Water Resistance and Optical Properties of Optical Adhesives Containing Strong Hydrophobic Components

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(Received October 6, 2003; Accepted December 29, 2003)

ABSTRACT: To produce high performance optical adhesives, adhesives were prepared by mixing triethoxy vinylsilane (TVSi) as a silane coupling agent into basic compositions consisting of 15 wt% 2-hydroxyethyl methacrylate (HEMA), *oligo*-siloxanyl dimethacrylate (SiMA) and acrylicacid tricyclo [5,2,1,0^{2,6}] decane (TCDA). When the composition includes TCDA from 43 to 69 wt%, copolymers polymerized from the composition exhibit high adhesion strength to glass, good optical transparency and excellent water-resistance. The high quality of the adhesives comes from microscopically homogeneous structures of the copolymers in which all components are mixed randomly.

KEY WORDS Adhesive Composition / Phase Structure / Water Resistance / Silane Coupling Agent /

In assembling optical devices, optical adhesives are important for combining optical parts such as optical fibers, lenses and prisms. The adhesives must have high adhesion strength to glass and excellent optical transparency. Fluorine-containing optical adhesives are such adhesives.^{1,2} We reported other optical adhesives consisting of dimethacryloxypropyl *oligo*-dimethylsiloxane (SiMA), 2-hydroxyethyl methacrylate (HEMA) and acrylicacid tricyclo[5,2,1,0^{2,6}]decane (TCDA).^{3,4}

For an optical device that needs higher-level reliability, optical adhesives having excellent water resistance are required, because moisture in air often deteriorates adhesion strength.^{5–7} This manuscript describes a trial to add high water resistance to adhesives and obtain excellent optical adhesives. We discuss the structural origin of the high efficiency that optical adhesives possess.

This paper proposes new adhesive compositions of SiMA, HEMA, TCDA and triethoxy vinylsilane (TVSi). These compositions include TVSi as a silane coupling agent to produce high-performance optical adhesives with good water resistance. Silane coupling agents, well known in the field of fiber-glass reinforced plastics, improve mechanical strength even in a humid atmosphere.^{8–10} Fiber glass and the coupling agent are connected by chemical bonds under suitable conditions.¹¹ Little research on adhesives including silane coupling agents has been performed so far, because the silane coupling agents added to the hydrophilic adhesives are unstable and are hydrolyzed and condensed easily by water absorbed by the hydrophilic groups.¹² For copolymers consisting of SiMA, HE-

MA, TCDA and TVSi, it is expected that the strong hydrophobicity of SiMA and TCDA protects the silane coupling agent from water.

EXPERIMENTAL

Materials

The chemical structures of components in the adhesive compositions are shown in Table I. HEMA includes a hydroxyl group and has good adhesive strength to glass in dry condition. SiMA has good wettability to glass surface because of the low cohesive force of polydimethylsiloxane chains. HEMA is not dissolved in SiMA. Substituting TCDA for a part of SiMA, however, makes SiMA and HEMA compatible. Adhesive compositions are shown in Table II. Triethoxy vinylsilane (TVSi) was used as a silane coupling agent. Ethoxy groups of TVSi produce Si–O–Si bonds with glass surface,⁹ and vinyl groups of TVSi are expected to have chemical affinity for the compositions. A small amount of 1-hydroxycyclohexyl phenylketone (HCPK) was added to initiate radical photopolymerization.

Adhesion Test

A pair of Pyrex glass rods with polished edge ($\phi 20 \times 25$ mmH and $\phi 6 \times 10$ mmH) was used as adherends for an adhesion test. The pair was bonded by the adhesive compositions photopolymerized by irradiation of ultraviolet rays 5 mW cm^{-2} from a 400 W high-pressure mercury lamp for 10 min.

Compressive shear force was applied to the interface of the bonded glass rods using a universal tester

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Table I. Properties of adhesive components

	Structural formula	Molecular weight	Purity % (GC)
HEMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$	130	≥ 98
SiMA	$ \begin{array}{ccccccc} \text{CH}_2=\text{C}-\text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 & & \text{H}_3\text{C}-\text{C}=\text{CH}_2 \\ & & & & & & \\ \text{COO}(\text{CH}_2)_3-[\text{Si}-\text{O}]_n-\text{Si}-\text{O}(\text{CH}_2)_3-\text{OCO} \\ & & & & \\ \text{CH}_3 & & \text{CH}_3 & & \end{array} $	$M_n = 1522$ $M_w/M_n = 1.537$ $n \approx 16$	≥ 97
TCDA	$ \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{COO} - \text{[Bicyclic structure]} \end{array} $	206	≥ 98
TVSi	$\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_2\text{CH}_2)_3$	146	≥ 98
HCPK	$ \begin{array}{c} \text{Ph}-\text{C} \\ \\ \text{O} \\ \\ \text{OH} \end{array} $	204	

Table II. Prepared adhesive compositions (wt%)

Run no.	SiMA	HEMA	TCDA	TVSi
1	70	15	15	
2	55	15	30	
3	35	15	50	
4	15	15	70	
5	0	15	85	
6	69	15	11	5
7	57	15	23	5
8	46	15	34	5
9	34	15	46	5
10	23	15	57	5
11	11	15	69	5
12	0	15	80	5
R1	100			
R2		100		
R3			100	
R4	95			5
R5		95		5
R6			95	5

with the apparatus shown in Figure 1. The adhesion test was carried out on dry and wet samples immersed in hot water at 80 °C for 20 h, or set in saturated water vapor at 40 °C for 168 h.

Transparency and Turbidity Measurements

Test films were made by photopolymerization from adhesive compositions with thickness 0.3 mm placed between transparent, low alkaline-glass substrates. The sample included a pair of glass substrates. The refractive index of the glass was 1.53. Theoretical upper-limit of optical transmittance of the sample was *ca.* 91%, because the measured transmittance included

Figure 1. Schematic diagram of adhesion test.

light reflection loss due to mismatching of refractive indices at the interfaces between low alkaline-glass and air, and between the glass and adhesives. Turbidity of the polymerized samples was estimated by optical transparency measured by a spectrometer.

Microscopic Observations

The polymerized samples of 50 μm thickness were tinted in 1 wt% Rhodamine B solution at 60 °C for 10 min. The phase structures of the samples were observed with a 900-power optical-microscope. Optical absorbance of the tinted samples was measured by a spectrometer.

Water Absorption of Samples

Water absorption was measured after immersion in water for 20 h at room temperature.

Table III. Properties of prepared polymers and copolymers

Run no.	Optical transmittance %T at 450 nm	Adhesion strength			Water absorption (%)
		Dry (N mm ⁻²)	80 °C Wet (N mm ⁻²)	40 °C Wet (N mm ⁻²)	
1	47.5	6.0	0.7	1.3	3.2
2	62.1	13.7	0.8	4.2	3.0
3	88.4	14.1	0.1	1.7	2.4
4	90.6	14.7	0.2	2.3	1.9
5	90.5	10.1	1.6	1.4	2.0
6	50.2	11.3	3.5	3.6	3.5
7	60.8	7.9	2.6	3.6	2.6
8	83.4	10.7	6.8	6.9	2.0
9	90.8	14.0	12.2	12.1	1.3
10	90.6	15.6	14.7	14.5	1.5
11	91.0	16.3	15.1	14.0	2.1
12	91.2	8.3	15.4	6.7	2.5
R1	90.6	4.5	0.2	1.9	0.5
R2	90.7	10.1	2.0	3.2	71.2
R3	90.8	6.0	1.3	5.0	0.7
R4	91.0	2.0	2.3	3.4	1.0
R5	39.5	8.0	1.4	5.8	65.8
R6	91.0	5.3	13.2	3.7	0.8

Figure 2. Adhesion strength of copoly(SiMA/HEMA/TCDA). ○: dry condition, ●: after immersion in hot water at 80 °C for 20 h, ▲: after kept in humid atmosphere at 40 °C for 168 h.

RESULTS AND DISCUSSION

Experimental results are summarized in Table III.

Adhesion Strength

Authors reported new optical adhesives consisting of SiMA, HEMA and TCDA easily copolymerized by ultraviolet irradiation at room temperature.^{3,4} Figure 2 shows adhesion strength of the copoly(SiMA/HEMA/TCDA) as a function of TCDA content and strength to increase with TCDA content in the dry condition and become 14 N mm⁻² at TCDA from

Figure 3. Adhesion strength of copoly(SiMA/HEMA/TCDA/TVSi). ○: dry condition, ●: after immersion in hot water at 80 °C for 20 h, ▲: after kept in humid atmosphere at 40 °C for 168 h.

30 to 70 wt%. Figure 2 shows adhesion strength to decrease remarkably in a humid atmosphere. The strength of the wet samples immersed in hot water significantly dropped to less than about 1 N mm⁻².

Figure 3 illustrates adhesion strength of copoly(SiMA/HEMA/TCDA/TVSi) samples at constant TVSi to enhance water-resistance. Adhesion strength increased with TCDA content in the dry condition. The strength of wet samples increased with TCDA content. Adhesives having high water resistance were obtained at TCDA from 46 to 69 wt%. Water resistance depends strongly on TCDA content. In samples with low TCDA, the water-resistant effect of TVSi

Figure 4. Adhesion strength of homopolymers of SiMA, HEMA and TCDA and copolymers with TVSi. □: dry condition, ▨: after immersion in hot water at 80 °C for 20 h. ■: after kept in humid atmosphere at 40 °C for 168 h.

was not found. In those samples, SiMA and HEMA are separated, resulting in the formation of regions of poly(HEMA) and poly(SiMA). Poly(HEMA) is invaded by water as seen in Table III and water-resistant effect of TVSi is lost.

Replacement of SiMA by TCDA promoted random copolymerization of SiMA, HEMA and TCDA and microscopically homogeneous structure was formed when TCDA content increased. The homogeneous structure of the copolymer in which all components are mixed randomly, improves water resistance.

Adhesive strength at TCDA content higher than 69% in dry and humid conditions at 40 °C decreased again due to plasticizer effect of residual monomers of TCDA.

Figure 4 compares adhesive strength of homopolymers of SiMA, HEMA, and TCDA and copolymers with TVSi with copoly(SiMA/HEMA/TCDA/TVSi). Adhesiveness was very bad in comparison with that of copoly(SiMA/HEMA/TCDA/TVSi). Copoly(TCDA/TVSi) showed strange behavior that wet samples immersed in hot water at 80 °C had stronger adhesion than dry samples. Residual monomers in samples after ultraviolet irradiation at room temperature may polymerize because of annealing at 80 °C for long time (20 h).

The cause of the survival of monomers and short chains is that the glass transition temperature of poly(TCDA) of *ca.* 120 °C is much higher than room temperature. Residual monomers and short chains of TCDA cannot meet with other molecules at room temperature when surrounded by immobile long chains. This does not occur in other samples except TCDA because the glass transition temperature of poly(SiMA) is below −100 °C due to *oligo*-dimethylsiloxane¹³ and poly(HEMA) is at most 60 °C.¹⁴

Optical Transparency

Optical transmittance at 450 nm of copoly(SiMA/HEMA/TCDA/TVSi) is plotted against TCDA con-

Figure 5. Optical transmittance of copoly(SiMA/HEMA/TCDA) and copoly(SiMA/HEMA/TCDA/TVSi). ○: copoly(SiMA/HEMA/TCDA/TVSi) ●: copoly(SiMA/HEMA/TCDA).

tent in Figure 5, where transmittance of copoly(SiMA/HEMA/TCDA) is plotted for comparison. Transmittance increased with TCDA and leveled off at 46 wt%. Transmittance at 46 wt% TCDA content was 91% nearly equal to the theoretical upper-limit of the sample, which includes the light reflection loss due to mismatching of refractive indices between air and glass.

The same was observed for samples without TVSi, but samples including TVSi showed higher transparency than without TVSi at TCDA content below *ca.* 50 wt%.

Transparency of the copolymer samples varied with TCDA. In Figure 6, absorbance spectra in the frequency range of visible radiation are plotted against reciprocals of the 4th power of wavelength. Samples No. 6 and No. 7 with TCDA at less than 23 wt% were turbid and light absorbance decreased with TCDA. Absorbance spectra increased nonlinearly with increase in λ^{-4} , indicating the existence of a fairly large heterogeneous structure that scatters light. Light absorbance of sample 8 with TCDA 34 wt% varied linearly with λ^{-4} . Rayleigh scattering may thus occur due to parti-

Figure 6. Optical absorbance vs. λ^{-4} plots of copoly(SiMA/HEMA/TCDA/TVSi).

Figure 7. Microscopic images of copoly(SiMA/HEMA/TCDA/TVSi), copoly(HEMA/TVSi), copoly(SiMA/TVSi) and copoly(TCDA/TVSi) after soaking in 1 wt% Rhodamine B solution at 60 °C.

cles less than 0.1λ .^{15,16} Samples with TCDA more than 46 wt% were colorless and transparent, and absorbance spectra were nearly constant against λ . There is thus no heterogeneous structure that scatters light. Samples 9, 10, 11 and 12 exhibited good transparency in all visible light regions like optical glass or resin such as PMMA.

Microscopic Observation

Microscopic images of samples 6 to 12 and from R4 to R6 are shown in Figure 7. In samples 6 and 7 with TCDA less than 23 wt%, heterogeneous structures were observed, showing regions tinted well by Rhodamine B and which are over $1\mu\text{m}$ in diameter. Rhodamine B tints only the HEMA component in these three homopolymers of SiMA, HEMA and TCDA as seen in Figure 7. The tinted regions thus form by the aggregation of the HEMA component. The size of a region decreased with TCDA content and a fine phase-separated structure was formed at 34 wt% of TCDA (No. 8). A microscopically homogeneous structure was obtained at TCDA more than 46 wt%, supporting the considerations in Figures 3, 5 and 6.

Optical absorbance of samples at 595 nm, due to the absorption of Rhodamine B, is plotted against TCDA in Figure 8. Absorbance at 650 nm was subtracted from the original value at 595 nm to eliminate the influence of light scattering. Absorbance at 0 wt% TCDA was calculated from sample R5 to make HEMA content equal to that of other samples. Absorbance decreased monotonically with TCDA up to

Figure 8. Optical absorbance of copoly(SiMA/HEMA/TCDA/TVSi) after soaking in 1 wt% Rhodamine B solution at 60 °C.

46 wt%, although the quantity of HEMA was the same. The structure of the copolymer may thus change continuously with TCDA content.

In samples with small amounts of TCDA, the HEMA component was condensed by itself, as indicated by the tinted regions for samples 6 and 7 in Figure 7. The size of the condensed region decreased with TCDA, because some HEMA monomers were copolymerized with SiMA and TCDA. Optical absorbance also decreased. Above TCDA content of 46 wt%, nearly all HEMA monomers were copolymerized with SiMA and TCDA randomly. A microscopically homogeneous structure was formed and not tinted by aqueous Rhodamine B solution, since HEMA component was mixed microscopically with SiMA and

TCDA components having strong hydrophobicity. Thus, the effect of TVSi was protected from water.

CONCLUSIONS

SiMA/HEMA/TCDA/TVSi with HEMA of 15 wt%, TVSi of 5 wt% and TCDA of 46 to 69 wt% was high-quality optical adhesives showing high adhesion strength to glass, excellent water resistance and good optical transparency in regions visible light. They are promising optical adhesives for assembling micro optical components in optical devices and medical apparatus. Excellent properties of the adhesives are due to homogeneous structures of polymers copolymerized randomly.

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