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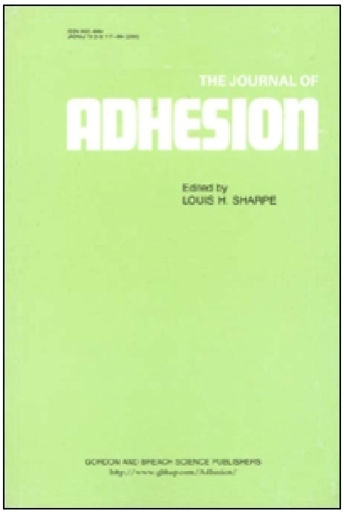

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Curable Optically Clear Pressure-Sensitive Adhesives

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Curable Optically Clear Pressure-Sensitive Adhesives

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A prototype transfer label construction that includes (a) an optically clear curable pressure-sensitive adhesive layer, (b) a curable epoxy layer, and (c) a transparent carrier layer has been developed. This transfer label construction is particularly useful for protective coatings in color filters for use in a liquid-crystal display panel structure. The curable epoxy and the curable pressure-sensitive adhesive (PSA) are applied to the color filter and then exposed to ultra violet (UV) radiation. The radiation transforms the PSA from a removable adhesive to a permanent adhesive. The color filter with the UV-cured adhesive is then baked to fully cure the adhesive layer, which further transforms the adhesive into an ultra-high-adhesion laminating adhesive. Such progressive transformation to different types of adhesive is monitored and confirmed by the shift in viscoelastic window.

Keywords: Pressure-sensitive adhesives; Optically clear; UV-curable; Viscoelastic window; Transfer labels; Liquid crystal display protective coatings

INTRODUCTION

Full-color liquid-crystal displays have become very common, in recent years, as flat-panel displays. They generally have a structure comprising a color filter that has a plurality of colors [*e.g*. red (R), green (G), and blue (B)] on a glass plate, a counter electrode substrate facing the color filter, and a liquid-crystal layer provided in a gap between the color filter and the counter electrode substrate as shown in Figure 1. In the color filter, a protective layer is needed to protect and flatten the colored layer as shown in Figure 2. In general, color

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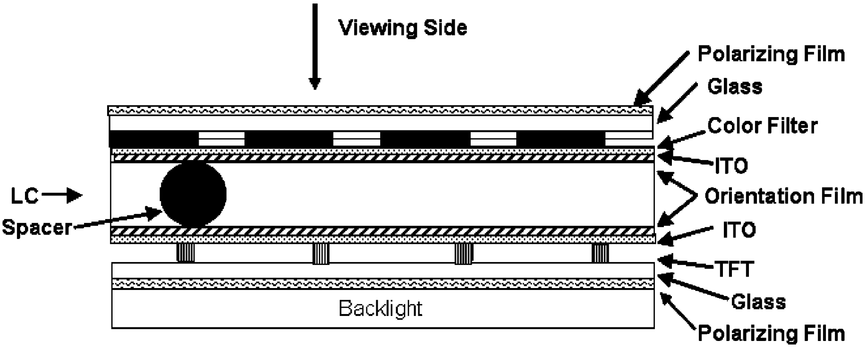

FIGURE 1 Schematic of multilayer components in a liquid crystal display.

liquid-crystal displays have a problem: the presence of an uneven gap among R, G, and B pixels that lowers the flatness of the transparent electrodes. This causes uneven colors and uneven contrast, resulting in lowered image quality. This effect is particularly pronounced in liquid-crystal displays of a super-twisted nematic (STN) system. This renders flattening by the protective layer very important.

In use, the color filter is adhered to the counter electrode. The assembly is then tested for display quality. In consideration of the reusability of the color filter, when the assembly is judged to be unacceptable in the display quality test, the protective layer is preferably provided only in specific regions so as to cover the colored layers on the transparent substrate (e.g. glass). Currently, the protective layer has been formed using a photo-curable resin that permits the portions to be cured to be easily limited through a mask. This usually involves an organic solvent used in development after exposure of the radiation-curable protective coating material to UV radiation. This is troublesome in handling and in wastewater treatment and further lacks profitability and stability. The current article describes a curable label construction comprising a curable PSA layer and curable epoxy layer coated onto a transparent carrier film. After removing release

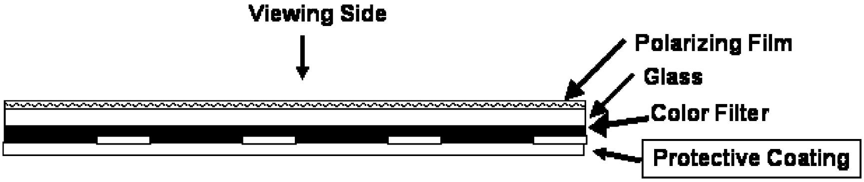

FIGURE 2 Protective coating for color filter.

liner and affixing the PSA side of the label to the surface of the color filter, the label construction is exposed to UV radiation. The transparent carrier film is then removed, leaving the cured epoxy layer and the cured PSA portions on the surface of the color filter. The structure consisting of the cured epoxy layer, cured PSA layer, color filter, and transparent substrate is then baked to further cure the epoxy and the adhesive to an ultra-high-adhesion (near structural) layer as shown in Figure 3.

The curable pressure-sensitive adhesive layer useful in this work should have adequate adhesion to the epoxy layer throughout the manufacturing process. The coated PSA should be repositionable or easily removable from the transparent substrate on which the color filter is formed. The UV cured PSA should adhere to the color filter and adhere to the epoxy layer so that the carrier film may be removed from the UV-cured epoxy layer. The baked PSA adhesive should anchor the baked epoxy layer to the color filter and should transmit light. The PSA of the present work transforms upon UV radiation exposure from a removable adhesive to a permanent adhesive, and upon heat treatment to an ultra-high-adhesion laminating adhesive to support the steps of the process of making a protective epoxy coating for the color filter.

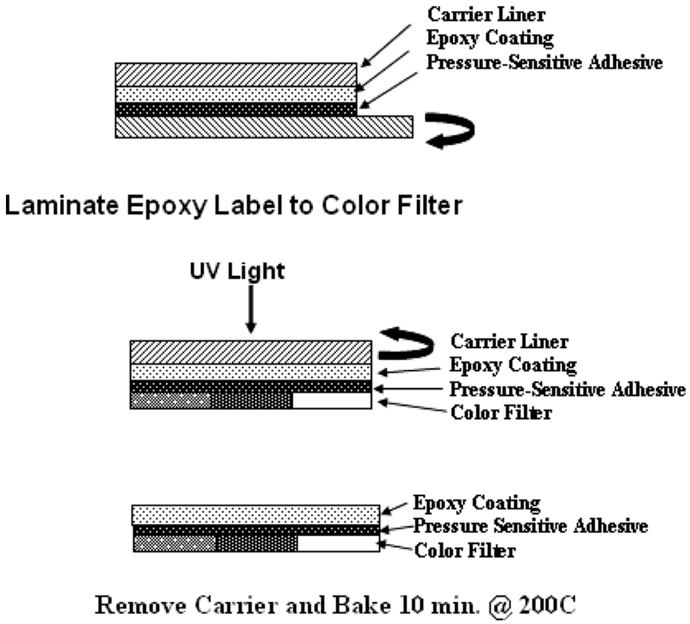

FIGURE 3 Three stages of preparing a protective epoxy-coating label.

The objective of this paper is to demonstrate, through different chemistries and curing processes, how the optically clear adhesive can transform from a removable to a permanent and finally to ultra-high-adhesion laminating adhesive as monitored and confirmed by the shift in viscoelastic windows proposed by Chang [1], and the utility of the curable optically clear adhesive in a functional label to adhere a protective epoxy coating onto a color filter.

EXPERIMENTAL

Curable Acrylic Pressure-sensitive Adhesive

The main component for the curable pressure-sensitive adhesive layer is a high-performance, pressure-sensitive adhesive, prepared in solvent, which contains acid and epoxy functionality. A typical acrylic pressure-sensitive adhesive has the following composition:

67.0% 2-ethylhexyl acrylate,
23.7% methyl acrylate,
7.0% acrylic acid,
2.0% vinyl pyrrolidone, and
0.3% glycidyl methacrylate (epoxy functionality).

A permanent PSA is obtained after drying off the solvent and cross-linking the polymer, utilizing the acid functionality with metal chelate ionic cross-linkers. The subsequent cross-linking of the epoxy functionality during the bake cycle yields an ultra-high-adhesion (near structural) adhesive.

Curable Pressure-Sensitive Adhesive Layer Blend, Preparation and Curing

The acrylic pressure-sensitive adhesive in solvent that contained acid and epoxy functionality as described was combined with an acrylated urethane oligomer, a methacrylated silane thermoset cross-linker, a photoinitiator, and metal chelate ionic cross-linker, forming the adhesive blend for the curable pressure-sensitive adhesive layer. A typical curable pressure-sensitive adhesive blend has the following composition:

70.0 parts acrylic pressure-sensitive adhesive (dry weight basis),
30.0 parts aliphatic urethane diacrylate (Ebecryl® 8803, UCB Chemicals Corp., Smyrna, GA, USA),

- 1.4 parts benzophenone (photoinitiator),
- 1.4 parts methyldiethanolamine (photoinitiator),
- 0.6 parts aluminum acetoacetonate metal chelate ionic crosslinker, and
- 0.6 parts methacrylated silane crosslinker (Witco Silquest A-174).

Stage 1. The adhesive blend was coated and dried, yielding a curable optically clear removable (or repositionable) pressure-sensitive adhesive consisting of ionic cross-linked acrylic polymer with epoxy functionality (Figure 4) that was plasticized with the acrylated

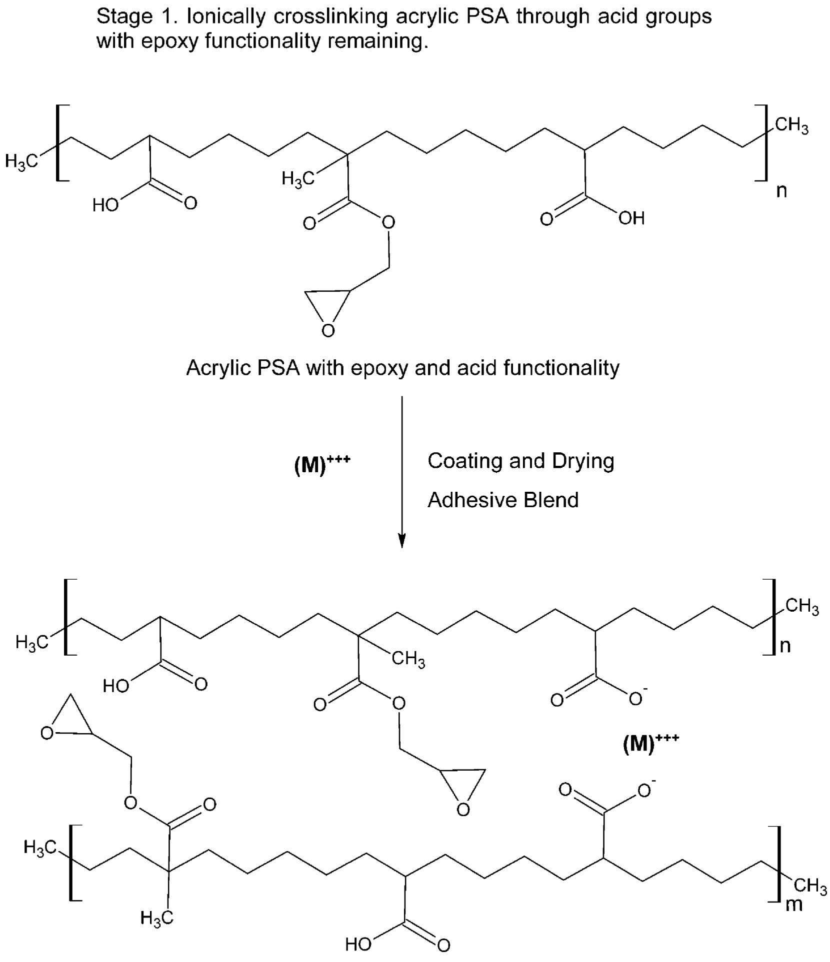
Stage 1. Ionically crosslinking acrylic PSA through acid groups with epoxy functionality remaining.

FIGURE 4 Crosslinking of acrylic PSA.

urethane oligomer (along with methacrylated silane cross-linker and photoinitiator).

Stage 2. The curable optically clear removable pressure-sensitive adhesive was then UV cured (with Fusion lamp bulb D at 5400 millijoules per square centimeter total dosage, Fusion, Gaithesburg, MD, USA), yielding a curable optically clear permanent adhesive consisting of ionic cross-linked acrylic polymer with epoxy functionality that formed an interpenetrating network with the tough cross-linked acrylated urethane oligomer (copolymerized with methacrylated silane cross-linker) as shown in Figure 5.

Stage 3. The curable optically clear permanent adhesive was then baked, yielding a cured optically clear near-structural adhesive consisting of an interpenetrating network of ionic, epoxy, and silane cross-linked acrylic polymer with a cross-linked urethane polymer as shown in Figure 6.

Protective Epoxy Coating Label Preparation

A protective epoxy coating consisting of

48.5 parts bisphenol A epichlorohydrin epoxy resin (Epon 825® Shell Chemical Co., Houston, TX, USA),
32.3 parts bisphenol A epoxy diacrylate (UCB Chemical Corp. Ebecryl 3700),
18.4 parts cycloaliphatic amine adduct (Shell Chemical Co. EPI-Cure 3382), and
1.0 part benzophenone

was prepared by combining an epoxy resin, epoxy-curing agent, epoxy diacrylate oligomer, and photoinitiator in solvent.

Step 1. The epoxy composition was coated onto an 1.5-mil (0.038-mm) polyethylene terephthalate (PET) transparent carrier film, and then oven-dried to remove the solvent and to make a gelled epoxy layer on the clear PET film (dry coating thickness: 0.5–1 μ).

Step 2. The adhesive mixture was then coated onto an epoxy-coated PET film so that the adhesive layer overlies the epoxy layer (dry adhesive thickness: 1–1.5 μ).

Step 3. The coated PET film from step 2 was then oven-dried to remove the solvent and form the gelled adhesive layer. The coated PET film was then laminated to release coated film and die-cut into square labels.

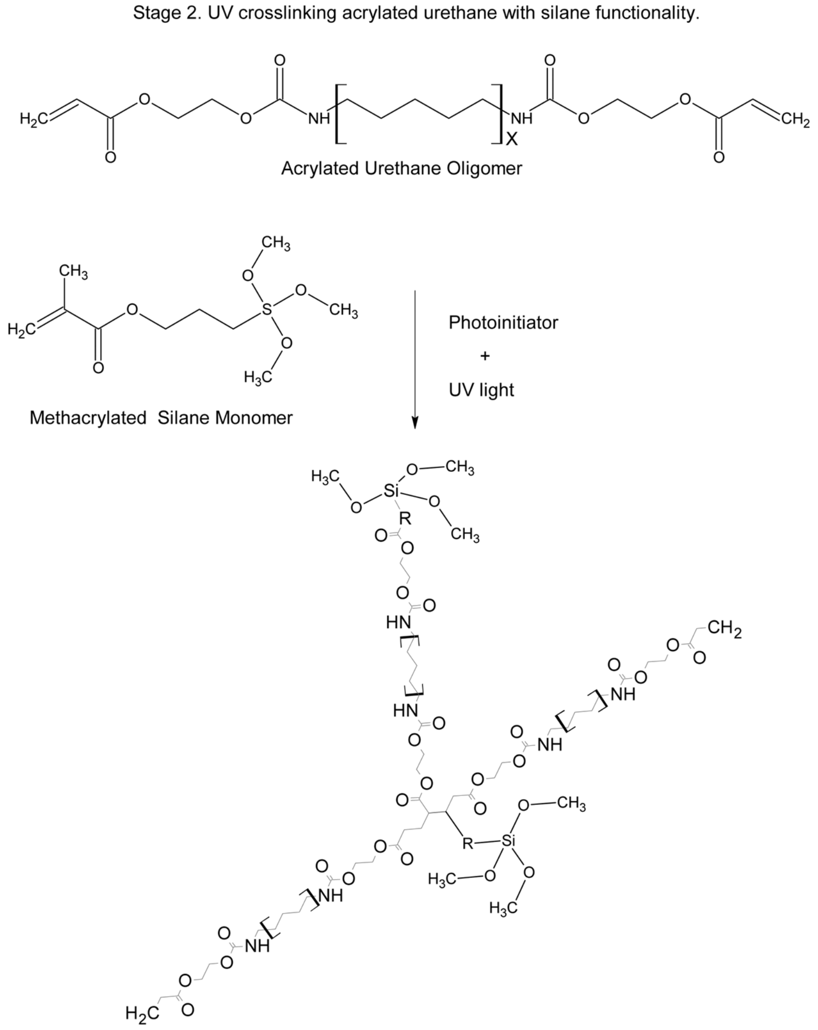

FIGURE 5 UV cross-linking of acrylated urethane oligomer.

Step 4. The release liner was cleanly removed from the label. The label was then laminated onto a color filter plate, adhesive side down. The label over the color filter was exposed to UV light.

Step 5. The carrier film was removed. The remaining cured epoxy/adhesive coated color filter was then baked for 10 min at 200°C and cooled.

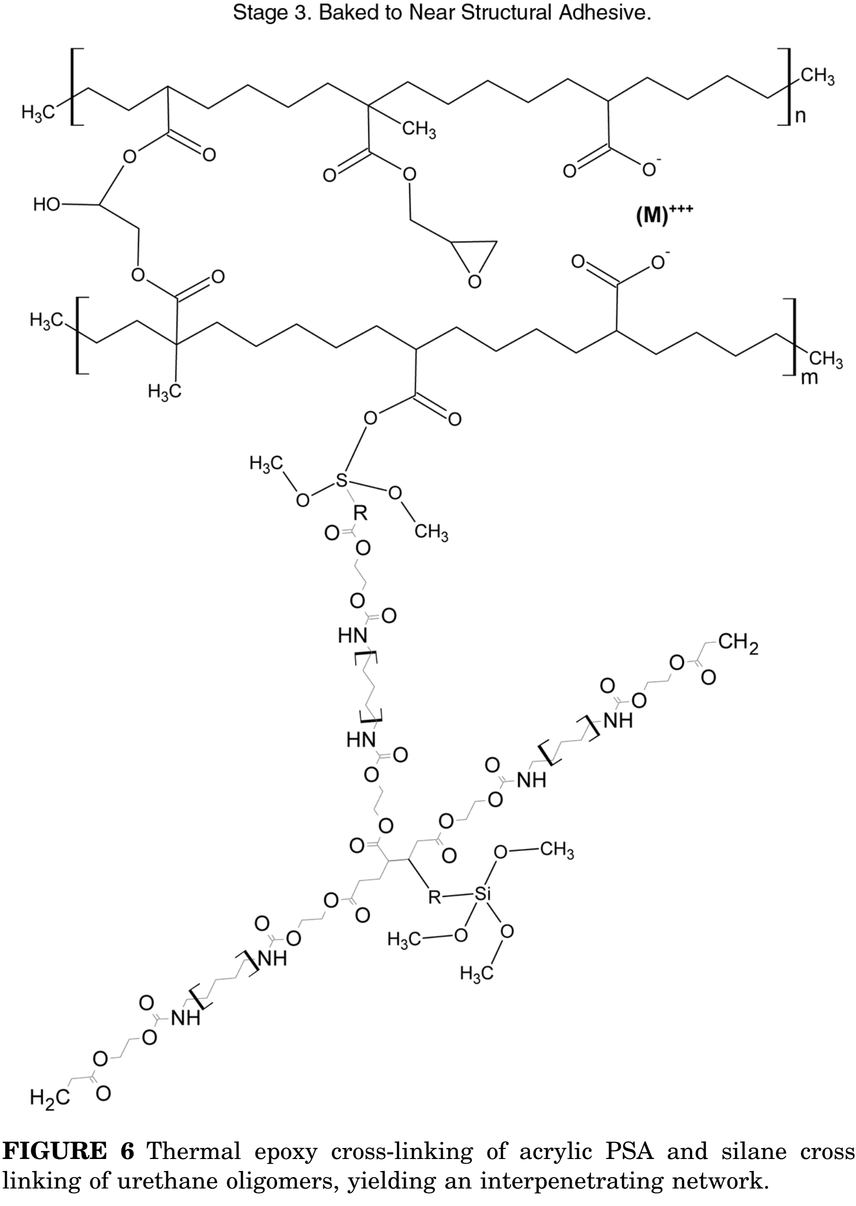

FIGURE 6 Thermal epoxy cross-linking of acrylic PSA and silane cross-linking of urethane oligomers, yielding an interpenetrating network.

Cross-Hatch Adhesion Test and Light Transmission Test

To determine the effectiveness of the curable pressure-sensitive adhesive layer for the protective coating, two tests were conducted:

Crosshatch adhesion test (ASTM-D 3359) was carried out using 3 M 610 tape (3 M, St. Paul, MN, USA). The test result of the cured epoxy/adhesive coated color filter was no "pick-off", showing that the adhesive performed well.

Optical clarity (ASTM-D1003) was measured using a Byk Gardner Haze-Gard Plus IIP-4725 (Byk Gardner, Columbia, MD, USA). The clarity and percentage of light transmission was measured for the adhesive blend on glass with a coating thickness of 20 μ, and the results were compared with a glass sample. The clarity and light transmission for the adhesive blend was the same as that of the glass sample, within experimental error, showing very good optical clarity.

Rheological Measurements of Acrylic Polymer and Adhesive Mixture

Dynamic mechanical measurements were carried out on a Rheometrics Mechanical Spectrometer (RMS-800) (TA Instruments, New Castle, DE, USA) using 8-mm parallel plates. Temperature scans were carried out at 3°C intervals on the investigated adhesive before and after radiation as well as after fully baking at elevated temperature. Master curves were also constructed from the frequency sweep data at different temperatures using the horizontal shift only. Good superposition of the data was observed with all the samples studied. Viscoelastic windows for each adhesive were constructed using the G′ and G″ values at 0.01 and 100 rad/s as described previously [1].

RESULTS AND DISCUSSION

Viscoelastic Window (VW) Concept

It has been well established by many investigators that the performance of adhesives (*e.g.* peel, tack, and shear) depends strongly on the bulk viscoelastic properties of the adhesives [2–12]. The Williams–Landel–Ferry (WLF) superposition procedure between rates and temperatures of the tests has been applied very successfully in adhesion tests both in peel [2, 3] and in other modes of debonding [5, 8, 9].

Using 10^{-2} and 10^{2} rad/s as the frequency window for the peel, tack, and shear tests, G′ and G″-measured values of different PSA samples at these two frequencies are constructed by plotting the four coordinates: (1) G′ at 10^{-2} rad/s, G″ at 10^{-2} rad/s, (2) G′ at 10^{2} rad/s, G″ at 10^{-2} rad/s, (3) G′ at 10^{-2} rad/s, G″ at 10^{2} rad/s, and (4) G′ at 10^{2} rad/s, s, G″ at 10^{2} rad/s on the log–log cross plot of G′ and G″. A hypothetical viscoelastic window is shown in Figure 7.

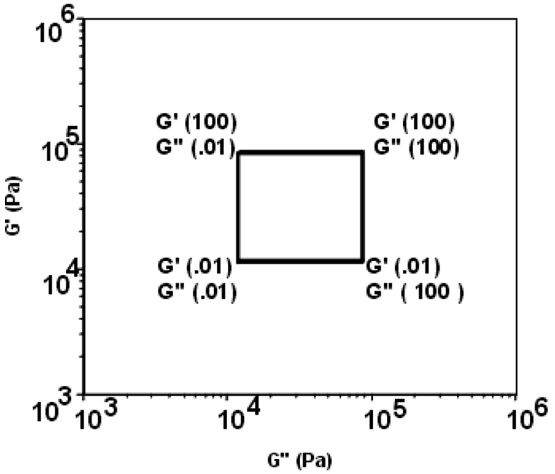

FIGURE 7 Construction of a viscoelastic window.

It was found that for most PSAs, the range of G′ and G″ at room temperature within the selected frequencies falls between 10^3 and 10^6 Pascals. In addition, there is a unique correlation between the adhesion performance of the PSAs *versus* the location of their Viscoelastic Windows (VWs). A four-quadrant concept was therefore adopted to categorize different types of PSAs [1].

The proposed four quadrants [1] (top-left hand quadrant of high G′ and low G″, top-right hand quadrant of high G′ and high G″, lower left hand quadrant of low G′ and low G″, and lower right-hand quadrant of low G′ and high G″) correspond, respectively, to (1) non-PSA or release coatings, (2) high shear PSAs, (3) removable PSAs and medical PSAs, and (4) quick and cold stick PSAs. It was also observed that the VWs of general-purpose permanent PSAs occupy the central region, which straddles part of the four quadrants as shown in Figure 8.

Viscoelastic Windows of Investigated Adhesives at Different Curing Stages

Curable Acrylic Pressure-Sensitive Adhesive

A high-performance acrylic pressure-sensitive adhesive, which contains acid and epoxy functionality, was prepared in solvent. A permanent PSA was obtained after drying off the solvent and cross-linking the polymer, utilizing the acid functionality with metal chelate ionic cross-linkers.

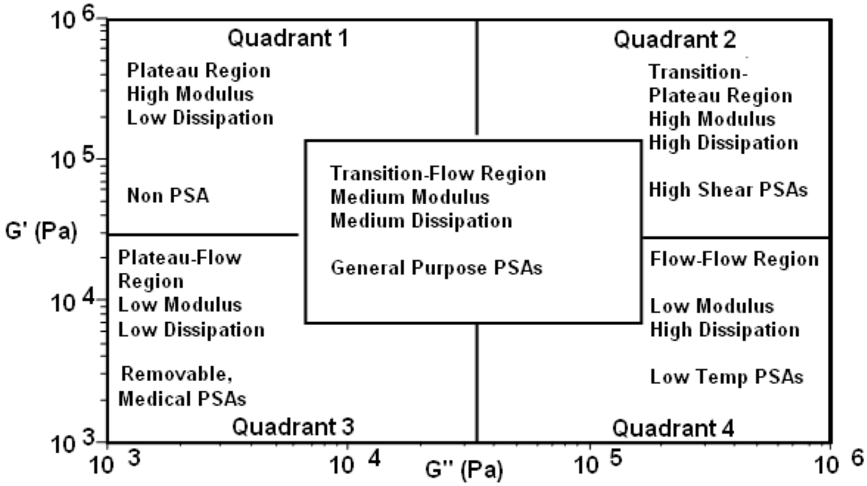

FIGURE 8 Location of viscoelastic windows for different pressure-sensitive adhesives.

Curable Pressure-Sensitive Adhesive Layer Blend

An adhesive composition was prepared by blending 70 parts by weight of the acrylic pressure sensitive adhesive and 30 parts by weight of an aliphatic urethane acrylated oligomer with methacrylated silane crosslinker, photoinitiator, and metal chelate ionic crosslinker.

Table 1 shows the viscoelastic properties of both the pre-UV-cured pressure-sensitive adhesive and the adhesive blend. Compared with the acrylic PSA, it can be observed that the adhesive blend containing the urethane oligomer generally shows lower G′ and G″ values at the bonding and debonding frequencies. This can be attributed to the plasticization effect of the urethane oligomer.

Table 2 shows correspondingly the viscoelastic properties of the pressure-sensitive adhesive and the adhesive blend after UV curing.

TABLE 1 Viscoelastic Properties of Pre-UV-Cured Acrylic PSA and Blend with Acrylated Urethane Oligomer

Property	Acrylic PSA	Acrylic/Urethane blend
Tg (°C)	0	−5
Tan δ at Tg	1.41	1.19
23°C G′ at 0.01 rad/s (Pa)	2.8×10^4	1.7×10^4
23°C G″ at 0.01 rad/s (Pa)	3.3×10^3	3.4×10^3
23°C G′ at 100 rad/s (Pa)	3.7×10^5	2.1×10^5
23°C G″ at 100 rad/s (Pa)	3.5×10^5	2.3×10^5

TABLE 2 Comparison of Viscoelastic Properties of UV-Cured Acrylic PSA and Blend with Acrylated Urethane Oligomer

Property	Acrylic PSA	Acrylic/Urethane blend
Tg (°C)	1	8
Tan δ at Tg	1.39	0.82
23°C G′ at 0.01 rad/s (Pa)	5.3×10^4	2.6×10^5
23°C G″ at 0.01 rad/s (Pa)	8.5×10^3	1.9×10^4
23°C G′ at 100 rad/s (Pa)	6.3×10^5	1.4×10^6
23°C G″ at 100 rad/s (Pa)	6.8×10^5	1.2×10^6

It is noteworthy that the originally plasticized lower G′ and G″ adhesive formulation now shows significantly higher G′ and G″ values than the acrylic PSA. Such an increase can be rationalized from the intra- and inter-cross-linking of both the adhesive components, forming, most probably, an interpenetrating network.

Table 3 shows correspondingly the subsequent viscoelastic properties of the two cured adhesives after baking. It can be observed that with baking, the G′ and G″ values further increased, forming a near-structural type of adhesive.

Figure 9 shows the viscoelastic window of the acrylic pressure-sensitive adhesive, whereas Figure 10 shows the viscoelastic window of its blend with urethane oligomer. The rheological footprints of the two adhesives at the successive stages of transformation from an uncured removable adhesive to a UV-cured permanent adhesive to an ultra-high-adhesion adhesive is well illustrated by the movement of the viscoelastic window. The rheological footprint of the adhesive blend correlates well with lap-shear testing. Lap-shear testing, using an Instron 5542 (Instron, Canton, MA, USA) at 10 mm/min, with 25 μ of adhesive blend bonding an aluminum test panel to a glass test panel with a 1″ × 1″ (2.5 × 2.5 cm) overlaps, showed a value of 16 psi

TABLE 3 Comparison of Viscoelastic Properties of Baked UV-Cured Acrylic PSA and Blend with Acrylated Urethane Oligomer

Property	Acrylic PSA	Acrylic/Urethane blend
Tg (°C)	2	10.5
Tan δ at Tg	1.37	0.45
23°C G′ at 0.01 rad/s (Pa)	1.9×10^6	9.4×10^5
23°C G″ at 0.01 rad/s (Pa)	6.7×10^5	1.2×10^5
23°C G′ at 100 rad/s (Pa)	7.8×10^6	4.7×10^6
23°C G″ at 100 rad/s (Pa)	2.6×10^6	2.3×10^6

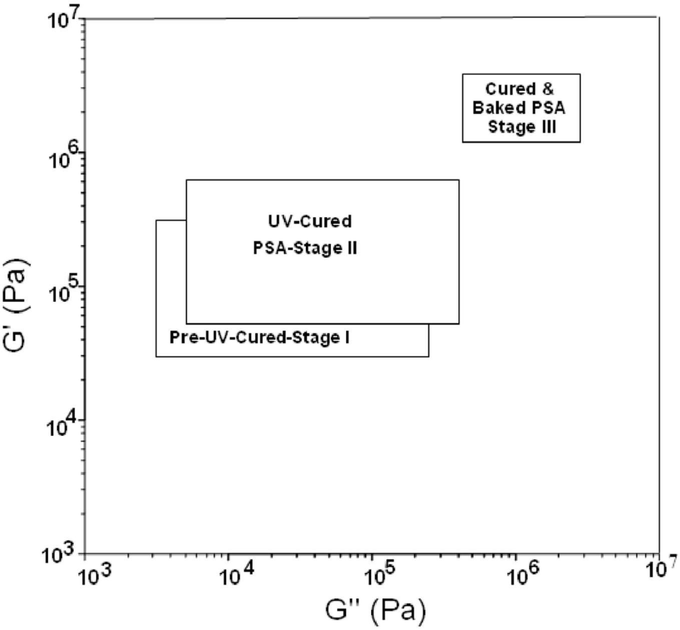

FIGURE 9 Viscoelastic windows of acrylic PSA at different stages of cure.

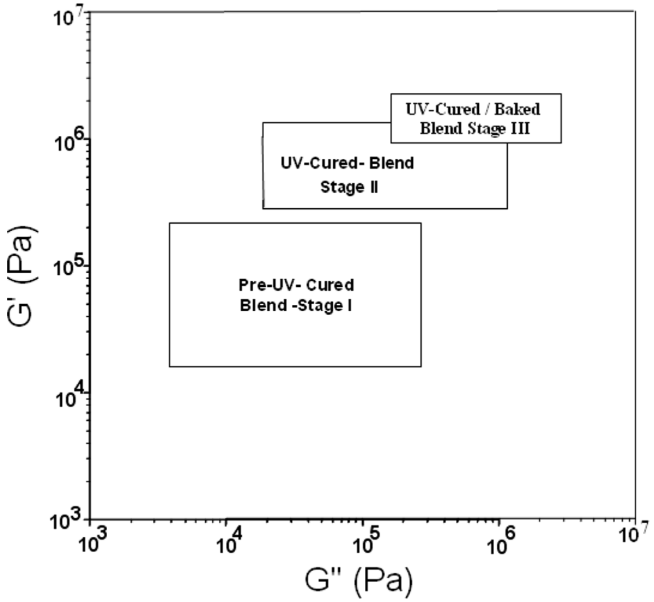

FIGURE 10 Viscoelastic windows of acrylic PSA/urethane blend at different stages of cure.

(110 kPa) for samples pre-UV-cured, 38.2 psi (263 kPa) after UV curing, and 50.4 psi (348 kPa) after baking.

SUMMARY

A curable, optically clear pressure-sensitive adhesive (PSA) mixture, which has been developed for a functional label, is particularly useful for adhering a protective epoxy coating onto color filters for use in a liquid-crystal display panel structure [13, 14]. The curable epoxy and the curable PSA are applied to the color filter and then exposed to UV radiation. The radiation transforms the PSA from a removable adhesive to a permanent adhesive. The color filter with the UV-cured adhesive is then baked to fully cure the adhesive layer, which further transforms the adhesive into a near-structural adhesive. Such a progressive transformation to different types of adhesive is monitored and confirmed by the viscoelastic window.

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