Influence of melt viscosity on the writing sensitivity of organic dye-binder optical-disk recording media

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The writing sensitivity of dye-binder optical recording media has been defined as the rate of change in the recording response of the medium as a function of laser power. That response was measured by the electronic readout of the recorded pits and shown to be a function of the viscosity of the binder. The variation in dye-binder media sensitivity was 98% accounted for by variations in binder viscosity and writing laser power. For nonpolymeric systems, a more general regression model was formulated using the glass-transition temperature of the recording medium as a substitute for its viscosity. Thus, for any given dye-binder system, writing sensitivity can be largely predicted from the dye T_g, the binder T_g, and their relative concentration, assuming optimum optical efficiency.

I. Introduction

The object of this work was to determine the relationship between the writing sensitivity of organic dye-binder media and media melt viscosity. Writing sensitivity was defined as the rate of change in the recording response as a function of writing laser power. That response was measured by the electronic readout of the recorded pits. As a theoretical framework, the mechanism of hole formation espoused by Wrobel *et al.*[1] was assumed. That is, pit formation was considered to be essentially a flow process in which the primary driving force is back pressure due to limited material ablation and decomposition. Thus it was believed that diffusion processes were unimportant; consequently, the glass-transition temperature T_g was not expected to be a controlling parameter, given that the mass flow involved has to occur at temperatures well beyond the T_g of the system. As theorized by Kivits *et al.*,[2] it was assumed that friction forces due to viscosity had to be overcome for pit formation. This work was not concerned with the influence of optical efficiency. The work of Howe and Wrobel[3] for optimizing the dye-binder layer for optimum optical performance has been followed.

II. Model System

To study the effect of viscosity on the writing sensitivity of dye-binder media, it would have been desirable ideally to design experiments in which viscosity was the only changing variable. In practice, this is not always easy. To vary viscosity and yet attempt to keep certain material properties constant, a technique of controlled oligomerization[4] was used, so as to minimize structural perturbation as much as possible. The properties of the oligoester series used for this study are tabulated in Table I and shown in Fig. 1. The melt viscosities, expressed at 260°C, range over 10 decades.

The dye system was kept constant and had absorption in the IR region. The structure of the recording system is reported elsewhere.[5] It is a bilayer structure consisting of the dye-binder sensitive layer coated over a reflector. The 30.5-cm (12-in.) glass substrate was smoothed with a radiation-cured lacquer. The nominal thickness of the dye-binder layer was 110 nm, a region where maximum absorption for optimum writing sensitivity and maximum phase shift for optimum readout sensitivity were matched.[3] Throughout this study the structure of the disk was kept constant. The coating conditions were the same, except for parameters that control the final thickness of the dye-binder layer. The formulations used for all the layers were constant except for the nature of the binder, which was the variable through which viscosity was adjusted. The dye-binder ratio was 50:50 by weight. Variations in actual thicknesses of the dye-binder layers were small and in the range where disk performance is virtually thickness independent. The disks were tested at a media velocity of 18.43 m/s and turntable speed of 1800 rpm. The carrier frequency was 8.6 MHz and the

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recording wavelength, nominally 830 nm. Readout was done by phase modulation at 633 nm.

III. Results and Discussion

A. Carrier/Noise Performance

One of the conventional ways of reporting dye-binder performance is a plot of carrier-to-noise ratio (CNR) vs writing laser power. Such plots are shown in Fig. 2. As expected, there was a clear trend between writing sensitivity and the nature of the binder. The binders with lower viscosities gave the higher CNRs at the lowest laser powers. Furthermore, the polymeric binder (the binder with the highest viscosity) gave by far the lowest performance. However, the CNR is very misleading for the purpose of this work; here the concern is writing sensitivity. CNR is a measure of sensitivity relative to the noise floor of the system. The best unbiased measure of layer sensitivity is the carrier signal. Moreover, the carrier signal is expressed in a logarithmic scale. Thus large differences in performance may appear insignificant. Consequently, a better way to compare the results is to convert to a linear scale. A decibel is defined as follows:

$$\mathrm{dB} = 10^{*} \log(P/P_0). \qquad (1)$$

Thus a linear carrier signal can be defined by

$$P/P_0 = \mathrm{antilog}(\mathrm{dB}/10). \qquad (2)$$

Figure 3 shows plots of P/P_0 as a function of laser power. The trend becomes more obvious. However, it is not certain that the trend is in fact due to the viscosity of the binder. Several structure-dependent properties could be responsible (solely or in combination). The proper way to establish the influence of viscosity is to analyze the data statistically through an appropriate model. A first-order multiple linear regression model with laser power and binder viscosity was used:

$$\log(P/P_0) = A + B^{*} \log(\mathrm{power}) + C^{*} \log(\mathrm{viscosity}). \qquad (3)$$

To account for machine drift, the carrier intensity was normalized relative to results for a calibration disk tested on the same day as the experimental disks. The slope of a linear regression of $\log(P/P_0)$ on log(power) was used as the reference value. The F and T statistics for model (3) were very significant. The R-square value suggested that 97.9% of the variation in writing sensitivity was explained by variations in laser power and binder viscosity (260°C). The F-test for regression relation between writing sensitivity and binder viscosity was very significant: $F = 95.53$ with prob $> F$ equal to 0.0001. The model is graphically displayed in Figs. 4 and 5.

Table I. Physical Properties of Binder Series

Binder	Mn[1]	Mw[1]	Viscosity[2] in cps	T_g°C
Monomer 1	—	—	2.1×10^{-2}	69
Monomer 2	425	446	0.5×10^{2}	130
Monomer 3	—	—	1.2×10^{2}	148
Oligomer 1	670	929	5.6×10^{2}	158
Oligomer 2	705	1,337	1.5×10^{3}	170
Oligomer 3	930	2,035	6.6×10^{4}	188
Oligomer 4	1,216	2,735	5.0×10^{5}	200
Oligomer 5	2,038	4,570	7.1×10^{6}	234
Oligomer 6	3,388	6,659	1.5×10^{7}	255
Polymer 1	16,422	31,678	—	310

(1) Polystyrene equivalent by GPC
(2) Measured at 260°C

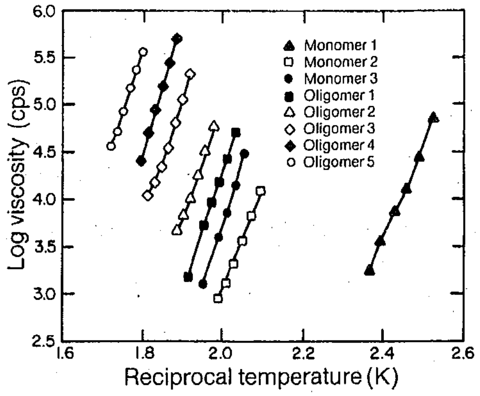

Fig. 1. Melt viscosities vs temperature for binder series.

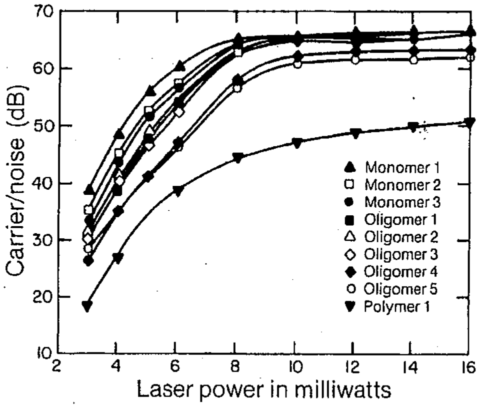

Fig. 2. Carrier-to-noise performance for binder series.

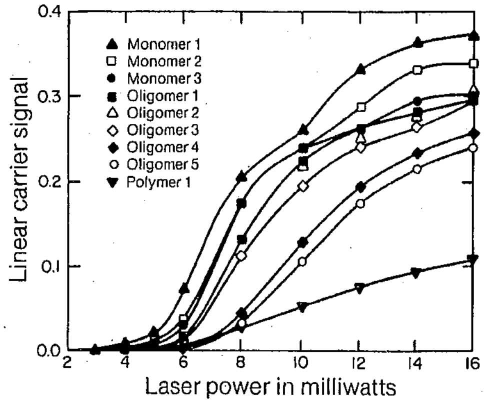

Fig. 3. Linear carrier performance for binder series.

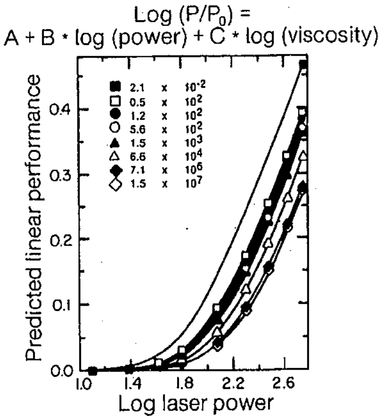

Fig. 4. Viscosity regression model: laser power as parameter.

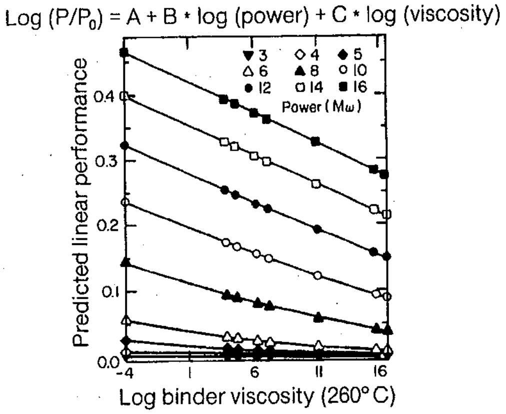

Fig. 5. Viscosity regression model: binder viscosity as parameter.

B. Glass-Transition Temperature—a Valid Substitute for Dye-Binder Layer Viscosity

The statistical model we have discussed so far relates the dye-binder layer sensitivity to the viscosity of the binder and the writing laser power. This is a very restricted model, because it only applies to the particular dye used in the experiments. However, the viscosity that matters is that of the sensitive mixture. That viscosity is a function of the binder viscosity, the dye viscosity, and their relative concentration. It was not possible to measure viscosity of the mixture directly because of dye decomposition at the required temperatures. However, for low-molecular-weight materials, below polymer-chain entanglement, viscosity is expected to be collinear with T_g. In fact, a strong correlation was obtained between T_g and viscosity with a coefficient of simple correlation of 0.989. Thus, for materials below the critical molecular weight, i.e., monomeric or oligomeric materials, it becomes conceivable to use the T_g of the dye-binder layer as a substitute for its viscosity. Now the model becomes

$$\log(P/P_0) = \alpha + \beta^* \log(\text{power}) + \gamma^* \log(T_{gC}), \tag{4}$$

where T_{gC} is the T_g of the dye-binder mixture measured or calculated.[6,7]

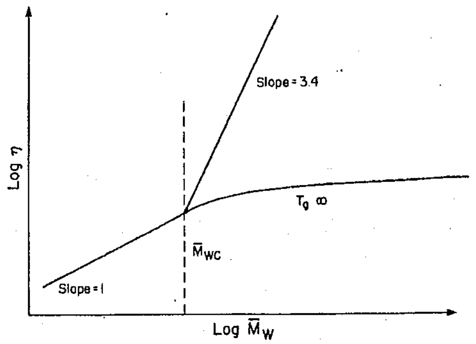

Fig. 6. Schematic relationship between melt viscosity, molecular weight, and T_g.

C. Viscosity vs T_g

One of the original assumptions was that T_g should not be a controlling parameter in the pit formation process, because the mass flow involved is at temperatures well beyond the T_g of the system. Yet a relationship between dye-binder sensitivity and its T_g has just been established. The strong collinearity between T_g and viscosity of low-molecular-weight materials has allowed us in effect to substitute one for the other. However, that collinearity complicates the task of determining the true operating parameter. Is it T_g? Is it viscosity?

Above the critical molecular weight, T_g should be independent of molecular weight. On the other hand, the viscosity/molecular-weight relationship steepens (Fig. 6). Thus, if viscosity is the true operating parameter as opposed to T_g, for polymeric materials, the actual experimental results should be substantially lower than predictions made using a glass-transition-temperature model, because the viscosity of the layer would be much higher than T_g would have predicted. This is exactly what is seen in Fig. 7 for the polymeric example. Additionally, statistical tests using dummy variables have shown a significant difference in the coefficient of correlation for the polymeric example, when compared to the lower molecular weight binders. However, when the same tests were repeated for the next highest molecular weight binder (oligomer 6), no significant difference was noted. That result suggests that the critical dye-binder combination where the slope change occurs is between the oligomer 6 and polymeric examples.

IV. Conclusions

The writing sensitivity of dye-binder recording media has been defined as the rate of change in the electronic readout of the written pits as a function of laser power and shown to be a function of the viscosity of the binder. The variation in dye-binder media sensitivity was 98% accounted for by variations in binder viscosity and writing laser power. For nonpolymeric systems, a more general regression model was formulated using the glass-transition temperature of the recording medium as a substitute for its viscosity. Thus, for any

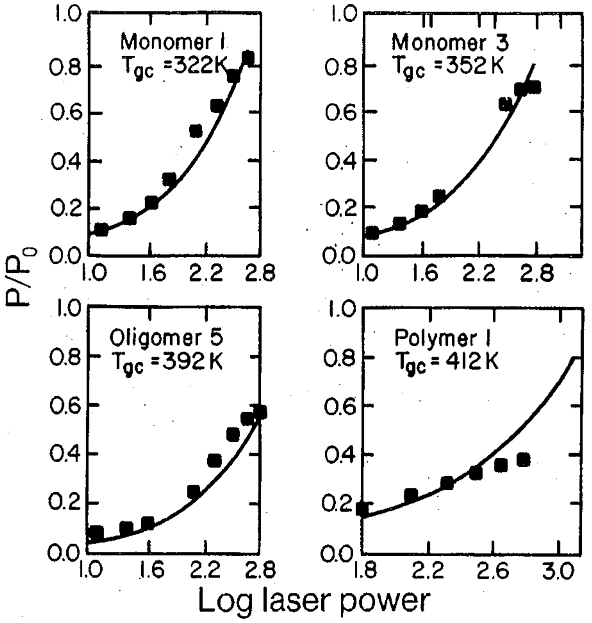

Fig. 7. Comparison of predicted curves to experimental results.

given dye-binder system, writing sensitivity can be largely predicted from the dye T_g, the binder T_g, and their relative concentration, assuming optimum optical efficiency. It has been shown that the true operating parameter in the pit-formation process is the viscosity of the dye-binder medium.

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NEW PATENT COVERS 3-D LASER MEASUREMENT SYSTEM

NBS researchers have received a patent for an automated laser tracking system that greatly simplifies the task of accurately measuring the dimensions of large shapes, such as aircraft wings or fuel tanks. The five-axis laser tracking system invented by Kam Lau and Robert Hocken of the NBS Center for Manufacturing Engineering includes a laser interferometer, a servo-controlled tracking mirror, a similar target mirror, and a computer to control the system. Once the laser is "locked" on the target mirror, the control system keeps the beam centered on the target as it is moved about the space to be measured. The interferometer constantly returns displacement measurements to the controller, and angle-sensitive transducers on the tracking and target mirrors send the data necessary for the computer to keep a running account of the three-dimensional position, pitch, and roll of the target mirror. A simpler 3-axis system, also covered by this patent, measures the position of the target without pitch and roll. The system is portable, fully automated, uses only one station, and can measure positions over a sizeable volume (a radius of 20 meters or greater over 360° in the horizontal and ± 40° in the vertical) to an accuracy of about one part in 100,000. This is about 3 times better than a close competitor: a multi-station, computer-assisted theodolite system (also invented at NBS.) Other applications include assessing the static and dynamic performance of robot arms and the accuracy of machine tools and coordinate measuring machines. The system is being marketed by Automated Precision, Inc., 7901-C Cessna Avenue, Gaithersburg, Md. 20879.