From rosin to high adhesive polyurethane acrylate: Synthesis and properties

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ABSTRACT

A high adhesion polyurethane acrylate (HPUA) was synthesized from isophorone diisocyanate (IPDI), hydroxyethyl acrylate (HEA) and hydrogenated rosin. The chemical structure was characterized by ^{1}H NMR and FTIR; storage modulus and glass transition temperature (T_g) were measured with dynamic mechanical analyzer. Real time infrared spectroscopy (RTIR) was used to investigate the effect of different concentrations of photoinitiator on the double bond conversion of HPUA. Real time volume shrinkage and adhesion on glass, poly(ethylene terephthalate) (PET), polycarbonate (PC) and polyvinyl chloride (PVC) substrates were also measured by laser micrometer and universal testing machine. Results showed that this kind of HPUA has a high photopolymerization rate, low volume shrinkage and high adhesion compared with commercial polyurethane acrylate competitor.

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1. Introduction

Owing to its numerous distinct advantages, such as instant drying, broad formulating range, reduced energy consumption, curing under mild conditions, and less space and capital requirement, UV-radiation technology has quickly developed in many high technical fields [1–3].

In a free radical UV-curing system, one of the biggest problems is low adhesion ability compared with solvent drying or thermo curing counterparts, which can be attributed to larger volume shrinkage and weaker bonding ability. It could lead to worse application properties and low fabrication resolution. The adhesion ability of UV-cured materials can be improved by a number of strategies including introducing organic-inorganic hybrid systems [4], long-chain structure compounds [5,6], and adding adhesion promoters [7] or inorganic nanoparticles [8,9]. However, even with such modifications, deficiencies still exist.

The most important component of UV curable formulations is the oligomer, which decides the polymerization kinetics and the mechanical properties of the cured material, such as hardness, adhesion, flexibility and solvent resistance [10–12]. Polyurethane acrylates, which are usually synthesized from polyols or diols, together with diisocyanates and hydroxyalkyl (meth)acrylates, are the most widely used oligomer types due to their diverse properties and characteristics. Thus, the design and synthesis of new polyurethane acrylates by the use of novel polyols or diols could be one of a promising range of solutions to alleviate this problem.

Rosin is a widely harvested and biodegradable natural product [13–15] which has been applied in many industrial fields. Hydrogenated rosin is the dominant variety of modified rosin with lower toxicity than rosin due to its bulky and high rigid alicyclic structure. This kind of alicyclic structure can decrease volume shrinkage during polymerization in comparison with linear analogues. Also, the carboxylic group of the hydrogenated rosin can react with a variety of groups resulting in structures which can, for example, lead to better adhesion to various materials via the molecular bonding adhesion mechanism [16]. It has been reported that reactions between carboxylic acid and isocyanate groups can result in the formation of amide and imide-urea moieties with the introduction of second isocyanate groups, which can form hydrogen bonding and chemical bonding with the polar groups such as hydroxyl, carboxyl on substrates surface [17–20]. Therefore, low volume shrinkage and high adhesion polymer films could be obtained when the hydrogenated rosin moiety is incorporated into an oligomer structure.

In this study, we aimed to synthesize a new type of bifunctional polyurethane acrylate by hydrogenated rosin, diisocyanate and hydroxyethyl acrylate. It is expected that this new polyurethane acrylate could exhibit smaller volume shrinkage caused by alicyclic structure and better adhesion resulting from imide-urea groups.

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2. Experimental

2.1. Materials

Triethylene propylene glycol diacrylate (TPGDA), 2-hydroxyethyl acrylate (HEA) and CN9001 (an aliphatic urethane acrylate with good adhesion) were supplied by Sartomer (Warrington, PA, USA). Isophorone diisocyanate (IPDI) and hydrogenated rosin were purchased from Shanghai First Reagent Co., (Shanghai, China). Magnesium chloride and butyl acetate were analytical reagent grade and provided by Beijing Chemical Plant (Beijing, China). Dibutyltin dilaurate (DBTL) and p-methoxyphenol (MEHQ) were analytical reagent grade and supplied by Tianjin Fucheng Chemical Plant (Tianjin, China). 2-hydroxy-2-methyl-phenyl-propan-1-one (Darocur1173) was supplied by Ciba (Basel, Switzerland). Butyl acetate was processed with standard method and all other reagents were used as received.

2.2. Synthesis of high adhesion polyurethane acrylate (HPUA)

HPUA was synthesized via a three-step reaction. IPDI (0.1 mol), DBTL (700 ppm) and MEHQ (1000 ppm) were added into a four-necked flask equipped with a mechanic stirrer, thermometer, reflux condenser and dropping funnel. HEA (0.105 mol) was slowly added dropwise to the IPDI through a dropping funnel and temperature was maintained at no more than 40 °C. The progress of reaction was determined by measuring the NCO value using the di-n-butylamine back titration method according to HG/T2409-92 (Industry Standard of China). When the NCO value decreased to 50% of the original value, the first step reaction was regarded as complete.

The reaction temperature was then raised to 75 °C and the hydrogenated rosin (0.05 mol) dissolved into 50 mL butyl acetate with MgCl$_2$ (0.1 wt%, as catalyst) was added. The second step reaction was monitored by FTIR. When the COOH peak (around 1690 cm^{-1}) disappeared, the second step reaction was regarded as complete.

Finally, the reaction temperature was raised to 100 °C and the mixture stirred at this temperature until the FTIR peak at 2267 cm^{-1} for the –NCO group disappeared. The reactant was precipitated by petroleum ether, filtrated and dried under a vacuum system, which was then purified by column chromatography with combination eluent of 70 wt% ethyl acetate and 30 wt% petroleum ether, giving a faint yellow solid HPUA after vacuum drying at 30 °C at 10 mmHg for 24 h. The synthetic route for this process is shown in Scheme 1.

2.3. Measurement

The ^{1}HNMR spectrum was recorded by a Bruker AV600 unity spectrometer operated at 600 MHz using CDCl$_3$ as solvent.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 instrument (Thermoelectric, USA). Real-time infrared spectroscopy (RTIR) was used to determine conversion of double bonds. The formulations (Table 1) were applied between two KBr crystals and irradiated with UV radiation with a UV spot light source (Rolence-100 UV, Taiwan, China) with 25 mW/cm^2 light intensity at room temperature. The degree of conversion (DC) of the double bond was calculated from the peak area at each reaction time by the following equation [21].
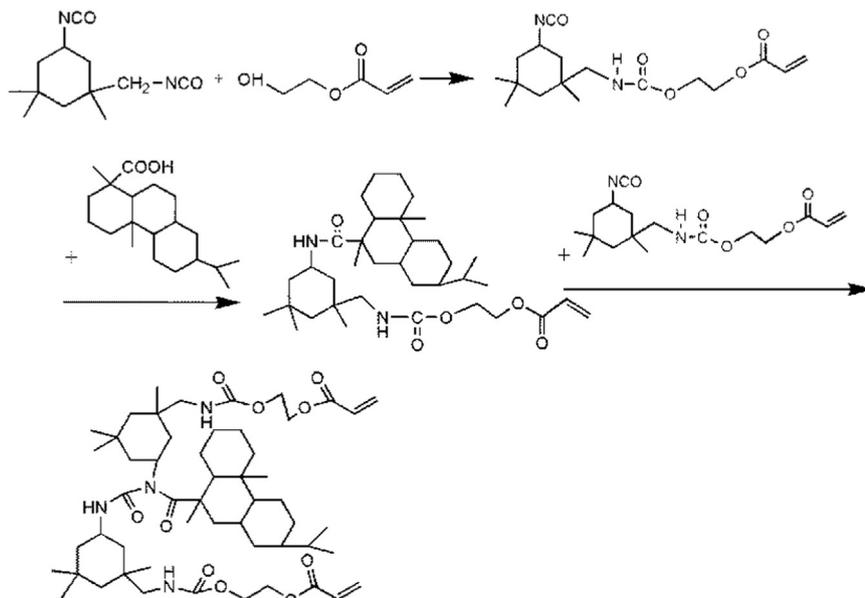
$$DC(\%) = (A_0 - A_t)/A_0 \times 100$$

DC is the degree of conversion of double bonds at time t, A_0 and A_t are the peak area of the double bond around 810 cm^{-1} before irradiation and at time t.

Glass transition temperature (T_g) was indicated by the peak in the tan δ curve measured through dynamic mechanical analyzer (METZSCH 242 C, Germany) with 1 Hz frequency and 5 mm strain amplitude. Temperature scans were carried out in a N$_2$ atmosphere from -50 to 140 °C with a heating rate of 5 °C/min. Specimen dimensions were $10 \times 5 \times 1$ mm^3. Specimens were irradiated by a UV plane light source (RW-UVAC301-40bh, Runwo Co., China) under light intensity at 30 mW/cm^2 for 60 s.

The photopolymerization volume shrinkage of the various formulations investigated were obtained using a LK-G laser micrometry technique developed by our lab [22]. The thickness of

Table 1
Formulations investigated (wt%).

Component	S1	S2	S3	S4	S5	S6
CN9001	80	60	50	40	20	0
HPUA	0	20	30	40	60	80
TPGDA	20	20	20	20	20	20

Scheme 1. Reaction route for the synthesis of HPUA.

the sample layer was controlled to around 100 μm by coating the sample on glass slides (1 mm thickness). The ø30 μm laser beam was initially zeroed onto the glass slide, then reflected off the surface of the sample to give the thickness of the sample layer. The measurements of dimensional changes were conducted at room temperature under a UV spot light source irradiation (Rolence-100 UV, Taiwan, China) with 25 mW/cm^2 light intensity, with a sampling interval of 10 ms.

Levels of adhesion were assessed on glass, PET, PVC and PC substrates with a universal testing machine (Model 1185, Instron USA) according to China national standards GB 7124-86. Formulations for adhesion testing were prepared by mixing different ratios of oligomer and TPGDA with 3 wt% Darocur1173 (to total mass of oligomer and monomer), as shown in Table 1. After uniformly coating formulations to form about 35 μm liquid film on the various 10 mm wide substrates, a piece of coated substrate was overlapped to a blank one with cross area of 10×20 mm^2, then irradiated by a UV plane light source (RW-UVAC301-40bh, Runwo Co., China) under light intensity 30 mW/cm^2 for 60 s. The UV-cured systems were tested by using the testing machine with a crosshead speed of 5 mm/min at room temperature. Five samples were measured for each experiment, and the average was reported.

3. Results and discussion

3.1. Synthesis of HPUA

The shrinkage or volume reduction of formulations during the UV curing process can affect adhesion strength, since high
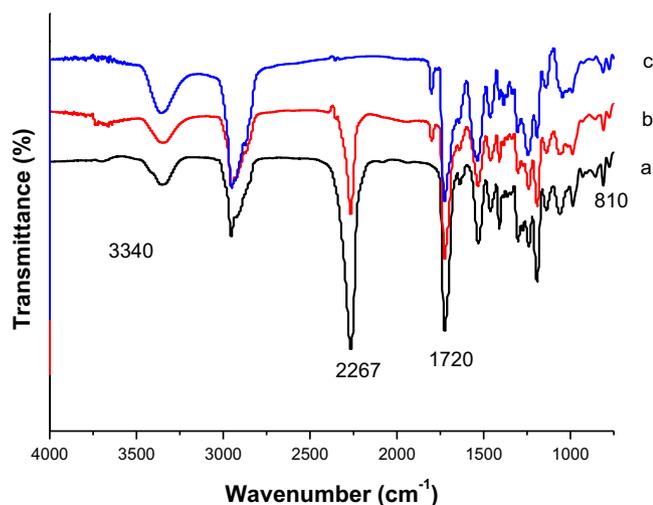

Fig. 1. The IR spectra of synthesized first step product (a), second step product (b) and HPUA (c).
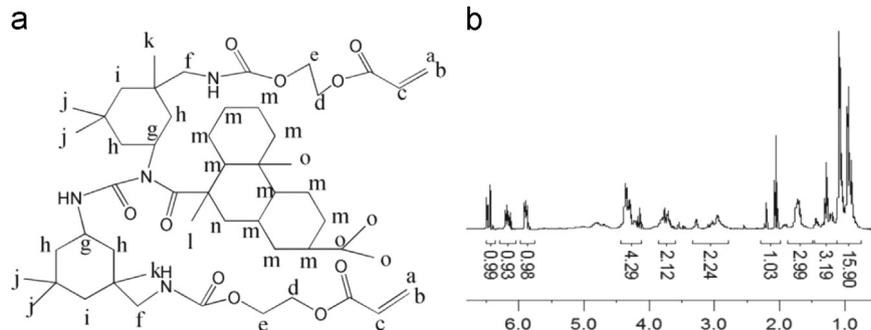
shrinkage can induce a considerable amount of internal stress which can lead to a cured film peeling away from a substrate [23]. If some functional groups of resins could form hydrogen or chemical bonding with polar groups such as hydroxyl or carboxyl on the surface substrates, the adhesion between cured film and substrate could be improved [24]. Therefore, in an attempt to mitigate such effects we designed a polyurethane acrylate oligomer containing a bulky alicyclic structure and imide-urea group, which was synthesized from IPDI, HEA and hydrogenated rosin.

In the synthesis of HPUA, the biggest problem is how to improve the reaction of hydrogenated rosin with the product of the first stage, because the reaction of isocyanate with carboxylic acids is one of the less utilized reactions in isocyanate chemistry. Typically, for the reaction of aliphatic carboxylic acids with aliphatic isocyanate, high reaction temperatures (about 140 °C) and long reaction times have been necessary [25]. However, high temperature will lead to polymerization of double bonds thus destroying the whole oligomer system. In order to solve this problem, MgCl$_2$ was selected as catalyst for the first time, because it has been reported that MgCl$_2$ could promote the extrusion of CO$_2$ from the addition product of the isocyanate and carboxylic acid [26,27]. Results showed that the reaction temperature and time could be reduced to within a reasonable range.

The FTIR spectra of synthesized HPUA (Fig. 1) showed that the absorption peak at 2267 cm^{-1} of the NCO group disappeared. The absorption peak at 810 cm^{-1} illustrates that the acrylate double bond has been incorporated into the polyurethane structure, and the absorption peak at 1800 cm^{-1} indicates the formation of an imide-urea structure. The absorption peak at 3330–3600 cm^{-1} belongs to N–H, 2855–2955 cm^{-1} can be assigned to C–H, and 1720 cm^{-1} is ascribed to C=O, respectively [28]. The chemical structure and ^{1}H NMR data of synthesized HPUA are shown in Fig. 2. The peaks at $\delta = 6.44$, 5.87 and 6.14 ppm belong to H$_a$, H$_b$ and H$_c$, which indicates the existence of acrylate groups in the HPUA structure. The peaks at 2.9, 3.7 and 4.3 ppm can be attributed to H$_d$, H$_e$, H$_f$ and H$_g$, with the peaks within the range 0.9–2.06 ppm being attributed to C–H$_2$ and C–H$_3$ containing structures [19,28]. The area integration of the peaks are consistent with theoretical calculated values.

3.2. Mechanical and thermal properties

Fig. 3(a) and (b) indicate the dependence of storage modulus (E') and tan δ on temperature for samples S1–S6, respectively. As indicated sample S6 exhibits the highest E', with E' of samples increasing as the ratio of HPUA increased. At the same time, the glass transition temperature (T_g) of samples increased as the content of HPUA was increased, with sample S6 exhibiting the highest value. One likely reason for this is a higher crosslinking degree of HPUA resulting from a higher double bond density. Although both the HPUA and CN9001 systems have two double

Fig. 2. The assignation of hydrogen atoms (a) and ^{1}H NMR spectrum (b) of HPUA.

bonds, much higher calculated molecular weight of CN9001 ($M=2813$) than HPUA ($Mn=942$) leads to much less double bond density. On the other hand, it can also be attributed to the high rigidity of the bulky alicyclic moiety in the molecular backbone of HPUA, which restrains the movements of polymer segments and consequently increases T_g [20,29,30].

3.3. Photopolymerization kinetics of synthesized oligomer

It can be seen (Fig. 4) that the double bond conversion of HPUA with different initiator concentrations (0.5, 1, 2 and 3 wt% Darocur1173) increases upon irradiation by UV light and reaches a maximum (around 50–80%) at very short time, which shows a very good photopolymerization activity. Also the double bond conversion increases with the initiator concentration resulting in more free radicals and higher initiating speed. It is also shown (Fig. 5) that the sample S1, consisting of 80 wt% CN9001 and 20 wt% TPGDA, exhibits the highest polymerization rate with sample S6, comprising 80 wt% HPUA and 20 wt% TPGDA, exhibiting the lowest. This could be attributed to a larger stereo effect and higher T_g of HPUA caused by bulky alicyclic moieties in comparison to CN9001, which would lead to a reduction in polymerization activity.

3.4. Volume shrinkage

Fig. 6 shows the volume shrinkage of the samples listed in Table 1 which occurs with 3 wt% Darocur1173 following UV-curing. It can be seen that sample S1 shows the highest volume shrinkage, which is about 4.20%, with sample S6 exhibiting the smallest volume shrinkage, at approximately 1.75%, even though it has the highest double bond density. The volume shrinkage of samples decreases as the content of HPUA is increased. This can be attributed to the bulky alicyclic structure inherent to the HPUA system thus resulting in lower volume shrinkage in comparison to CN 9001 following UV cure.

3.5. Adhesion ability

From Fig. 7, it shows that the HPUA system exhibits better adhesion on glass, PVC, PC and PET than CN9001, because the adhesion on these substrates is gradually improved as the content of HPUA is increased. This result could be explained with two reasons: one is very small volume shrinkage of the HPUA, which leads to less internal stress during UV-curing; second reason is the existence of an imide-urea structure in HPUA, which could form strong hydrogen and chemical bonding with various substrate surfaces. One example worthy of note is that the adhesion of S6 on PET is also improved by about 50% compared with S1. Because it is well known that PET is largely non-polar in character and therefore difficult to achieve good adhesion, [31,32], the adhesion of HPUA on glass, PVC or PC substrates is better than with a PET substrate. Also, the higher polarity of glass leads to a greater improvement in adhesion in relation to the other substrates with increasing HPUA content.

4. Conclusions

A novel polyurethane acrylate was synthesized from IPDI, HEA and hydrogenated rosin. The photopolymerization kinetics, characterized by real time FTIR, shows good reaction rate and photo-initiator concentration dependence. The storage modulus and the glass transition temperature of HPUA are about 3.25 GPa and 54.4 °C respectively according to DMA results. The volume shrinkage of HPUA is about 1.75%, much lower than commercial oligomer CN9001 and the adhesion to glass, PET, PVC and PC substrates are 4.56, 0.82, 1.91 and 2.01 MPa respectively, much higher than its comparing sample. The results indicate that HPUA is promising as a UV curing oligomer for low volume shrinkage and high adhesion demand.
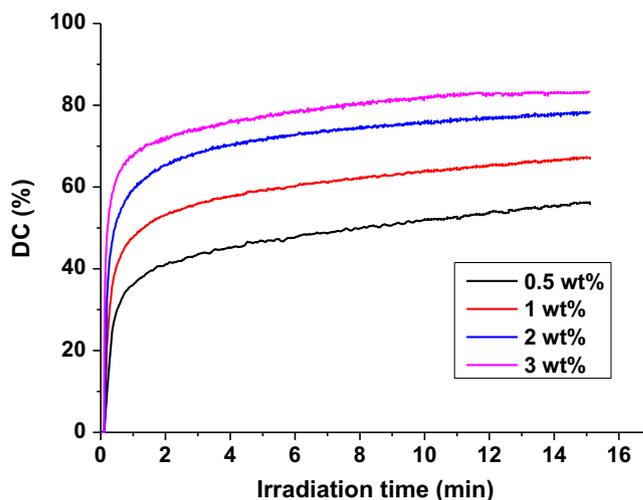

Fig. 4. Effect of initiator Darocur 1173 concentration on photopolymerization of HPUA, $I=25$ mW/cm^2.
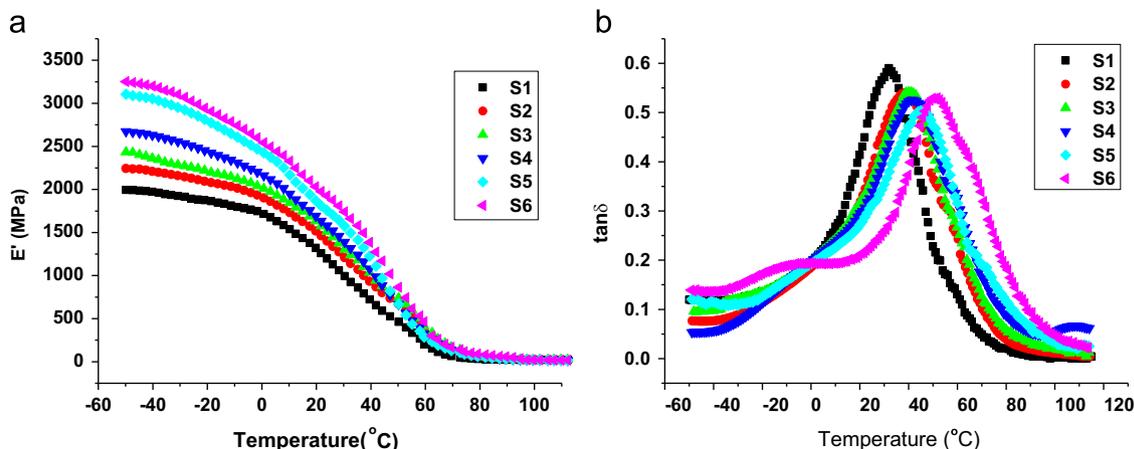

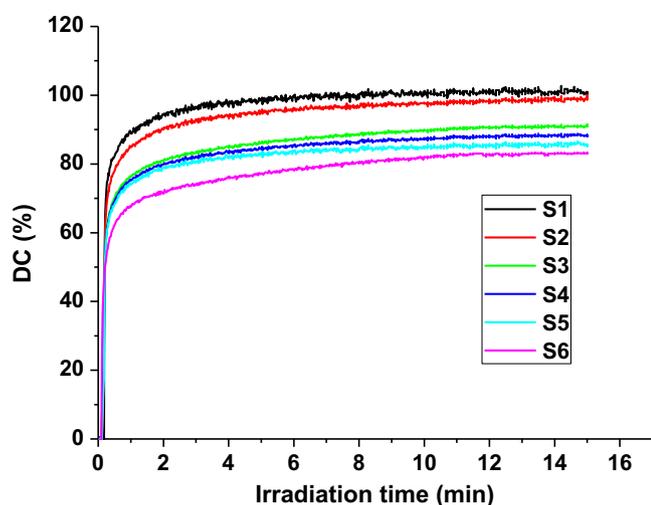**Fig. 3.** The storage modulus E' (a) and tan δ (b) curves for the various formulations.

Fig. 5. Double bond conversion as a function of irradiation time for the various formulations, $I = 25$ mW/cm^2, Photoinitiator: 3 wt% Darocur 1173.
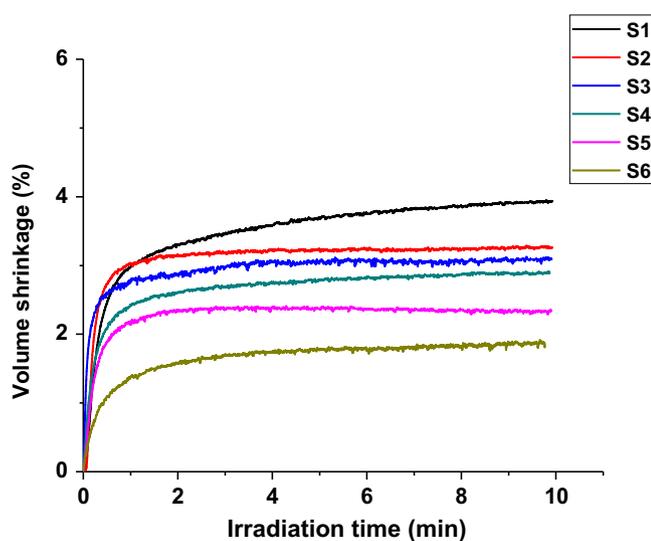

Fig. 6. Volume shrinkage as a function of irradiation time for the various formulations, $I = 25$ mW/cm^2, Photoinitiator: 3 wt% Darocur 1173.
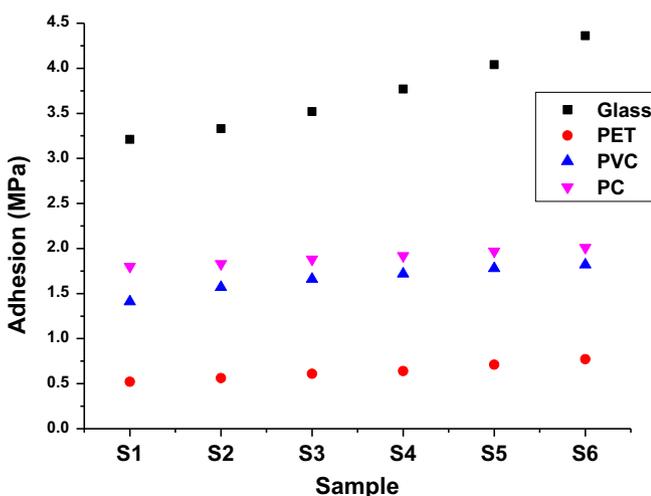

Fig. 7. Adhesion values for the various formulations as a function of substrate type, $I = 30$ mW/cm^2, Photoinitiator: 3 wt% Darocur1173.

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