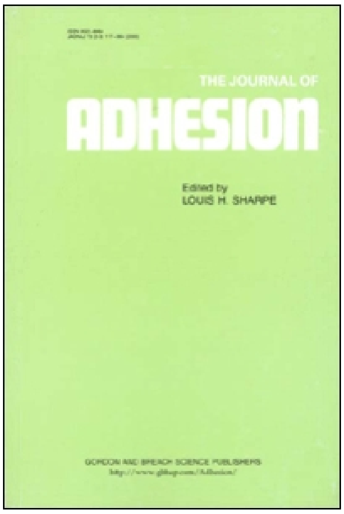

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Mechanical and Optical Properties of UV-Curable Modified Acrylic Adhesives

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Ultraviolet (UV) curable modified acrylics constitute a unique class of polymers for optical bonding applications due to their transparency. To elucidate their adhesion characteristics two UV-curable modified acrylics, including rigid and flexible formulations, were evaluated. Two main aspects were investigated. First, durability in hot-humid environment, in combination with epoxy, amine and methacryl terminated silanes, was assessed. Secondly, the optical transparency of the modified acrylic adhesives in the visible and infra-red regions of the spectra was measured. Transmittance was evaluated for the neat adhesives and for the cases where silanes were used both as surface primers as well as additives incorporated into the adhesives.

Experimental results show conclusively that enhanced mechanical properties are obtained when silanes are utilized as primers, especially for strength endurance in humid environments. Best performance for the rigid and flexible UV-curable adhesives was obtained when the methacrylic-terminated silane was used. Furthermore, when silanes were used as primers or directly incorporated into the adhesives, some improvement in transmittance was observed in all regions of the spectra. Generally, the UV-curable adhesives studied exhibited more than 90% transparency in the visible and near infra-red regions. Due to inherent absorbing bands, close to 3.5 and 5.5 μm and in the whole range of 8 to 12 μm, transmittance levels are low in these regions. These results indicate that acrylic adhesives in particular and polymer adhesives generally are inadequate optical adhesives in the latter region.

KEY WORDS UV-curing; acrylic adhesives; silanes; optical properties; mechanical properties; durability.

INTRODUCTION

Preparation of adhesively bonded joints requires that, at some time in the bonding operation, a liquid adhesive with good wettability characteristics should be transformed to a solid state with appropriate interfacial as well as cohesive properties.

The liquid-to-solid transformation may be accomplished by solvent removal in the case of solubilized adhesives, cooling for thermoplastic adhesives, or by chemical reaction for condensation or addition-type thermosetting adhesives. The latter group of adhesives comprise three distinct steps in the curing reaction—initiation, propagation and termination. Initiation is the critical step in the reaction and may be obtained in elevated or room temperature conditions, provided it is catalysed by some source, such as dissolved peroxide, mechanical rupture of encapsulated hardener, presence of moisture (e.g. RTV silicones), absence of oxygen (e.g. anaerobics) or by ultra-violet (UV) light. Commonly, room-temperature-curing adhesives are single-part formulations protected from the catalyzing source until needed for use. Initiation of the cross-linking reaction in UV-curable adhesives is triggered at a wavelength of 200–400 nm followed by free radical formation and subsequently an addition-type polymerization proceeds.[1–6] Commonly, UV-curable adhesives are based on acrylic, epoxy and urethane polymers that include an acrylate (or methacrylate) moiety[2] through which propagation takes place.

The ability to control the initiation step of the curing reaction by both the radiation wavelength and its intensity leads to wide use of UV-curable resins. However, in bonding applications at least one of the adherends has to be transparent to UV radiation. Consequently, UV-curable adhesives are commonly used for bonding transparent optical components such as lenses and glass sheets. For optical applications, UV-curable modified acrylics are used,[3] as a result of their low shrinkage, good interfacial strength, enhanced environmental endurance and good high temperature properties.[4,5]

The optical, mechanical and durability properties of UV-curable, modified-acrylic adhesives were characterized, among other optical adhesives for bonding applications of transparent glasses.[7]

The objectives of the present study were to investigate rigid and flexible formulations of UV-curable acrylic adhesives with respect to the resulting mechanical, optical and durability properties of adhesively-bonded borosilicate glass adherends. The interfacial as well as cohesive characteristics of the adhesives were studied following application of three selected silane coupling agents to the glass surfaces or after direct addition of the silanes into the adhesives.[8,9]

METHODOLOGY AND OBJECTIVES

Two UV-curable, modified acrylic adhesives were characterized with respect to their optical, mechanical and durability properties. The methodology used in the present study followed that used in our previous investigation.[7]

The two selected UV-curable acrylics were of high and low moduli, respectively, commonly used for optical bonding of glasses or for bonding glass to metal.

Joints composed of borosilicate glass adherends were characterized with regard to adhesion strength and durability following application of silanes to the adhesive-adherend interface. The silanes were selected on the basis of their functional groups[8,9] to match those of the glass and adhesive respectively. Consequently, epoxy, amine and methacryloxy-terminated silanes were chosen on the basis of their chemical affinity to the modified-acrylic adhesives.

In the initial stage of the study, the mechanical properties of the adhesive-silane combination, using a modified flat-wise tensile specimen, were investigated. In the next stage, the effect of heat and humidity on the mechanical properties of the UV-curable adhesive and the respective silane coupling agents, was evaluated.

In a subsequent part of the study, the transmission properties of the rigid and flexible acrylics were evaluated in the 0.4–0.7 μm, 0.9–1.2 μm, 3–5 μm and 8–12 μm regions of the spectrum. In this case, the effect of application of the silanes on the optical properties was studied. The various silane types were applied either as surface primers or directly incorporated into the acrylic adhesives prior to radiation. The latter case was aimed at determining the effect of viscosity reduction of the adhesive due to silane addition. Lower viscosity was envisioned to reduce interface scattering and reflection as a result of better penetration of the adhesive into the glass surface imperfections. Furthermore, addition of silanes directly to the adhesives may be a necessity in order to avoid direct contact of the aqueous silane solution with a water-sensitive substrate, as may be the case with NaCl optical elements.

MATERIALS AND PROCESSES

Adhesives

Two UV-curable adhesives were included in the present study. The first was a high modulus (150 ksi), high strength (3 ksi) adhesive (Noa 61). The second was a low modulus (20 ksi), low-strength (1.5 ksi) adhesive (Noa 65). Both adhesives are products of Norland Products Inc., North Brunswick, NJ, U.S.A. The adhesives are one-part, 100% solids, low viscosity, clear and colorless liquids at room temperature. Curing time is relatively short and depends on the adhesive thickness and the light intensity at 350–380 nanometers.

Coupling agents

Three silane types were used in the investigation. The first was γ-glycidoxypropyltrimethoxy silane (A-187), the second—γ-methacryloxypropyltrimethoxy silane (A-174), and the third—γ-aminopropyltriethoxy silane (A-1100). All three are manufactured by Union Carbide.

The silanes were either dissolved in water/ethanol (50/50 v/v) to 1% and applied by brushing to the glass adherends or added directly to the adhesive (1% by weight) prior to application of the adhesive to the adherends.

Curing conditions

Curing was carried out in three steps. In the first step, the joint was exposed to UV for a short duration (a few seconds) to achieve initial setting. In the second step, the joint was exposed for 5 minutes at a distance of 5 inches from a 100-watt lamp.† Finally, specimens were kept at room temperature (20–25°C) for 30 days, prior to environmental conditioning and testing.

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† Mercury lamp, Model B-100A, manufactured by Ultraviolet Products, U.S.A.

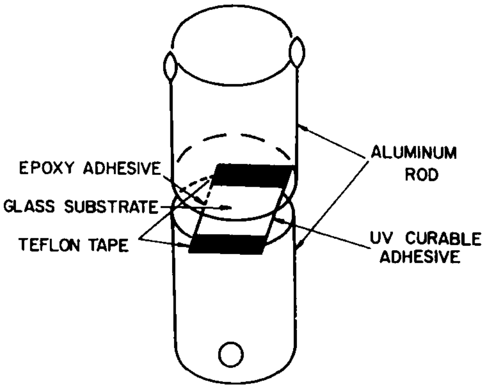

FIGURE 1 Exploded view of the modified flat-wise tensile specimen used for evaluation of mechanical properties.

Mechanical Testing

A modified flat-wise specimen was used throughout the present study, see Figure 1. The testing assembly consisted of two aluminum cylinders 1" in diameter and a central BK-7 glass plate (Borosilicate glass manufactured by Schott, W. Germany) 1 mm thick and 25 × 25 mm square. One side of the glass was bonded to the aluminum cylinder by the acrylic adhesive using UV radiation. After curing, the second side of the glass was bonded to the other aluminum adherend with an epoxy adhesive (Scotch Weld 1614 by 3M). Using this method, the failure was forced to occur in the aluminum-acrylic-glass region. The bonded area was 25.4 × 12.7 mm, defined by Teflon film 0.1 mm thick that had been inserted between the glass and metal interface.

The BK-7 glass was wiped with methylethylketone (MEK) and degreased in Freon-isopropanol solution before bonding. The aluminum was grit blasted and wiped with isopropanol prior to adhesive application.

Durability was evaluated by conditioning of the modified flat-wise samples at 95% relative humidity and 50°C for 7 days.

An Instron Mechanical Tester was used for loading the specimens to failure at 0.2 cm/min. Mode of failure, whether interfacial or cohesive, was evaluated by visual inspection.

Transmission Testing

Specimens for optical transmission characterization were prepared from BK-7 glass or sodium chloride substrates that served as adherends. BK-7 was used for the visible and near I.R. range, while NaCl was used for the I.R. regions. The NaCl or BK-7 round disks were part of the spectrophotometer windows, 25.4 mm in diameter and 5.1 mm thick, polished on both sides (see cross section in Figure 2).

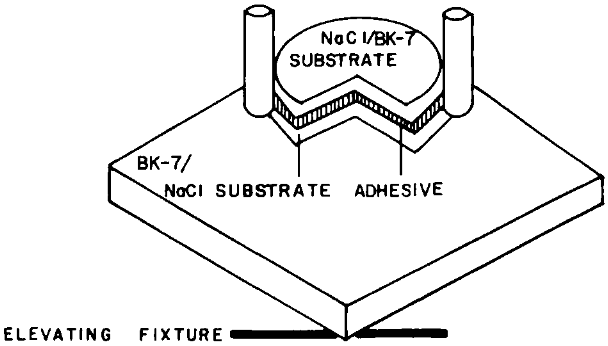

FIGURE 2 Schematic description of bonding fixture, for preparation of doublets for transmission measurements. The fixture is made of a plate with two rods holding the doublet (cross section is shown).

The adhesives were applied between the NaCl or BK-7 substrates using a special bonding fixture with two rods so that the two round disks will have a joint outer circumference (see Figure 2) to ensure optical alignment and bondline thickness of 0.05 mm throughout the curing process. Following bonding, care was exercised to prevent contamination of the substrate surfaces and to avoid moisture absorption by the bonded assembly. A sealed desiccator containing silica gel powder was used for this purpose.

The transmission measurements were carried out using a Beckman Acta IV Spectrophotometer for the visible (0.4–0.7 μm) and near I.R. (0.4–1.2 μm) regions, and a Perkin Elmer 283B Spectrophotometer for the 3 to 12 μm region.

RESULTS AND DISCUSSION

Strength and durability

The first part of the study was devoted to the evaluation of the effects of epoxy, amine and methacryl-terminated silanes on the mechanical properties of the adhesively-bonded glass joint.

Figure 3 summarizes the flat-wise tensile properties of the two adhesives before and after environmental exposure, with and without silanes. As can be concluded, application of the three silanes to the glass substrates resulted in a remarkable increase in the load bearing capabilities of the joints. The enhancement of strength is more pronounced following exposure to the environmental conditions, indicating that silane coupling agents impart increased protection to the adhesive-glass interface, as manifested in the mode of failure. While the non-primed glass samples exhibited adhesive failure, in all cases, at the adhesive-glass interface, it moved, in some cases, to the aluminum-adhesive interface when silanes were used.

For the rigid adhesive (Noa 61) the most noticeable effect was accomplished

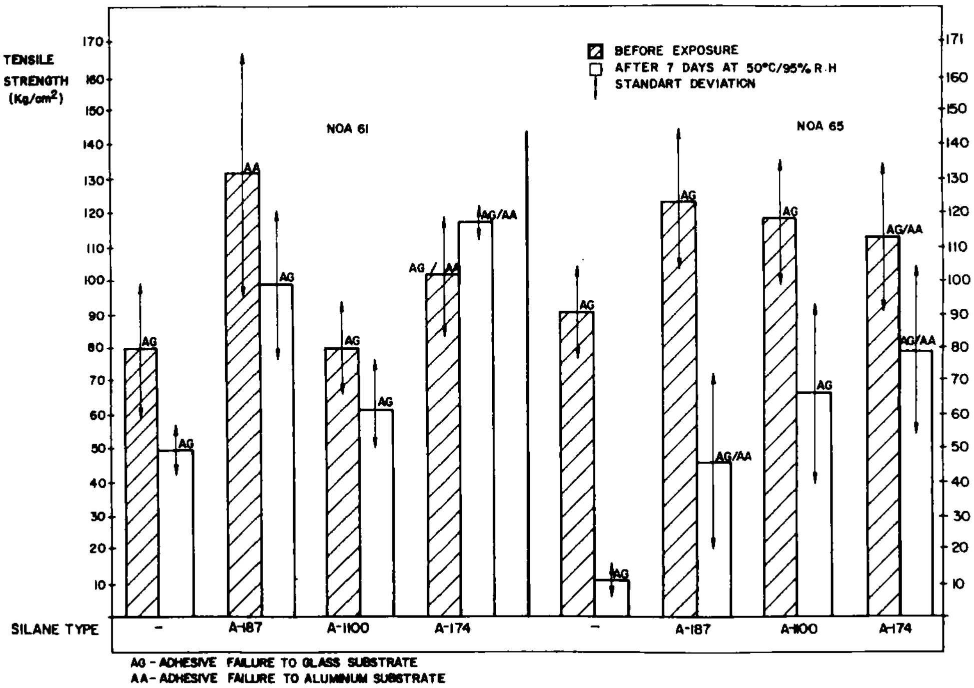

FIGURE 3 Schematic representation of Noa 61 and Noa 65 tensile strengths with or without silane before and after exposure to 50°C/95% R.H. for 7 days. The failure mode is interfacial (AA—Adhesive-Aluminum, AG—Adhesive-Glass).

with the use of the epoxy-terminated silane (A-187). In this case, the tensile strength increased by 50% for the unconditioned specimens and close to 100% for the environmentally-exposed samples. Failure occurred in the glass-adhesive interface for non-primed glass, and it transferred to the aluminum-adhesive interface when the epoxy silane was used. The methacryl-terminated silane was the most effective compared to the other two silanes when the testing specimens were conditioned in heat and humidity. This result suggests that the methacryl end-group may react with the acrylic moiety of the adhesive and thus provide a durable interface.

For the flexible adhesive (Noa 65), the silanes used similarly improved bond strength at ambient conditions. However, upon exposure for 7 days to 95% R.H. at 50°C, bond strength was reduced remarkably for non-primed specimens, while the decrease for primed specimens was moderated by the use of silanes. Once again, the effectiveness of the methacryl-terminated silane was most pronounced. However, the amine-terminated silane (A-1100) did not cause any change in failure mode, which remained at the adhesive-glass interface. This could be attributed to a stronger bond to the aluminum.[10]

TABLE I
Percent transmission at 0.4–0.7 μm

	0.4 μm	0.5 μm	0.6 μm	0.7 μm	Average
Noa 61	89.0	92.0	92.0	92.0	91.2
Noa 61 + A 187 (AS)	89.0	92.0	92.0	92.0	91.2
Noa 61 + A 174 (AS)	90.0	92.0	92.0	92.0	91.3
Noa 61 + A 187 (AB)	87.0	90.5	91.0	91.5	90.0
Noa 61 + A 174 (AB)	87.5	92.0	92.0	92.0	90.3
Noa 65	90.0	92.0	92.0	92.0	91.5
Noa 65 + A 174 (AS)	90.0	91.5	92.0	92.0	91.4
Noa 65 + A 174 (AB)	88.0	90.0	90.0	90.5	89.7

AS—Applied on surface
AB—Added to bulk

Transmission properties

The final stage of the present investigation concentrated on the optical properties of the rigid and flexible modified acrylic adhesives. Tables I, II and III summarize the transmission properties of the studied adhesives for the visible (0.4–0.7 μm), near infra-red (0.9–1.2 μm) and the 3–5 μm regions, respectively. It should be emphasized that measurements in each region were taken at 3–4 points, and that average transmission level is given in percentage relative to the transmission of BK-7 glass or NaCl substrate.

Visible range (0.4–0.7 μm)

In the visible range the higher transmissions were obtained for the combination of the rigid adhesive (Noa 61) and methacryl silane applied on the glass substrate, and for the Noa 65 on untreated glass. Generally, transmission levels were high (~90%). In all cases, direct incorporation of silanes into the adhesive reduced the transmittance.

TABLE II
Percent transmission at 0.9–1.2 μm

	0.9 μm	1.0 μm	1.1 μm	1.2 μm	Average
Noa 61	92.0	92.0	92.0	93.0	92.2
Noa 61 + A 187 (AS)	93.0	93.0	93.0	93.0	93.0
Noa 61 + A 174 (AS)	91.5	92.0	92.0	92.0	91.9
Noa 61 + A 187 (AB)	93.0	93.0	93.0	93.0	93.0
Noa 61 + A 174 (AB)	93.0	93.0	93.5	93.5	93.2
Noa 65	93.0	93.0	93.0	93.0	93.0
Noa 65 + A 174 (AS)	93.0	93.0	93.0	93.0	93.0
Noa 65 + A 174 (AB)	92.0	92.5	92.5	92.0	92.2

AS—Applied on surface
AB—Added to bulk

TABLE III
Percent transmission at 3–5 µm

	3.25 µm	3.3 µm	3.4 µm	3.8 µm	3.9 µm
Noa 61	65.0		6.0	74.0	55.0
Noa 61 + A 187 (AS)	70.0		9.0	79.0	73.0
Noa 61 + A 174 (AS)	69.0		9.0	77.0	73.0
Noa 61 + A 187 (AB)	68.0		8.0	77.0	70.0
Noa 61 + A 174 (AB)	75.0		15.0	82.0	77.0
Noa 65		7.0	3.0		72.0
Noa 65 + A 174 (AS)		13.0	3.0		79.0
Noa 65 + A 174 (AB)		18.0	3.0		80.0

AS—Applied on surface
AB—Added to bulk

Near I.R. range (0.9–1.2 µm)

As in the visible range, in this region the two UV-curing adhesives with treated or untreated substrates are mostly transparent and show transmission above 90%. Also, in this spectral range, direct addition of silanes to the adhesives results in equal or lower transmissions compared with the surface-applied cases (Figures 4 and 5).

I.R. range (3–5 µm)

The 3 to 5 µm region includes inherent absorbance peaks which are characteristic of organic compounds, and especially of the alkyl groups present in the acrylic polymer backbone (CH_3, CH_2CH_3, etc.) and in the silane coupling agents (see Figure 4, 5). Hence, the calculated average transmission value has no real meaning. A similar behavior was found for the previously studied optical adhesives.[7] The main two absorption peaks are in 2.8–2.9 µm (NH or OH groups) and 3.35 µm (alkyl groups). The best transmission (~70%) for both adhesives appears in the 3.6–5.4 µm window. It seems that silane addition improves the transmission level, especially for the rigid acrylic formulations, at 3.6 µm–4.9 µm. Generally, the average transmission levels are 77% and 80% in the range of 3.6 µm–5.5 µm for the rigid and flexible adhesives, respectively.

I.R. range (8–12 µm)

The 8 to 12 µm range is the least transparent region for polymeric adhesives.[7] This region of the spectrum has wide inherent absorbance bands for the UV-curing acrylic adhesives with or without the silane coupling agents. Results indicate that the incorporation of silane slightly improves the optical transparency in the upper limit of this range (10–12 µm), but the transmittance in the 7–9 µm range is very low, as shown in Figures 4 and 5, and no quantitative comparison is possible.

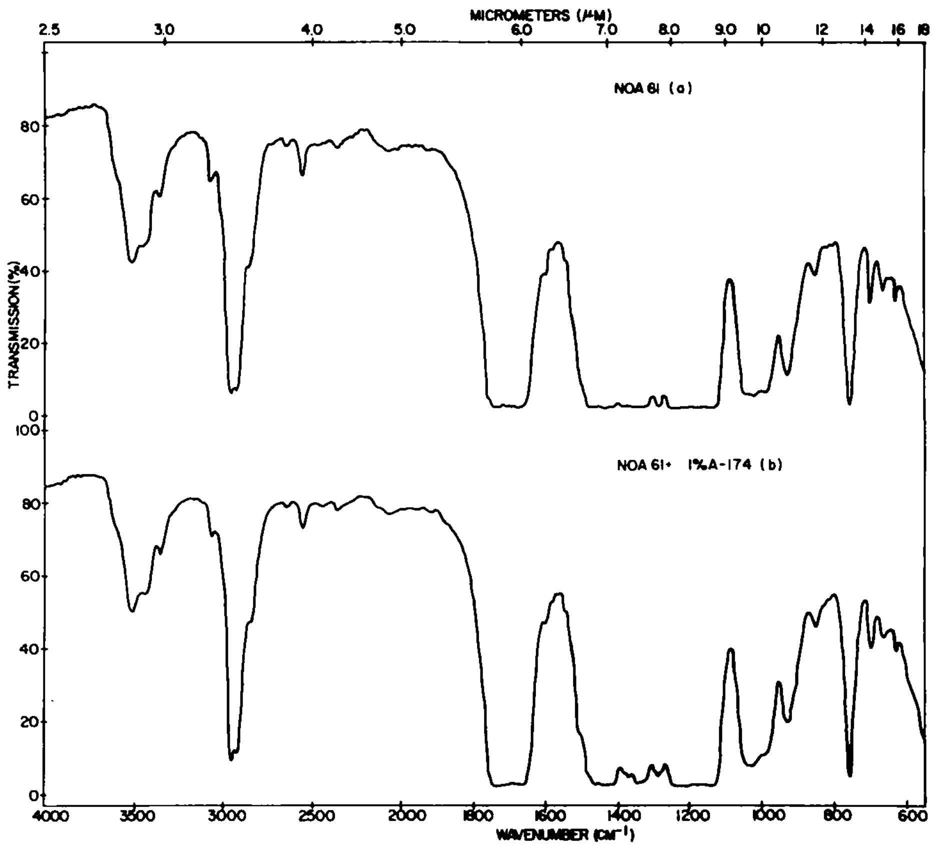

FIGURE 4 I.R. spectra of Noa 61 (a) and Noa 61 + A − 174 (1%) (b).

The improvement in transparency obtained with silanes may be due to better adhesion of the adhesive to the glass substrate (resulted from better wetting) preventing light and reflection scattering at the transition between the glass and the adhesive.

Generally, silane coupling agents either applied on the substrate or incorporated into the adhesive do not degrade the good optical transparency in the 0.4–0.7 μm and 0.9–1.2 μm ranges. Furthermore, in the 3.6–5.2 μm and 108–12 μm ranges some improvement is obtained.

CONCLUSIONS

The mechanical, durability endurance and optical properties of UV-curable rigid and flexible acrylic adhesives were studied.

Silanes were found to be very effective in enhancing the flat-wise tensile properties of bonded glass assemblies, especially their long-term performance.

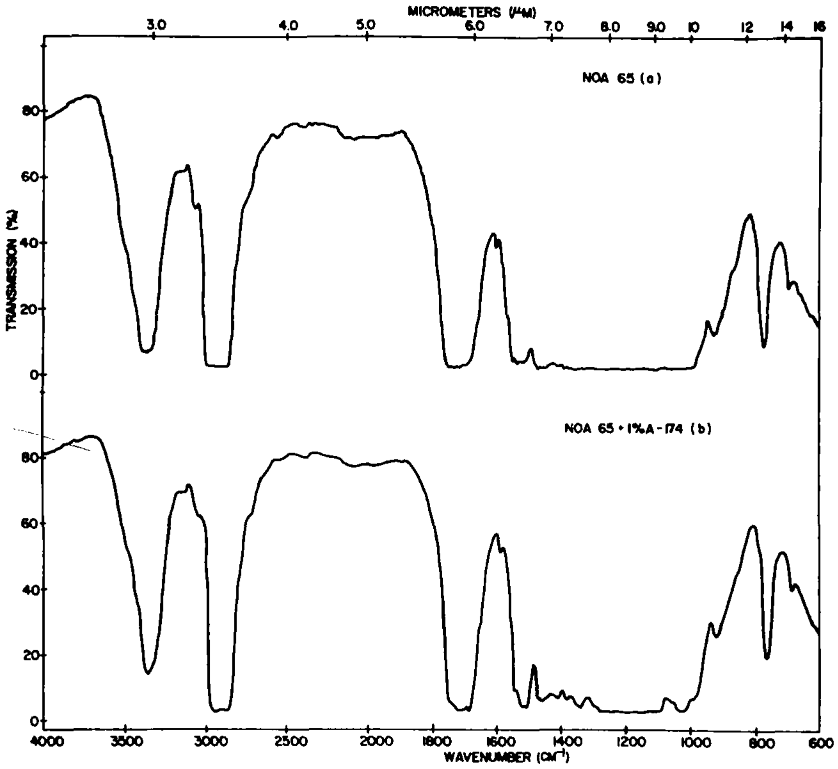

FIGURE 5 I.R. spectra of Noa 65 (a) and Noa 65 + A – 174 (1%) (b).

Among the three functionally-terminated silanes selected, the methacryl end group was shown to be most effective, probably due to its chemical compatibility with the acrylic adhesives studied. In addition to the improved mechanical properties, silanes slightly improve transmittance characteristics to glass doublets, probably due to reduced scattering at the adhesive-glass interfaces.

Generally, UV-curable acrylic adhesives exhibit high transmittance levels in the visible and near infra-red regions, while they demonstrate low transparency in the 3.5, 5.5 and most of the 8–12 μm regions due to inherent absorbances of NH, OH and alkyl moieties. Consequently, acrylics are inadequate to serve as adhesives in applications which require transparency in these regions.

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