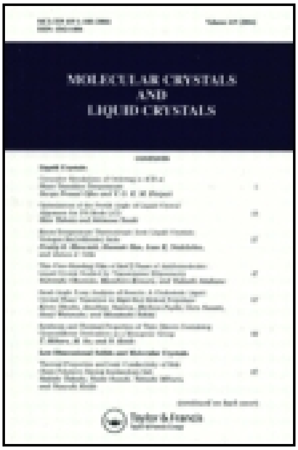

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Liquid Crystal-Rubber Dispersions

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Liquid Crystal–Rubber Dispersions†

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Cholesteric liquid crystals have been dispersed in a variety of rubbers to produce thin films with intense color displays. The integrity of laminates, made with these films between plastic sheets, is improved due to the increase in peel strengths that the rubbers provide.

INTRODUCTION

Cholesteric liquid crystals are organic, grease-like materials with the mechanical properties of fluids. When used in thermography, for non-destructive testing or medical applications, the liquid crystals are normally dissolved in an organic solvent then painted onto the substrate or device having a dark background. This method of use creates difficulties in handling the painted devices and the open tacky surface traps atmospheric dust which is known to cause deterioration of the color properties.[1,2] Further, the coating must be removed after the testing by a solvent wash.

Attempts have been made to encapsulate the liquid crystal so that it is present as a dry film with its own black background, easily applied to a surface, and readily removed. One technique is that of microencapsulation developed by the National Cash Register Corporation. Hoffmann La Roche have developed a product in which the liquid crystal is embedded in a polymer matrix and coated onto a supporting film. The liquid crystal surface is then protected by an acrylic coating.

Another technique is to laminate the liquid crystal between two transparent plastic films.[3] However, the adhesion of a liquid crystal to most surfaces is minimal so attempts have been made to blend the liquid crystal with an inert material which will improve adhesion between the laminating films

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or will produce a dry film of its own accord. This method of encapsulation also produces an increase in the life-time of the liquid crystal.

An excellent encapsulating material is the polyurethane system being developed by Benton and Quigley,[4] and we have found that synthetic rubbers are also compatible with cholesteric liquid crystals. Consequently, we have examined a series of rubbers and have found that appreciable quantities can be solvent blended with cholesteric liquid crystals to obtain cast films with brilliant color displays. Further, the adhesive properties of the rubbers, which range in consistency from semifluid to hard solids, improve the integrity of packages when these materials are laminated between transparent plastic films, such as Mylar.†

EXPERIMENTAL

Toluene or hexane solutions of rubber and liquid crystal were prepared and cast onto Mylar film substrates. Solvent evaporation left a coating 0.001 in. thick onto which another Mylar layer was laminated.

The laminates were examined for intensity of color response, temperature at which the response occurred, and peel strength. Peel strength was measured on an Instron Universal testing machine, Model TT-D, operating at 10 in/min, according to ASTM D-1876.

The rubbers evaluated were SMR 5 natural rubber (Malaysian Rubber Producers), SBR 1502 (Firestone), Hycar 1014 (B. F. Goodrich), LM 450 and butyl 065 (Exxon), bromobutyl X2 (Polysar), Neoprene W (DuPont), Kraton 1101 and 1107 (Shell), and Lithene S (Lithium Corp.).

The liquid crystal consisted of cholesteryl nonanoate (9 parts by weight) and cholesteryl myristate (1 part by weight).

The liquid crystals produce a full spectral range of colors on heating, but the composition examined produced a predominantly blue response. Consequently, in order to determine comparative effects of the rubber dispersions, the temperature of the maximum intensity was measured through a 450 nm filter. The sample was heated and cooled on a thermoelectric heater, and illuminated by a series of incandescent lamps arranged to give an angle of incidence of 20° to reduce glare from the top surface of the sample. A thermocouple embedded in the surface of the heater provided a temperature signal which was fed into the X-axis of an X–Y recorder. The reflected light was collimated through a tube vertically above the sample, through a 450 nm narrow band pass filter, and was detected by an S4 photomultiplier tube. This signal was fed into the Y-axis of the X–Y recorder.

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† Tradename of DuPont.

RESULTS AND DISCUSSION

As expected, the intensity of the color response decreased when the liquid crystal was dispersed in a rubber, the actual intensity varying with the rubber used. The responses due to the different rubbers (containing 80 wt% liquid crystal) are shown in Figures 1, 2, and 3, together with that for the liquid crystal alone for comparison. These figures indicate that the butyl and bromobutyl X2 rubbers (Figure 1) produce the smallest reduction in the color intensity, whereas SBR, Lithene S, and natural rubber (Figure 3) have the most deleterious effect on the color response.

The reduction in intensity may arise from several causes. Certainly, dilution of the liquid crystal is expected to reduce the intensity; however, there may be some chemical interaction with antioxidants or catalyst fragments from the rubber polymerization step. Also, the rubbers are not water-white which can result in internal absorption of the display. A simple dissolution and precipitation step could reduce internal absorption.

The rubbers shown in Figures 2 and 3 produce a marked decrease in the color intensity compared to those in Figure 1. At the present time, no estimate can be made on how the chemical structures of the rubbers affect the molecular ordering of the liquid crystal and, hence, the intensity of the color display.

Figures 1, 2, and 3 also show that there is a change in the temperature at which the responses occurs. This again may arise from chemical interactions

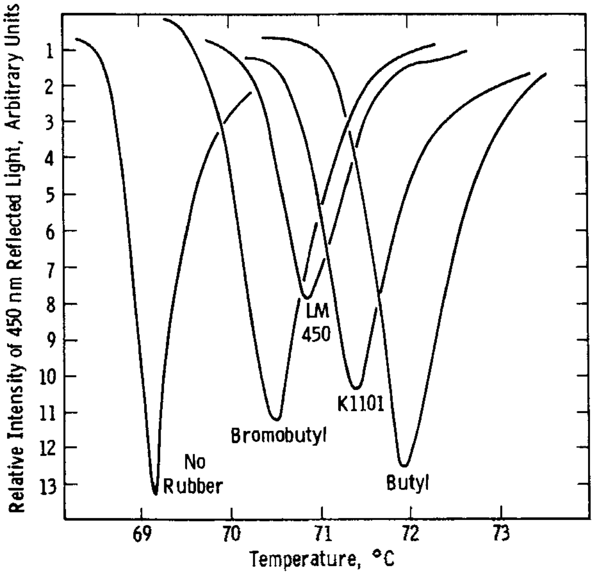

FIGURE 1 Thermal response of rubber/liquid crystal mixtures (at constant LC concentration).

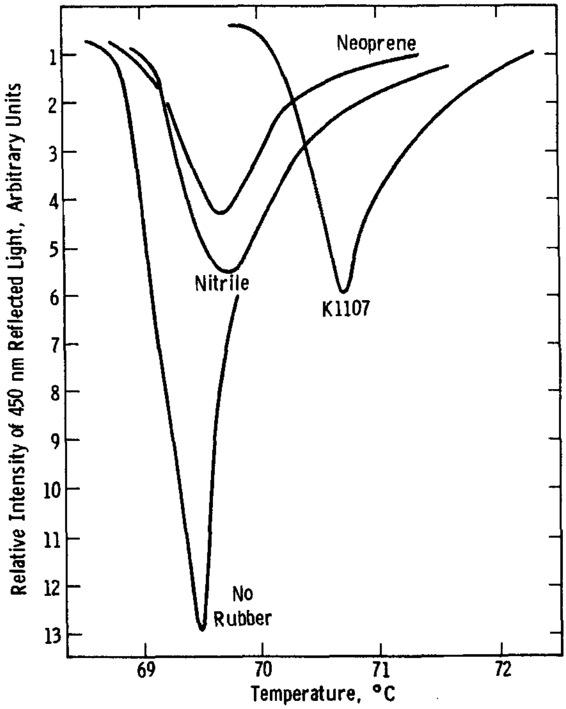

FIGURE 2 Thermal response of rubber/liquid crystal mixtures (at constant LC concentration).

or constraints on the molecular ordering of the liquid crystals induced by the rubber structure.

Since bromobutyl X2 produced the least reduction in intensity, at a concentration of 20%, the effect on the temperature and intensity of the response was examined in greater detail for different concentrations of this rubber. These results are shown in Table I and Figure 4, where increasing rubber concentration results in an orderly increase in the temperature at which 450 nm light is reflected. However, this increase cannot be extrapolated much beyond 30 wt% rubber because there is about 50% reduction in color response at this concentration, and there is virtually no color response at 40 wt% rubber.

When using a laminated liquid crystal package, it is essential that the integrity of the laminate be sufficient to allow a reasonable amount of handling and manipulation. Consequently, the peel strength of the Mylar laminates, as shown in Figure 5, was used as the measure of laminate integrity.

The optimum concentration of rubber in liquid crystal, in order to maximize both color response and laminate peel strength, was about 20 wt% and

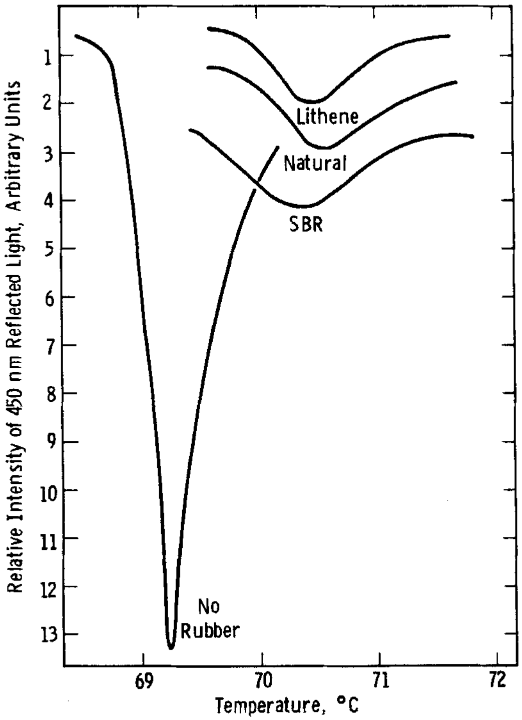

FIGURE 3 Thermal response of rubber/liquid crystal mixtures (at constant LC concentration)

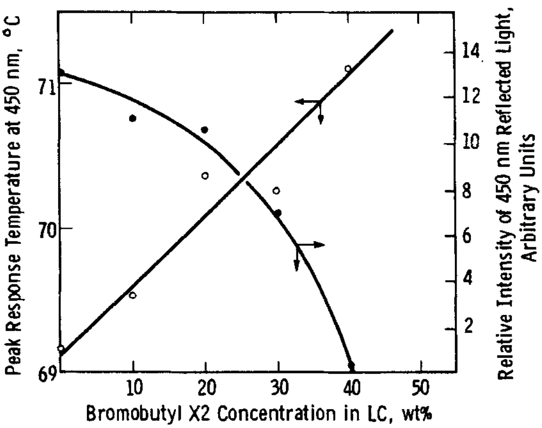

FIGURE 4 Effect of increasing bromobutyl X2 concentration on liquid crystal response.

TABLE I

Color response for 450 nm reflected light in bromobutyl X2/LC mixtures

	Peak response	
Bromobutyl concentration, wt%	Temperature, °C[a]	Intensity, arbitrary units
0	69.16	13.0
10	69.53	11.0
20	70.36	10.5
30	70.26	7.0
40	71.10	<1.0

[a] The standard deviation for these temperatures is 0.4°C.

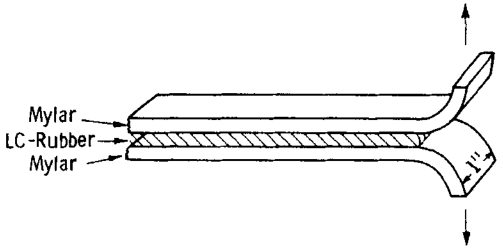

FIGURE 5 Laminate construction for peel strength tests.

this concentration was used to compare the peel strengths of each of the rubbers. These results are shown in Table II. The value for the liquid crystal alone was too low to be measured by our method, and the values for many of the rubber–liquid crystal mixtures are so low that there is no actual adhesion between the coating and the Mylar. The Kratons (1101 and 1107) and natural rubber did provide much higher values but these are still much lower than the values for the rubbers alone, in which the tack or self-adhesion is limited by the cohesive strength of the rubber. In the case of the Kratons, the well ordered domain structure, as shown by Bi and Fetters,[5] may be responsible for the increased peel strength, albeit so small. It appears more likely that the surface tension of the rubber-liquid crystal mixture is being measured rather than an adhesive force.

Peel strength tests on the bromobutyl X2-liquid crystal laminates, shown in Figure 6, indicate how rapidly peel strength decreases with increasing liquid crystal concentration.

The main requirements of these laminates are intense color displays and handleability or conformability to substrate surfaces. If more rugged laminates are required, it may be possible to increase the level of adhesion by several means, including chemical modification of the Mylar surface.

TABLE II

Peel strengths of LC-rubber laminates

Material 20 wt % in LC	Peel Strength lb per linear inch
No rubber	<0.01
Lithene S	0.016
Butyl 065	0.020
LM 450	0.035
Bromobutyl X2	0.040
SBR 1502	0.053
1014 Nitrile	0.052
Neoprene	0.100
Kraton 1107	0.100
Natural (SMR5)	0.115
Kraton 1101	0.250

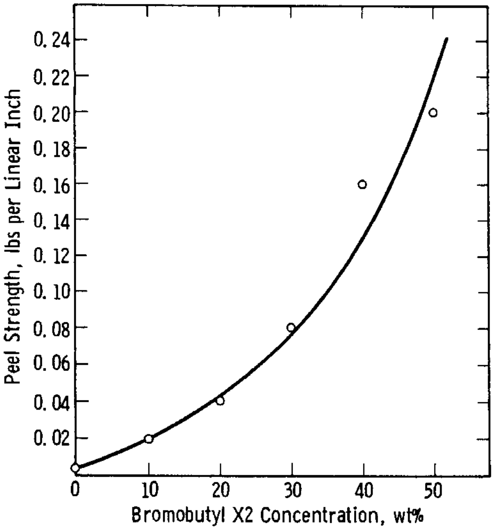

FIGURE 6 Peel strength of LC : bromobutyl X2 laminates.

This can be achieved by a surface etch with 20 wt% aqueous sodium hydroxide[6] (10 min at 70° to 95°C); the casing technique,[7] whereby the Mylar is exposed to a plasma; or the application of a "tie coat,"[8] such as DuPont 46911 adhesive. It is considered that the etch or casing techniques offer the best potentials for increasing laminate peel strength with minimal effect on the liquid crystal color response.

CONCLUSIONS

It is possible to disperse liquid crystals in rubber matrices to give films about 0.001 in. thick with intense color displays. When these films are laminated between Mylar sheets, the peel strength of the laminates, which is related to laminate integrity and handleability, increases with increasing rubber concentration with a corresponding decrease in color response intensity. The optimum composition to maximize color intensity and laminate peel strength in thin films consists of 80 wt% liquid crystals and 20 wt% rubber.

Acknowledgement

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