Lower Critical Solution Temperature (LCST) Polymer Solution for Clear/Cloud Glazing Applications

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SYNOPSIS

An aqueous-based clear/cloud solution was developed using poly(vinyl methyl ether) and an antifreeze mixture of ethylene and propylene glycols. The solution has a controllable cloud point from 15 to 90°C, freeze protection to −46°C, and a density that prevents the precipitated polymer from settling and is fairly stable to UV degradation. A significantly smaller heat gain is achieved through the clear/cloud glazing when compared to a normal double-pane window. © 1994 John Wiley & Sons, Inc.

BACKGROUND

In the late 1970s and early 1980s, there was a major thrust in the area of solar energy devices to reduce heat loads through modified glazings. The objective was to allow useful solar energy and derived warmth through the windows when it was needed, but reject the solar energy when it was not needed. A major market existed with skylights, sloped glazings, greenhouses, and row tunnels.

Light transmission is the premier goal of these devices. However, during periods of high solar insolation, the amount of radiant energy transmitted through the glazing can exceed what is required. The overheating can be controlled by added ventilation or air conditioning in buildings and greenhouses. However, these approaches do not ease the energy requirements of the structure. Other modifications including manually operated shades and blinds, semipermanent white wash (greenhouses), and permanent metallized coating have been used effectively. All these modifications have their drawbacks whether it is cost, time-consuming adjustment of shading devices, or continual shade whether it is needed or not.

What the industry needs for both the skylight and films applications is a completely automatic system that would reduce excess solar heat gain when necessary, yet would transmit desired solar radiation during cold periods. It was envisioned that a clear/cloud glazing system would be the answer. The change from transparent (radiation passing) to cloudy (radiation rejecting) would be triggered by the temperature of the clear/cloud system. This article details the development of such a fluid.

The most active workup until just recently in creating a clear/cloud glazing system has been based on the concept of lower critical solution temperature (LCST).[1-3] This simply describes the phenomenon of one material (solute) being insoluble at a second higher temperature. This is in contrast to many familiar multicomponent systems that show enhanced solubility with increased temperature. The LCST phenomenon is largely a behavior unique to a system in which one of the components is a polymer.

Below the LCST, the miscible solution is transparent or clear because the two phases are interdispersed on a molecular level. Above the LCST, the two-phase immiscible mixture is opaque because the particles of the dispersed phase begin to grow large enough to act as scattering centers. If the two materials' refractive indexes differ by more than 0.01, then the maximum scatter can occur when the particles' diameters reach ½ the wavelength of light.[4] For the visible range that contains the peak solar radiant energy, this optimum particle size ranges from 200 to 400 nm. This scattering can lead to opacity even at low loading (< 10%) for the dispersed phase.

There are several prerequisites recognized for a clear/cloud fluid to be useful in a thin plastic (25–250 microns) film application. The most important is deliquescence. The solution must retain enough water during dry periods so that it simply does not dry out and leave a clear film of polymer. The high surface area-to-volume ratio of a sandwich film makes this a particularly difficult challenge. Since all plastic films have a measurable water permeability, eventual drying out of the solution is expected. Addition of salts or humectants may help to control the loss of water. The desired LCST range is 25–30°C and must be adjustable due to the particular application and the addition of salts or thickeners, both of which can move the LCST of a system. The LCST phase-separation phenomenon must be reversible over many cycles and this requires stability toward settling. A high concentration of solid precipitated polymer at the bottom of the glazing becomes difficult to redisperse naturally and the system becomes irreversible. Matching the density of the solvent to the polymer is one possible solution to the settling problem. The use of viscosifiers is another approach used in a cloud-gel system.[5] Freeze protection was important for the aqueous media, but probably would be achieved as a by product of addition of hydroscopic salts.

RESULTS AND DISCUSSION

Several homo- and copolymers known to have LCST behavior in water were screened for cloud-point behavior in either 40% LiCl or 50% LiBr (see Table I). The response of the LCST polymer to the brine

Table I Polymers Tested for LCST Behavior

Poly(N-vinyl propylene carbamate)
Poly(ethyl oxazoline)
Hydroxy propyl methyl cellulose
Hydroxypropyl cellulose
Poly(vinyl methyl ether)
HEA/HPA[a]
VOM[b]/styrene
VOM/vinylidene chloride
Acrylamide/HPA
VOM/methyl methacrylate
VOM/t-butyl styrene
VOM/acrylonitrile
VOM/butyl acrylate

[a] Hydroxyethyl acrylate/hydroxypropyl acrylate.
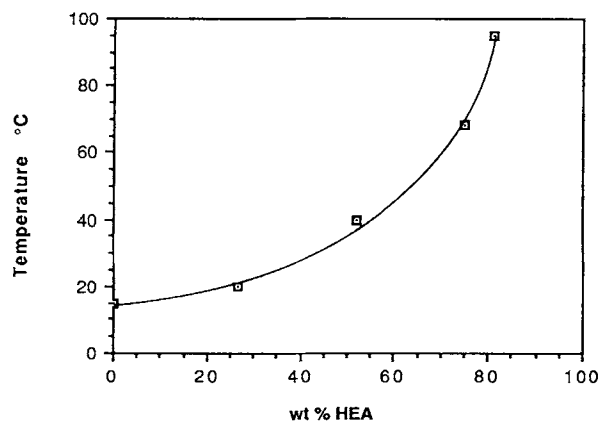[b] N-Vinyl-5-methyl oxazolidinone.

Figure 1 LCST data for HEA/HPA copolymers.

solution was striking as all the cloud points were driven either very low, < 0°C, or very high, > 50°C.

It became evident that by balancing the composition of a copolymer between a hydrophylic monomer and a hydrophobic monomer an LCST copolymer could be prepared that has a controllable LCST temperature. An example is shown in Figure 1.[6]

The HPA composition of the copolymer is found by 100 − wt % HEA = wt % HPA (HPA, hydroxypropyl acrylate; HEA, hydroxyethyl acrylate). Although some trend has been observed with the copolymer brine work, no truly compatible system has been developed. Further, the necessary integration of the surfactant and thickener package promised to further complicate the system. A less complex system was envisioned with glass as the glazing where the loss of water is no longer a problem. The top priority then becomes freeze protection as the expansion of the fluid upon freezing would rupture the glass.

Freeze Protection and Control of LCST

In addressing the vital need for freeze resistance in an aqueous clear/cloud polymer solution, two classes of additives were determined to be worthy of further attention. These were inorganic salts and water-miscible organic solvents. However, the large effect on the LCST by the inorganic salts, as mentioned earlier, led us to investigate water-miscible solvents. The most promising compounds are the glycols that exhibit potent freezing-point depression capacities (see Fig. 2).[7]

Protection to −46°C can be gained with ∼ 58% by weight with either ethylene or propylene glycol in water. They are relatively inexpensive, readily available, and have moderate to low toxicity.
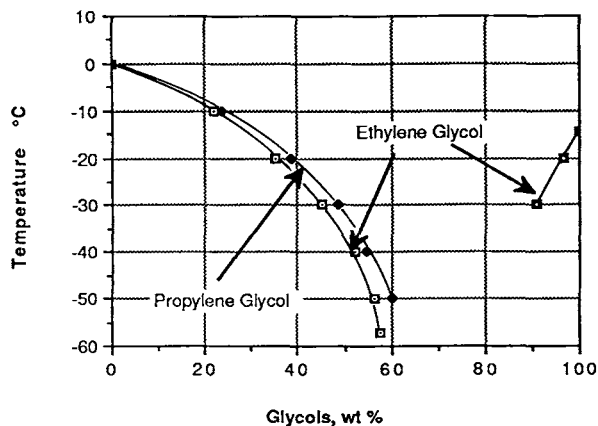
Figure 2   Freezing points of aqueous glycol solutions.

Table II   Composite Densities for a Stable Cloud-Point Solution

Pure Component	Density (80°F)	Wt. Fraction (%)	Weighted Densities (g/cm³)
Ethylene glycol (EG)	1.1	29	0.32
Propylene glycol (PG)	1.07	29	0.31
Water	1.00	40	0.40
PVM	1.05	2	0.02
		100	1.05

Screening of the copolymers listed in Table I (as 2 wt % solutions) and a solution of 58 wt % ethylene and/or propylene glycol yielded a single system that showed promise. The combination of poly(vinyl methyl ether) (PVM) and a blend of ethylene and propylene glycols in water yielded a good, yet controlled reversible cloud point, with a predicted freezing point of below −46°C.

The PVM/glycols system concentrations were set at 2% by weight PVM and 58% total glycol, with the remainder being water. The polymer level of 2% was determined to be adequate to cause a $\frac{1}{16}$ in. layer to be opaque above its LCST. It was determined that the ratio of ethylene to propylene glycol could also be used to control the cloud point. Figure 3 shows the cloud point as a function of the levels of the individual glycols with ethylene glycol (EG) depressing the cloud point from the normal cloud point of PVM in water ($\sim$ 32°C) to 14°C.

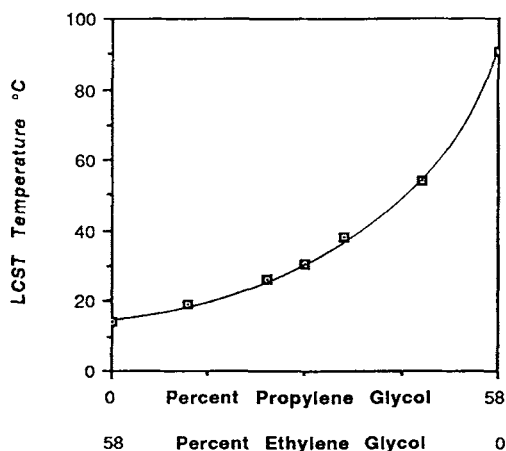In contrast, propylene glycol (PG) is more com-patible with the polymer and raises the cloud point to 94°C. A mixture of 29% EG and 29% PG yields a desirable intermediate LCST of $\sim$ 30°C. The capability to adjust this cloud point by simply altering this glycol ratio is an important tool in optimizing the system for diverse applications. The added feature of not substantially altering the freeze protection during cloud-point manipulation is an added asset.

Settling Stability

A further requirement of a freeze-protected LCST system is to avoid irreversible phase separation. Often, this occurs with polymers that have a markedly greater density than that of their solvent. In the case of PVM, in the aqueous 1 : 1 glycols solution, no such density gradient exists to drive a gravity separation. The composite solution density matched that of the PVM polymer; thus, no settling will occur. The perfect match at 1.05 g/cm² was calculated in Table II. The measurement is strictly valid only at 1 : 1 EG : PG ratio. It has been determined that the entire 58% glycol spectrum from 0 : 1 to 1 : 0 falls within a 10% density range about PVM's density. Centrifugation tests (20,000 rpm) on the two-phase systems above the LCST temperature confirmed that no settling took place.

Long-term Photochemical Stability

The long-term stability of the clear/cloud solution toward insidious photodegradation became a primary concern when the permanence of skylights was considered. A design life of 20–50 years requires almost complete inhibition of photochemistry of the fluid. Although glass screens much of the high-energy solar radiation, a window of 400–320 nm light in passed into the solution.

Figure 3   LCST vs. % PG.

An accelerated degradation study of the fluid was undertaken with a Rayonet[‡] photochemical reactor equipped with 300 nm lamps. The intensity of one of these lamps was determined to be 624 $\mu W/cm^2/$ 10 nm with an International Light Inc. IL783 spectroradiometer. There were 15 of the lamps arranged in a cylindrical fashion around a quartz tube fitted with a cold finger condenser. Literature values for natural sun intensity vary from 0.005 (Ref. 8) to 50 $\mu W/cm^2/nm$ (Ref. 9). A value of 1.0 μW was used for this study.

A Rayonet irradiation of 15 h was then taken as approximately equal to 50 years of natural sunlight. Irradiation under either a nitrogen or air atmosphere yielded the same results. There was an initial bleaching of the light amber-colored solution along with a sharp drop in the pH. The virgin cloud solution had a pH of 7.0, while the irradiated samples had a pH of 3.6–4.6. Capillary GC analysis of the solutions (50 m SE-54 column 0–150°C at 30°/min) indicated that $\sim$ 38 different compounds were formed. Analysis on a Finnigan 9610 GC/MS indicated that some of the major products were consistent with acetone, acetaldehyde, 2,4-dimethyl-1,3-dioxolane, 1,3-dioxane, and 2,2,4-trimethyl-1,3-dioxolane. The presence of these compounds were further confirmed by coinjection of authentic samples, except 1,3-dioxane. Formation of the carbonyl compound can be derived from dehydration of the propylene and ethylene glycols, a known photochemical process,[11] whereas the dioxolane arise from simple acid-catalyzed cyclization of the glycols and the carbonyl compounds. An internal standard analysis was made to quantitate the acetone at 0.78 wt % in the irradiated solution. This translates to a $\sim$ 2.7% conversion of PG over the 50 year life of the window. This above value represents the maximum amount of conversion as there was no filtering of the light by the quartz as window glass would have done. The cloud point of the irradiated solution was within experimental error of the virgin solution, but there did appear to be coagulative problems of the precipitated polymer above the LCST. Coagulation could be controlled by addition of a 0.1 wt % sodium lauryl sulfonate solution. However, the effect on the LCST must be addressed.

Laboratory Performance

The LCST system was evaluated via the ASTM test E424-71, which is the "Standard Test Method for Solar Energy Transmittance and Reflectance (Terrestrial) of Sheet Materials." The scanning results for percent transmittance by the clear/cloud samples as well as competitive systems are shown in Figure 4.

The 2% LCST polymer samples were measured both in the cool and in the clouded mode for comparison with the unchanging empty cell, tinted double-strength ($\frac{1}{8}$ in.) poly(propylene glycol) (PPG) glass and tinted coated double-strength PPG glass. The best shading afforded in the visible region comes from the tinted glass with the reflective coating, with the clouded LCST next. The advantage of the variable transmittance system is shown by its ability to become highly transmittant when cool as the 2% polymer curve illustrates. This system even exceeds the empty cell in the cool state when maximum solar gain would be welcome.

A quantitative summary of the transmittance, reflectance, and absorbance values is given in Table III. These values were integrated from the curves of Figure 4 according to the ASTM method to simulate actual performance based on the sun's spectral intensities at these different wavelengths.

Thus, the figures represent a solar energy balance around the glazing. The PVM/glycols cell has an overall performance range of 39–75% transmittance, which is as good as the clear empty cell during the cool months, but is just slightly less effective in shading during the warm months as the state-of-the-art "low e" coated and tinted glass sample. However, the transmittance data alone cannot predict total performance. The absorbance values for the PVM/glycols system were substantially higher than that for the other samples, though adding impetus to actual testing of the clear/cloud fluid in a glazing system. The fate of the absorbed energy was not readily discernible, and the possibility of a major fraction of it being conducted or convected into the shaded space, rather than being rejected to the outside like the reflected energy, suggested actual testing would be necessary.

Field Testing of the Clear/Cloud Glazing

A large plywood box was constructed with two 2 $\times$ 3 $\times$ 1.25 ft compartments. Each compartment was insulated with Styrofoam® and outfitted with several thermocouples connected to the strip chart recorder. One side was covered with a clear/cloud composite glazing, while the other was fitted with a double-pane insulating glass window. The windows were each made of two 2 $\times$ 3 ft double-strength pieces of
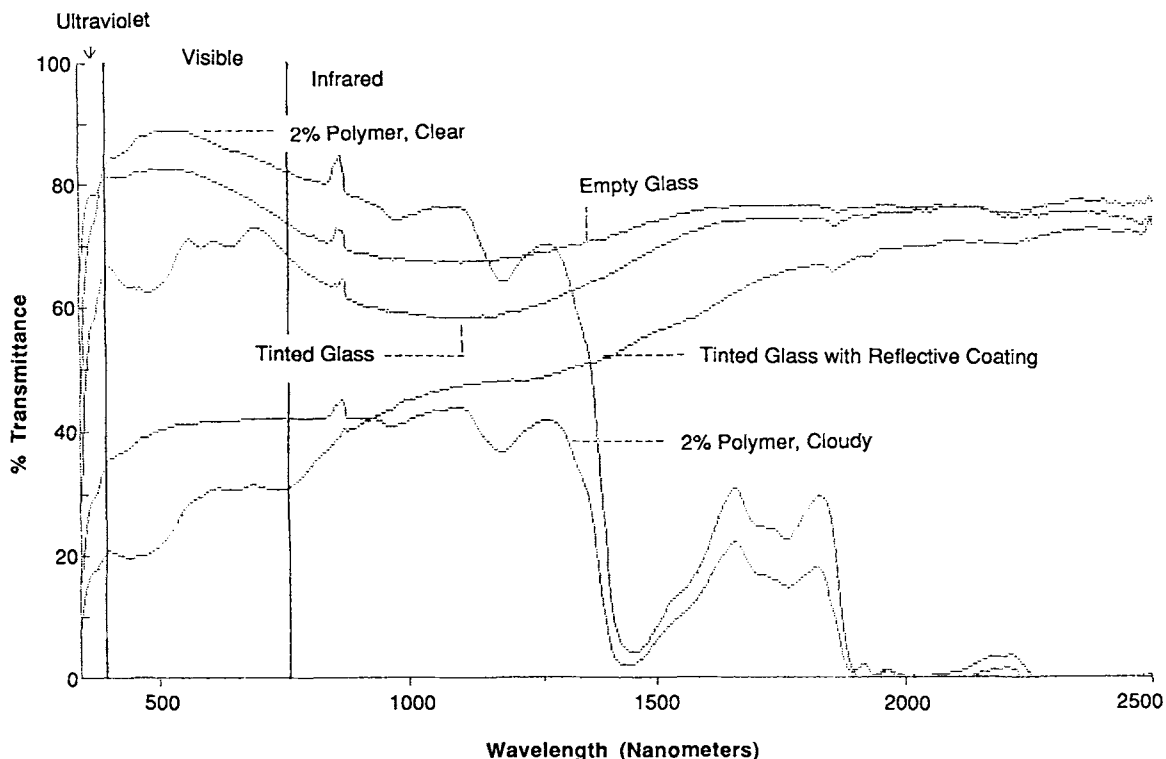
Figure 4   Solar energy transmittance by spectophotometry.

tempered glass and were spaced apart with a 63 mil (0.0063 in) Monel wire. Polyisobutylene sealant flanked the wire spacer to contain the 2% PVM/ 58% glycols solution in one window and dry nitrogen in the other. Temperature data were recorded during a mid-September period in Midland, Michigan. A representative set of data is plotted in Figure 5. The shading effect of the clear/cloud glazing is again evident when the internal temperature maximum is compared to the substantially higher maximum in the box with the conventional double-pane enclosure.

Although the field tests confirmed the heat-rejection capability of this system in a practical life-size application, they also identified a significant structural pressure problem created in glass skylights by such aqueous solutions. The presence of a hydrostatic pressure within a liquid-filled glazing was recognized early in the research, however, only as it related to sealing the liquid in. Once this sealing was successfully demonstrated in the laboratory, the pressure problem was ignored until larger windows were fabricated. Although small 1 sq ft windows showed no pressure effects, the 2 × 3 ft windows conspicuously deflected. When the filled unit was raised to a vertical position, the glass bowed in at the top of the window and out at the bottom. When the window was heated to the liquid's LCST, a clear oval appeared in the upper portion of the window as the panes touched and squeezed the fluid out from

Table III   Solar Energy Transmittance by Various Glazings

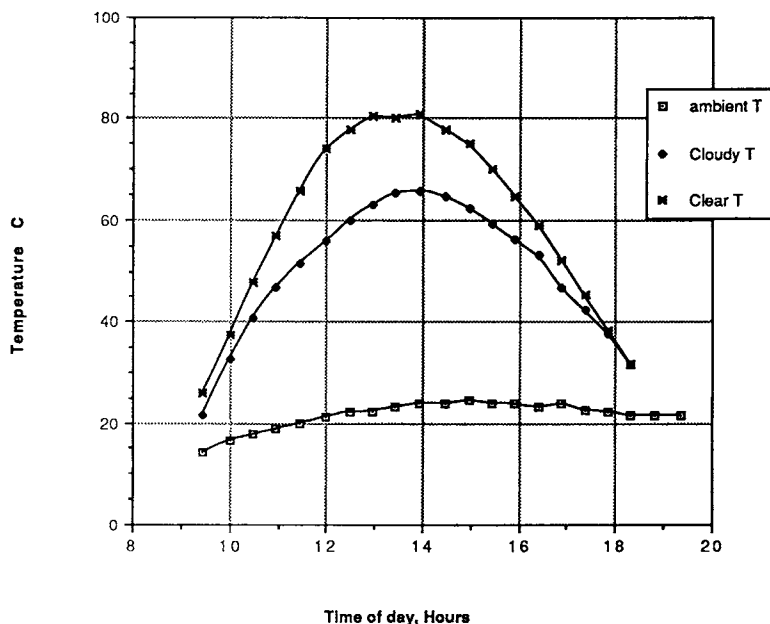|	Transmittance (%)	Reflectance (%)	Absorbance (%)
Empty glass cell	75	—	—
Tinted glass	66	8	26
Tinted and coated	35	37	28
PVM/glycols cell			
Clear	75	—	—
Cloudy	39	13	48

Figure 5 Solar exposure.

between them. This deflection and the associated stress caused a fracture of a glass edge 2 × 3 ft annealed window after standing for 2 days.

No adequate solution to the deflection problem was identified for use in standard glass skylights. Structural plastic sheet extrusions used in greenhouse glazing may offer the strength necessary to prevent this dangerous deflection. However, water vapor loss from such plastic glazing would need to be addressed.

CONCLUSION

A completely automatic system was developed to reduce heat gain through skylights when such a heat load is not needed (summer) and to allow useful heat gain when desired (winter). Laboratory tests show there is reduced light transmittance through the clouded window, which was confirmed by field test results that showed lower heat gain. The polymer solution system developed has an adjustable LCST, freeze protection to −46°C, matched solute/solution densities to prevent settling, and moderate photochemical stability. This technology will not be ready to be implemented until the deflection problem of the large pane windows is resolved.

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