

A THERMAL WAVE TECHNIQUE TO DETERMINE THERMAL DIFFUSIVITIES OF POLYMER  
FOILS

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INTRODUCTION

The increasing use of polymers sets more demands on nondestructive characterization and testing of both raw materials and ready products. Thus far, plastics have been considered to be poor electric and thermal conductors but manipulation of electric conductivity has already become an important factor for many applications. Also the more profound knowledge of thermal conductivity mechanisms and the measurement of thermal characteristics is gaining increasing importance in the future.

There are many standard methods to determine thermal conductivity of bulk polymer samples [1], but the measuring of thin foils is difficult because the area of the sample is large when compared with its volume which causes large heat losses. When the thermal conductivity through the foil is measured, a flash technique has already been used for several decades [2], but only very few methods have recently been presented [3,4,5] for measuring the thermal conductivity parallel to the sample surface. In the case of polymers the ability to measure the anisotropic conductivity parallel to the surface is especially important because the drawing of polymer foils changes the molecular orientation so that originally randomly oriented chains become oriented in the direction of the drawing. This molecular orientation affects the thermal conductivity so that the conductivity is better parallel to the orientation direction [6]. The anisotropy ratio depends on the structure of the molecules and the drawing ratio.

Here we present a method to measure anisotropic thermal diffusivities of less than 100  $\mu\text{m}$  thick polyethylene and poly(3-octylthiophene) (P3OT) foils. The method is based on the mirage technique [7]. Numerical simulation is used to emphasize the specific

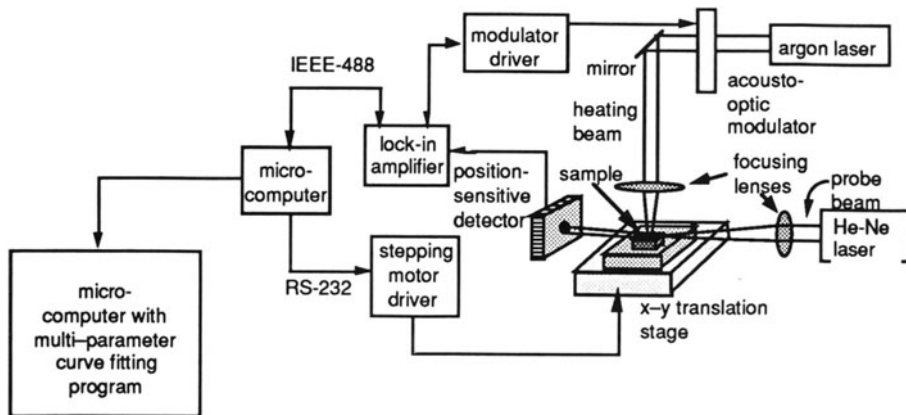


Fig. 1. The measurement setup.

features of the mirage technique in the case of low thermal diffusivity materials. The experimental data are fitted to a three dimensional thermal diffusion model for a multilayer structure. One of the outputs of the fitting is the thermal diffusivity of the polymer foil sample.

#### THE MEASUREMENT EQUIPMENT AND THE SAMPLES

The measurement setup is shown in Fig. 1. The line-shaped heating beam was an acousto-optically modulated Argon laser beam that was slightly focused on the sample with a cylindrical lens. A HeNe laser was used as the probe beam the deflection of which was detected as a function of transverse offset, i.e. the distance between the centers of the heating beam and the probe beam. The samples were mounted on a plexiglass holder that was placed on a translational stage. In the case of polyethylene samples silicon grease was used to fix the sample onto the holder; when P30T was measured no grease was needed between the foil and the holder because P30T foil is quite adhesive.

One difficulty arising from the laser heating is that polymers that are transparent for the green Ar<sup>+</sup> laser light have to be covered with an absorption layer. For this purpose our polyethylene samples were coated with a vacuum-evaporated gold layer that was approximately 0.1  $\mu\text{m}$  thick. Because the P30T samples were opaque, no absorption layer was needed for them. The measurement was controlled and the data were collected using a microcomputer.

The data were analyzed with a program that calculates theoretical mirage signal values according to a three dimensional thermal diffusion model, and fits these to the measured data. The results of the theoretical calculations depend on 13 different parameters characterizing the thermal properties of the sample and the measurement conditions. The parameters are the radius of the heating beam and the probe beam, the height of the probe beam from the sample surface, the thermal diffusivity of air, the thicknesses, the thermal diffusivities, and the volume heat capacities of the two sample layers, the normalized amplitude and phase of the measured signal, and the modulation frequency of the heating beam. There are still more parameters characterizing the numerical calculations the program does, but these are normally fixed and thus they do not affect the results.

This system has been successfully used before for the determination of thermal diffusivities of materials with high thermal conductivity, e.g. diamonds [8]. This paper presents the first low conductivity applications.

## SIMULATIONS

The behavior of the mirage signal was theoretically studied to find out how well different diffusivities can be distinguished from each other. A numerically simulated graph for polyethylene foils coated with gold layer is shown in Fig. 2. The diffusivities of the foils were chosen to be 0.0005, 0.001, 0.005, and 0.01  $\text{cm}^2/\text{s}$ . The value of the modulation frequency of the heating beam was selected to be 12 Hz, which is the frequency used also in the experimental part of this study. This frequency is a compromise between two facts: when measuring low diffusivity materials the frequency should be low to keep the diffusion length long enough but on the other hand the noise of the measurement signal increases when the frequency decreases.

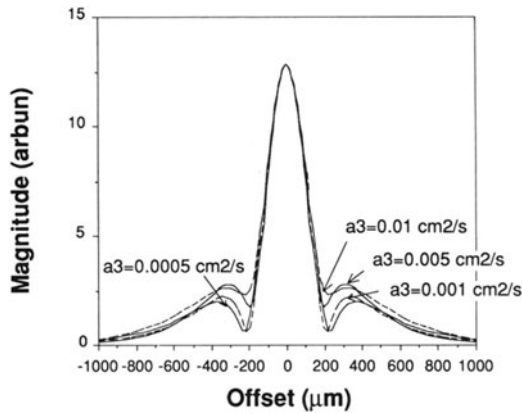


Fig. 2. A simulated magnitude of the normal deflection mirage signal. The sample is 100  $\mu\text{m}$  thick polymer foil with diffusivities of 0.0005, 0.001, 0.005, and 0.01  $\text{cm}^2/\text{s}$  coated with 0.1  $\mu\text{m}$  thick gold layer. The modulation frequency of the heating is 12 Hz. Graphs are normalized to the peak.

In these graphs a characteristic feature of mirage signal obtained from poor thermal conductors can be seen: at the distance of 150  $\mu\text{m}$  from the center of the heating beam there is a steep minimum in the magnitude signal. In the case of good thermal conductors this kind of behavior cannot be seen; the magnitude signal is a monotonously decreasing function of the transverse offset. The reason for this behavior is the difference between the sample and the air thermal diffusivities. When the diffusivity of the sample is larger than that of air, the sample dominates the temperature distribution near the surface and thus the deflection of the probe beam. In that case the temperature decreases monotonously as a function of the distance from the heating point; in the reversal case the local minimum is seen. This is clarified in Fig. 3

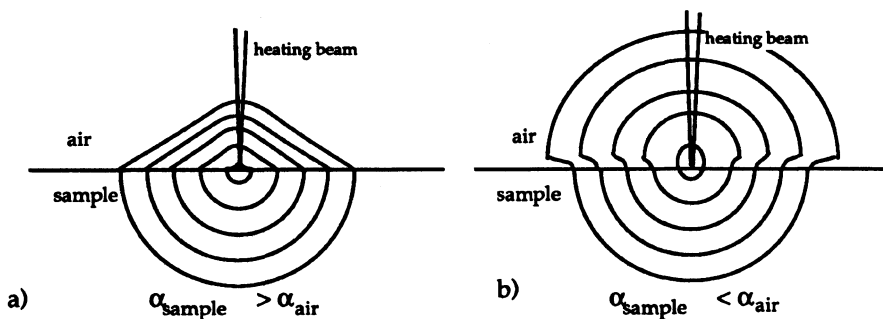


Fig. 3. Contours of constant temperature for cases where the thermal diffusivity of the sample is 1) larger and b) smaller than that of air (according to [9]).

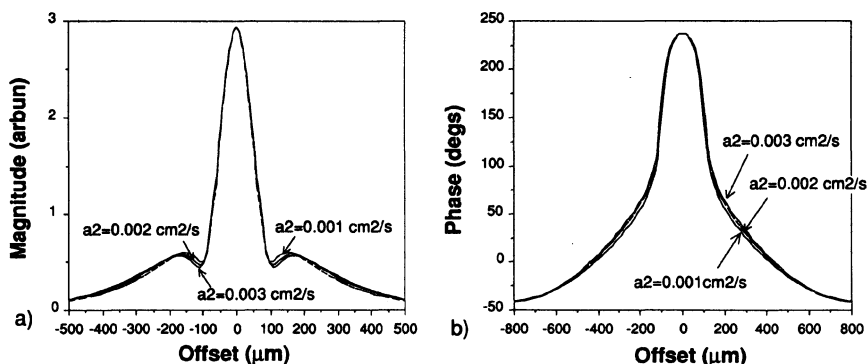


Fig. 4. A simulated a) magnitude and b) phase of the normal deflection mirage signal. The sample is a 50  $\mu\text{m}$  thick opaque polymer foil with diffusivities of 0.001, 0.002, and 0.003  $\text{cm}^2/\text{s}$  placed on a sample holder the diffusivity of which is 0.01  $\text{cm}^2/\text{s}$ . The value of the modulation frequency of the heating is 12 Hz.

with help of constant temperature curves in the sample and in the air. The temperature distribution above the samples of various diffusivities has been earlier studied by Reyes [9].

The other simulation case deals with opaque samples and thus no extra absorption layer is needed on the sample surface. Fig. 4 shows the simulated magnitude and phase of normal deflection signal when the foil diffusivity is 0.001, 0.002, and 0.003  $\text{cm}^2/\text{s}$ . The 50  $\mu\text{m}$  thick sample is simulated to be placed on a holder whose thermal diffusivity was selected to be 0.01  $\text{cm}^2/\text{s}$ . This corresponds to a fairly poor thermal conductor, e.g. glass.

Also here the characteristic dip of the magnitude signal is clearly seen. The differences of the signal are small even if the value of the diffusivity changes proportionately greater. In the magnitude signal the most significant difference between the different diffusivity values occurs at the slope of the secondary peak. The phase values are about the same for all the diffusivities near the center of the heating, but at the distances between 150 and 500  $\mu\text{m}$  from the heating the slopes of the curves are different. By measuring this the diffusivities might be able to be determined.

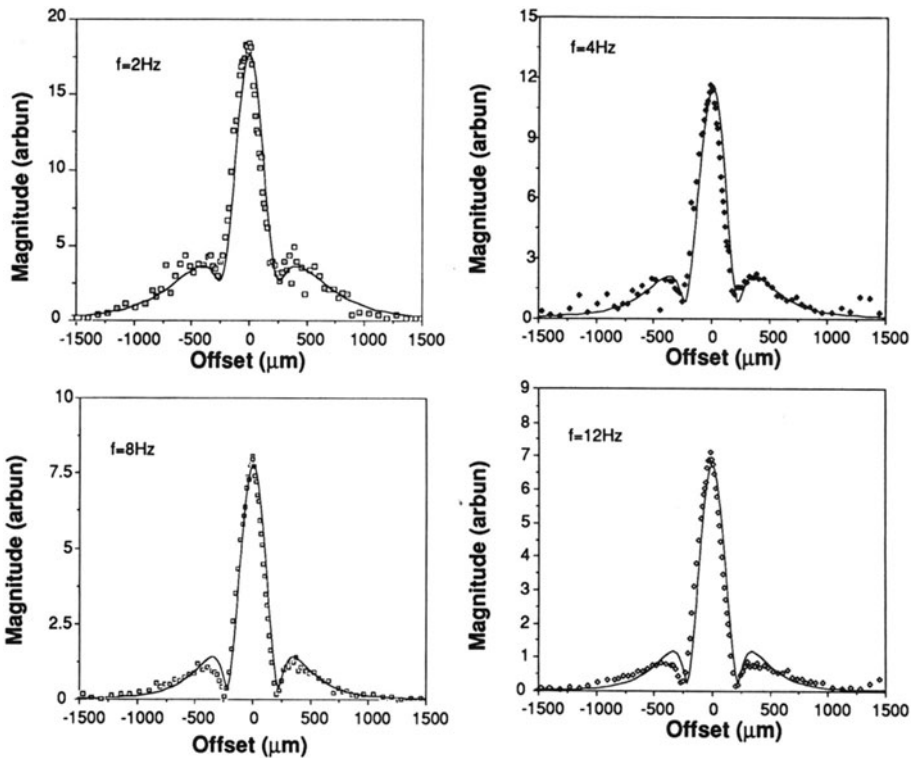


Fig. 5. The measured magnitude of the normal deflection mirage signal (dots) and the fitted theoretical curve (solid lines). The modulation frequencies of the heating beam are 2, 4, 8, and 12 Hz. The sample is a 100  $\mu\text{m}$  thick polyethylene foil that was covered with a 0.1  $\mu\text{m}$  thick gold layer.

## EXPERIMENTAL STUDY

The effect of the heating beam modulation frequency on the magnitude signal is shown in Fig. 5. A gold plated polymer foil was measured perpendicular to the polymer orientation and data were analyzed by fitting to the theoretical model. Because the diffusivity of the sample is small, low frequencies, 2-12 Hz, were used. The dip predicted by the theory is clearly seen. Although the theory favors the use of low frequencies it is to be noted that the noise increases with decreasing frequency, which is an example of  $1/f$  - noise. The quality of the fitting is good but some problems are seen at the dip, especially at the modulation frequency of 12 Hz.

Examples of the measurements made with opaque poly(3-octylthiophene) polymer are shown in Fig. 6. Also in these figures it can be seen that the fitting is better for the smaller frequency.

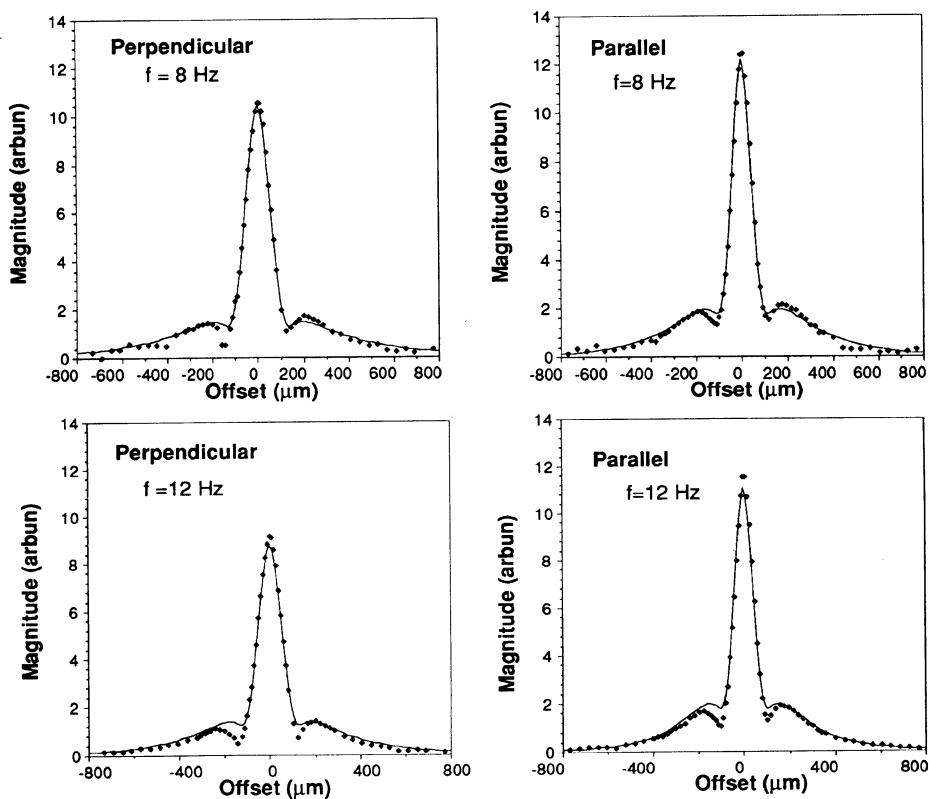


Fig. 6. Curve fitting (solid lines) to measured magnitude of normal reflection signals of a drawn 50  $\mu\text{m}$  thick poly(3-octylthiophene) foil sample. Measurements were made both perpendicular and parallel to the polymer orientation. Modulation frequency of the heating beam was 8 and 12 Hz.

Table 1. Measurement results of POT foil perpendicular and parallel to the molecular orientation. Measurements were made using both normal ( $\Phi_n$ ) and transversal ( $\Phi_t$ ) mirage deflection signal. Units are  $\text{mm}^2/\text{s}$ .

	measurement 1		measurement 2	
	$\Phi_n$	$\Phi_t$	$\Phi_n$	$\Phi_t$
perpendicular	0.10	0.10	0.10	0.10
parallel	0.17	0.10	0.17	0.14

The diffusivity values obtained from curve fitting are shown in Table 1. Two repetitive measurements were made both perpendicular and parallel to the orientation for the same samples and both normal and transversal deflection mirage signals were used for curve fitting. In all the cases the diffusivity perpendicular to the orientation is  $0.10 \text{ mm}^2/\text{s}$ . The diffusivity obtained parallel to the orientation varies between  $0.10$  and  $0.17 \text{ mm}^2/\text{s}$  so that the normal deflection signal gives larger values. This is assumed to be a result from the thermal expansion of the plastic during the heating. This causes extra reflection to the probe beam which is not yet included in the theoretical analysis. The thermal expansion of plastics is larger and thus, more disturbing than with most other materials due to the large thermal expansion coefficient and poor thermal conductivity. Principally it can be said that the conductivity parallel to the orientation is larger than perpendicular.

#### CONCLUSIONS AND DISCUSSION

In this paper we have studied the applicability of the thermal wave mirage technique to the determination of the thermal diffusivity of polymer foils. The mirage method shows a promising possibility to the detection of the orientational dependence of the thermal diffusivity of drawn polymer foils. We have theoretically and experimentally demonstrated that the thermal magnitude signal is non-monotonous in the case of the diffusivity of the sample being smaller than that of air. This is due to the fact that close to the heating volume the sample dominates the heat flow but further away, the propagation of the thermal waves is dominated by the air.

The measuring of poly(3-octylthiophene) samples is easier than transparent polyethylene foils because no special light absorbing layer is needed. The processing of this layer is time consuming and also the molecular orientation of the foil can be annealed due to the temperature rise during the vacuum evaporation process of the gold layer. Because the adhesion between polyethylene foil and gold is not very good, the gold layer might very easily become inhomogeneous which can cause large local variations on the light absorption. Therefore tightly focused heating beams cannot be used.

#### ACKNOWLEDGEMENTS

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