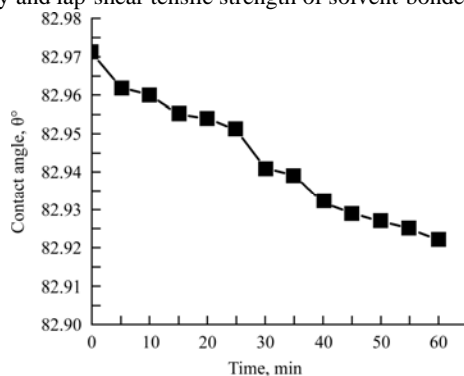
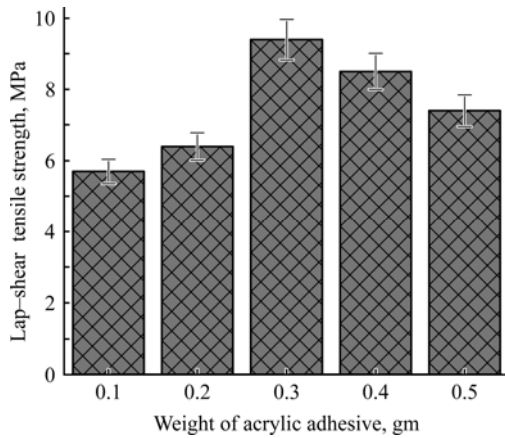
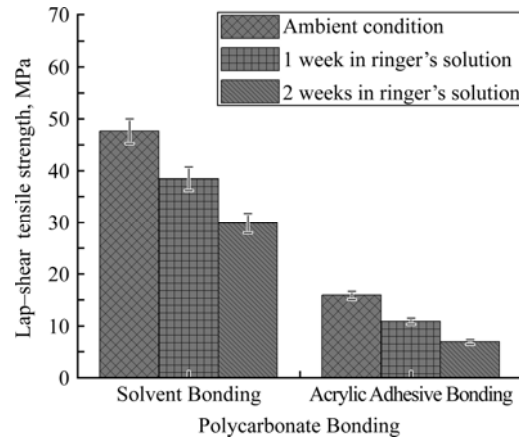


Fig. 7. Contact angle data of polycarbonate surface by water droplet vs. time.

Table 4. Contact angle and work of adhesion results vs. time

Time (min)	Contact angle (θ°)	Work of adhesion (N/m^2)
0	82.971	92.236
5	82.962	92.859
10	82.960	92.998
15	82.955	93.343
20	82.954	93.412
25	82.951	93.619
30	82.941	94.308
35	82.939	94.445
40	82.932	94.925
45	82.929	95.131
50	82.927	95.268
55	82.925	95.404
60	82.922	95.609

**Fig. 8.** Lap-shear tensile results of acrylic-adhesive bonded polycarbonate vs. weight.**Fig. 9.** Lap-shear tensile strengths of solvent bonding and acrylic adhesive bonding of polycarbonate after immersion in Ringer's solution for 1 and 2 weeks at 40°C.**Table 5.** Bond strength deteriorated (%) into Ringer's solution at 40°C after 1 and 2 weeks

Polycarbonate bonding	Bond strength in ambient condition (MPa)	Bond strength in Ringer's solution (MPa)		Bond strength deteriorated in Ringer's solution (%)	
		1 week	2 week	1 week	2 week
Solvent bonding	46.45	38.46	29.8	20.77	55.87
Acrylic adhesive bonding	16.7	12.7	8.7	31.49	91.95

increase in the quantity of acrylic adhesive, there is an increase in the lap-shear tensile strength. The lap-shear tensile strength reaches the maximum when polycarbonate is fabricated with 0.3 gm of an acrylic adhesive. Any further increase in quantity of adhesive lowers the lap-shear tensile strength as evident in Figure 8.

3.9. Performance study of solvent bonding and acrylic adhesive bonding of polycarbonate in Ringer's solution

Performance of the solvent bonding and the acrylic adhesive bonding of polycarbonate into Ringer's solution is shown in Figure 9. Due to exposure under Ringer's solution, lap-shear tensile strength of solvent bonding and acrylic adhesive

bonding of polycarbonate deteriorates. The result revealed that in the case of acrylic adhesive bonding, lap shear tensile strength decreases significantly in comparison with solvent bonding of polycarbonate. Therefore, it can be concluded that solvent bonding of polycarbonate is not only stronger but also more durable in respect of adhesive bonding. The retention of bond strength in ambient condition and in Ringer's solution is shown in Table 5.

3.10. Fracture surface analysis of the solvent bonding and the acrylic adhesive bonding of polycarbonate by scanning electron microscope (SEM)

The fracture surfaces of the DCM-solvent-bonded and the acrylic-adhesive-bonded polycar-

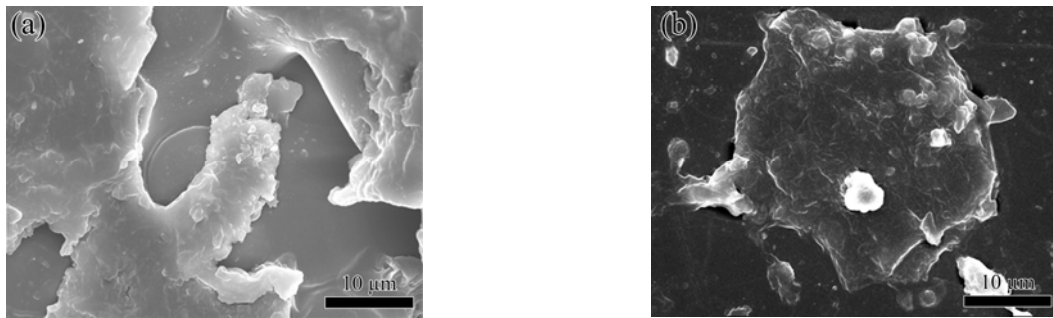


Fig. 10. Fracture surfaces of (a) solvent-bonded polycarbonate and (b) acrylic-adhesive-bonded polycarbonate.

bonate are shown in Figure 10a and b. It may be supposed that the adhesive joints for polycarbonate fail from polycarbonate-adhesive interface as shown in Fig. 10b resulting in a low joint strength. However, the fractography of the solvent bonding of the polycarbonate sample shows a cohesive failure from the adherent as depicted in Fig. 10a, thus resulting in a higher strength.

4. DISCUSSION

This investigation demonstrates the advantages of the solvent bonding over the adhesive bonding for fabrication of polycarbonate and its durability under aggressive surrounding conditions. The basic mechanism of the solvent bonding of a polymer is essentially governed by its solubility in a selected solvent in order to meet the entanglement of polymer chains across the interface and joining two polymer surfaces. Rimdusit et al. [16] have revealed that once solvated, the polymer molecules become mobile and can diffuse across the solvated layer, leading to the entanglement with other similarly dissolved molecules from another polymer piece and, consequently, the mechanical strength depends on polymer solvent interactions.

The mechanical load is homogeneously distributed when the solvent molecules are uniformly dispersed into the matrix of the polymer. Optical microscopic images (Fig. 2) show that the solvent molecules are uniformly distributed into the polycarbonate matrix. This uniformity helps to increase the joining strength of the DCM solvent polycarbonate sheets. When two different phases (gas/liquid, liquid/liquid, gas/solid or liquid/solid) are in contact with each other, the molecules at the interface show imbalance forces. Major cohesive interactions happen in organic materials due to the van der Waals forces, dipole-dipole interaction and hydrogen bonding. Chlorine shows more electronegativity than carbon, and therefore, the chlorine atoms pull out more electrons than the carbon atoms. In addition, carbon is more electronegative than hydrogen; consequently, the central carbon atom has pulled out an electron towards the hydrogen atom. Therefore, chlorine shows partially negative (δ^-) ions and hydrogen partially positive (δ^+) ions,

resulting in the formation of a permanent dipole. Apparently, there is a number of polar groups in polycarbonate chains and consequently, polycarbonate is compatible with polar solvent.

Rios et al. [17] demonstrate that when the contact angle is less than 90° , the substrate has a hydrophilic nature and has polar functional groups. Subedi et al. [18] consider that the contact angle of water on polycarbonate is 70° . Findings of our investigation are in line of those of Rios et al [17] and Subedi et al. [18]. However, due to partial wetting, as evident from Fig. 7, an intimate contact cannot occur when the adhesive spreads over the surface of polycarbonate resulting in a low adhesive bond strength compared to the solvent bonding strength.

The peak at 3452 cm^{-1} may be attributed to the presence of the $-\text{OH}$ group formed *in-situ* by the interaction between the polycarbonate and the acrylic adhesive. When polycarbonate sheets are joined by an acrylic adhesive, there is a possibility of formation of hydrogen bonding between the $-\text{OH}$ group and oxygen atom of the $\text{C}=\text{O}$ group of polycarbonate, resulting in the blue shift of the corresponding $\text{C}=\text{O}$ peak from 1765 to 1732 cm^{-1} . This is clearly supported by the FTIR spectra and shown in Figure 4. The lap-shear tensile strength shown in Figure 8 indicates that even after applying a sufficient quantity of adhesive, the adhesive bond strength is still relatively weak. This is because an increase in quantity of an adhesive increases the stress concentration at the overlap, resulting in deterioration of the adhesive bond strength. However, in the case of the solvent bonding, the solubility parameter of the solvent matches with the substrate, and, therefore, failure changes from an interfacial failure to a cohesive failure as revealed by Ng et al [19]. In our experiments, the solubility parameter is nearly between that of polycarbonate ($\delta = 21$) and dichloromethane [$\delta = (20.2\text{ MJ/m}^3)^{1/2}$], and, consequently, the solvent bonding of polycarbonate shows cohesive failure within the substrate as shown in Fig. 10a and an interfacial failure in the case of the adhesive bonding of polycarbonate as shown in Figure 10b. Therefore, it can be concluded with a high note that the solvent bonding is not only a high-throughput process for fabrication of polycarbonate but also shows much stronger and durable bonding

in comparison to that of the adhesive bonding of polycarbonate.

5. CONCLUSIONS

The solvent bonding is more prominent than the adhesive bonding due to the formations of a strong bond with the shortest curing time under elevated temperature. The solvent bonding of polycarbonate shows dipole-dipole interaction whereas a hydrogen bond is formed in the case of the acrylic adhesive bonding of polycarbonate. The fracture surfaces of the solvent bonding of polycarbonate indicate a cohesive failure from polycarbonate whereas an interfacial failure is observed when polycarbonate is joined by an acrylic adhesive. The solvent bonding is a more durable and high-throughput process than the adhesive bonding. Therefore, solvent bonding will have significant application not only for biomedical but also for joining of transparent polymers for automotive and transportation.

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Реферат

Это исследование способствует обоснованию выбора высокопроизводительного процесса склеивания с использованием растворителя или клея для изготовления изделий из прозрачного полимера, такого как поликарбонат. Исследования с облучением в ультрафиолетовом спектре и в спектре видимого света показывают, что по сравнению с клеевым соединением полимера, диффузионное склеивание с применением растворителя дает более прозрачное соединение. Поликарбонат по своей природе гидрофильный и имеет малый краевой угол в воде, а также обладает полярными функциональными группами на поверхности полимера. Отмечено, что прочность на разрыв при соединении внахлест полимера, склеенного с использованием растворителя, значительно выше, чем у поликарбоната соединенного акриловым клеем, причем склеивание поликарбоната растворителем занимает лишь несколько секунд. По результатам сканирующей электронной микроскопии, разрушение полимера при склеивании с применением растворителя происходит по когезионному механизму и поэтому склеивание растворителем показывает значительно более высокую прочность соединения.

Ключевые слова: адгезия, смачивание, поликарбонат, склеивание растворителем, механические свойства, промышленное применение.