

Time-Resolved, Pulsed Laser Sensitized Acoustic Technology: Application to On-Line Sorting of Waste Plastics

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SYNOPSIS

In industrial recycling of waste plastics the on-line sorting of different kinds of consumer plastics often represents the key to the successful commercial operation. The principle and a limited feasibility study of a novel wavelength independent photoacoustic sensor applied to this problem are presented. This wavelength independent sensor offers the advantages of low cost, portability, and is not limited by the surface modifications such as color, printed labels, etc. in the commercial products. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Today and in the coming century, environmental issues will increasingly be a major concern in most significant business decisions in all sectors of the economy, including the plastic industry. There is little doubt that the principles of the 3 Rs (reduction, reuse, and recycling) will become the norm of consumer plastics. In a successful commercial scale of plastic recycling, the first concern is a fast, reliable, and economical means of sorting various consumer plastics, in all shapes and forms as well as their various commercial surface modifications, such as color, printed labels, etc. Because different plastics do have distinguishable IR absorption spectra, a simple way to sort them out would have been accomplished by modified Fourier transform IR (FTIR) absorption and reflectance measurements. However, because most consumer plastics carry different types of commercial labelling, it is often not possible to obtain any surface IR spectral measurement reliably. Another common sensor for surface measurements is the photoacoustic (PA) technique, particularly the time-resolved mode. To the best of our knowledge, most, if not all, PA sensors are based upon direct absorption of the excitation energy by the

sample system. As a result, such measurements are wavelength specific or dependent and would suffer the same limitations as the IR spectral sensors. Our novel concept of wavelength independent photosensitized acoustic measurements removes such limitations and offers significant advantages and convenience to industrial processing.

This report represents the principle of the sensor and describes the generation and detection of pulsed laser induced acoustic signals in commercial container plastics. The aim of our study is to develop a novel measurement method to distinguish different kinds of polymer samples at room temperature and under circumstances making it possible to use this method in on-line measurements as part of a sorting control system in a plastic recycling plant. Naturally, this technique must also be nondestructive for the samples.

EXPERIMENTAL

Apparatus/Sensor System

For the PA excitation we used green light ($\lambda = 532$ nm) produced by a Nd : YAG laser (Quanta-Ray GCR-11) as short pulses of 6–7 ns width at the repetition rate of 10 Hz. For a comparison, a few measurements were carried out with a UV laser beam ($\lambda = 355$ nm). The output energy could be varied

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up to 135 mJ/pulse. However, in a long-pulse laser operation mode (200 μ s), we did not obtain any detectable acoustic signals due to significantly lower peak power. Two mirrors and a convex lens with a diaphragm were used to focus the laser beam onto the sensitizer placed on the surface of the sample. PA signals were detected with a piezoelectric sensor connected to a wide band amplifier. The sensor consisted of a circular β -polyvinylidene difluoride (PVF₂) foil, 28 μ m thick and 4 mm in diameter, in a stainless steel casing 19 mm in diameter.¹ A thin layer of Apiezon N grease was applied as an interface between the sample and the detector to ensure optimum transmission of acoustic waves. Experimental arrangements with the different positions of the exciting beam and the detector are shown in Figure 1. The arrows A and B indicate the direction of the exciting laser beam and the positions where the laser beam was focused on the sensitizer attached to the sample. When the detector was set up in the D position, it had to be pressed to the sample to obtain a good PA signal.

The amplified signals were acquired as a 256 sweep average using a Hitachi VC-6023 digital storage oscilloscope, and then transferred to an IBM PC for the treatment through an RS-232 C bus. The frequency characteristics of the measuring system employed (the pulsed laser/sensor) were used in the Fourier analysis of the transient structure of the PA signals. All experiments were carried out at a constant ambient temperature of 294 K.

Test Samples

The choice of test samples in this study was purely arbitrary and was mainly governed by the availability of consumer plastic containers in our labo-

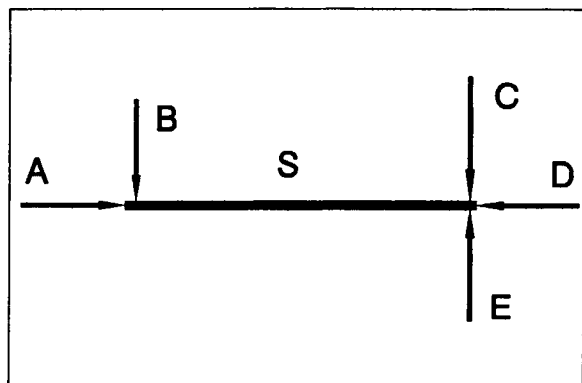


Figure 1 The scheme of experimental arrangements: S, a plastic sample; A, B, directions of the exciting laser beam; C, D, E, orientations of the piezoelectric detector.

ratory. However, they do represent a limited range of popular consumer plastics. Rectangular samples with the length of 82 mm were cut from used commercial plastic containers as well as random and irregular forms in a simulated real-world condition. Three different, common plastic containers were used in this feasibility study. Their plastic codes recorded by the manufacturers are:

1. sample HDPE #2: a white container used for powdered detergents, with a color printed paper label; approximate thickness of the plastics is 1.0 mm, the width, $w = 19.5$ mm;
2. sample HDPE #7: a white bottle used for fruit juice, thickness of 0.8 mm, $w = 25.4$ mm, with color printed paper label;
3. sample PP #5: a yellow container used for cream with a thickness of 0.6 mm and color prints, $w = 25.5$ mm.

RESULTS AND DISCUSSION

The presence of a sensitizer is a very important parameter in the technology under consideration. An intrinsic advantage of using a sensitizer is that the light absorption is localized to a rather thin layer, which produces more accurate time measurements. It is also obvious that the sensitizer, being a black body, is independent of the wavelength of the light source. Thus the light absorption does not depend on the color of the tested sample or the presence of colored labels on its surface. Because our aim was only to determine the sound velocity in plastics, we were not interested in applying the PA technique as a spectroscopic tool.² The utilization of strongly absorbing thin films acting as periodical heater is a popular method in PAs,³ however, our approach was to use a thermally thick black body, acting as an energy transformer to absorb the radiation and generate the acoustic wave. We have tested a 0.5–1 mm thick layer of copper oxide mixed into black Apiezon T grease as a sensitizer. As expected, we did not find any difference in the results obtained with two excitation wavelengths (355 and 532 nm) employed. The greased sensitizer was noted to “melt” after a few minutes of measurements with a crater formation; the “effective” thickness of the sensitizer at this point was evaluated to be less than 0.5 mm. Later, with the ablation of the grease we could see a drop in the PA signal intensity. Subsequent irradiation of the plastics could lead to the damage of the sample surface. Noncolored samples without the sensitizer gave sufficient but very weak PA signals.

It was possible to obtain strong PA signals with colored samples without the sensitizer; however, the magnitude of the signal decreased during the course of the measurements due to local melting of the polymer in the sharply focussed irradiation zone. Thus the sensitizer is required to preserve the sample from radiation damage and to make the measurements nondestructive.

In order to increase the stability of the sensitizer, we have tested oxidized 0.12 and 0.25 mm thick copper foils. The black oxide layer was obtained by heating a foil in air for a few seconds. A thin layer of Apiezon N grease between the copper foil and a sample was used for acoustic coupling. The evaluation of the thermal diffusion length in copper,

$$\mu = (K\tau / \pi\rho C_p)^{1/2},$$

where K is the thermal conductivity, with τ the laser pulse duration, ρ the density, and C_p the heat capacity, gave the value of $\mu = 5 \cdot 10^{-4}$ mm, which is considerably smaller than the thickness of the sensitizers used. Although the copper sensitizers were substantially more stable under the laser beam, the PA signal magnitude was significantly higher with the greased sensitizer.

Determination of PA Wave Propagation Time and Sound Velocity

A peculiarity of the plastic containers involved in the recycling is that their wall thickness is consid-

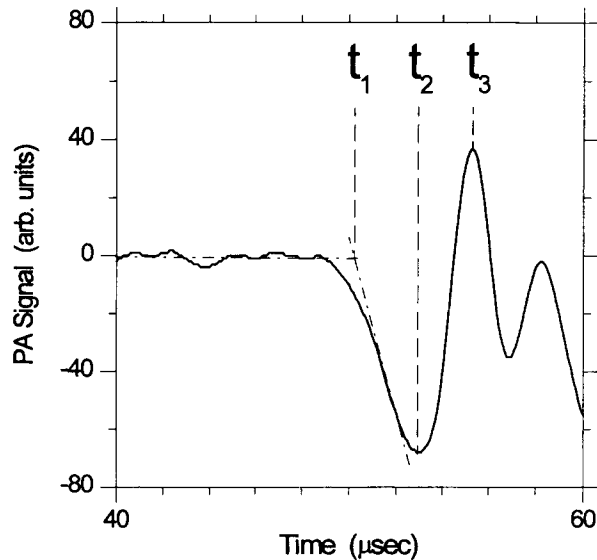


Figure 2 The primary peak on a typical PA signal of plastic samples. The points t_1 , t_2 , and t_3 were used for the determination of the acoustic wave propagation time.

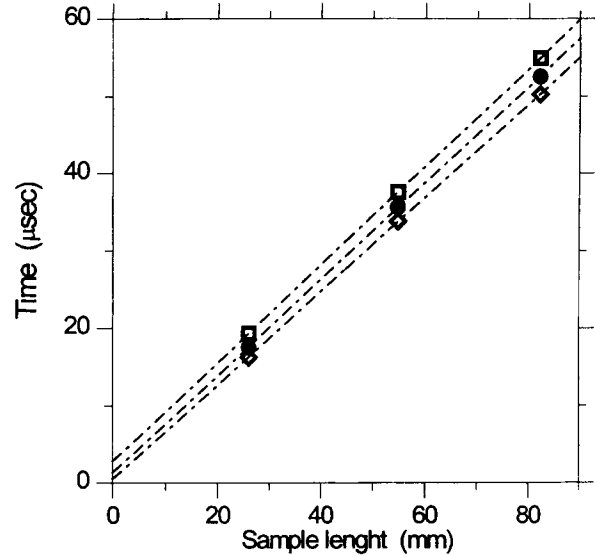


Figure 3 Plot of the times (\diamond) t_1 , (\bullet) t_2 , and (\square) t_3 vs. the length of sample HDPE #7. The dashed lines represent the least-square fittings. The data were obtained with a set-up "A-D" (Fig. 1) using the greased sensitizer.

erably less than the other dimensions. Therefore, the samples under investigation may be considered as membranes, and the wave velocity of transverse waves in membranes can be represented as

$$v = (f_0 / \sigma_0)^{1/2},$$

where f_0 is a surface tension per unit length, and σ_0 the mass density per unit area.⁴

In order to determine the velocities of acoustic waves in the plastic samples tested, we used different distinctive points on the primary PA peak (Fig. 2). The point t_1 was determined as the intersection of the background and the front slope of the primary peak and corresponds to the arrival of the acoustic wave front. The points t_2 and t_3 correspond to the maximum and minimum pressure on the sensor film.¹ Presented in Figure 3, there is a plot of these times versus the length of sample HDPE #7 together with the least-square fits. The results were obtained with the excitation in A position and the detection in D position, as shown in Figure 1, using the greased sensitizer. The t_1 least-square fit extrapolated to zero sample length is equal to $0.5 \mu\text{s}$, thus providing the most correct time determination for the PA wave travelling. This residual time can be explained by a small time delay that has been found while testing the time response characteristics of the "pulsed laser-piezo detector" system. The standard deviation of a single propagation time determination was better than $1 \mu\text{s}$. The extrapolated t_2 and t_3 values are

Table I Sound Velocities for Samples

Sample	Velocity (m/s)	
	t_1	t_2
HDPE #2	1710	1643
HDPE #7	1635	1565
PP #5	1822	1756

shifted to 1.3 and 2.8 μs , respectively, and this difference increases with increasing sample length, as is seen in Figure 3. Hence, some broadening of the primary PA peak with the increasing sample length takes place. However, the determination of the primary peak position, t_2 , is easier, especially with the noisy PA signal. A comparison of the averaged sound velocities measured for the tested samples is presented in Table I. The reproducibility of a single sound velocity measurement was 3%. The difference between the sound velocities determined with t_1 and t_2 values is of 4% for the samples tested. However, either of the points t_1 or t_2 can be used to distinguish the plastic samples based on the sound velocity.

The sound velocities depend on several factors, which can be separated into two groups: (1) factors related to the material composition and structure (e.g., the degree of polymer orientation) and (2) experimental factors associated with the measurement conditions. For the group (1) factors, we expect that such parameters as composition, density, crystallinity, and the degree of orientation are relatively specific for a particular manufacturing code. That is why we have presented the data for two samples of high-density polyethylene, HDPE #2 and HDPE #7. A linear dependence of the sound velocity on the density of PE has been demonstrated.⁵ We conclude that the difference in the sound velocities in the two test samples in our work is due to different manufacturing conditions.

As far as the industrial applications of PA testing are concerned, the “longitudinal” excitation and detection (directions A and D, Fig. 1) is difficult to carry out with commercial plastic objects, so we have tested set-ups with “transverse” excitation (direction B) and the detector in a transverse position (C or E, Fig. 1) to simulate more practical conditions. In this case it was necessary to increase the laser pulse energy by 20–50% to obtain the same PA signal magnitude as in the “A–D” arrangement.

In order to determine the feasibility of measuring the sound velocity with the detector in the C and E positions, it is necessary to consider two questions:

the type of the acoustic wave that can be detected with such set-ups, and the influence of the finite size of the detector on the output signal.

Our measurements showed that the PA signals detected with the detector in positions C or E resemble those obtained in the D position, and the determined sound velocities are very similar to the values presented in Table I. Thus, it appears that the detector measured the same type of waves in any of the C, D, or E positions. This result is consistent with the hypothesis that the acoustic waves generated in the samples under investigation can be considered as transverse waves in membranes. It also shows the feasibility of determining the sound velocities in thin plastics with the aim of distinguishing them using both transverse excitation and detection.

The sensor PVF₂ foil was 4 mm in diameter, and this size could cause an uncertainty of 2.5 μs in the acoustic wave propagation time determination. Additional distortions could be caused by the stainless steel casing of the detector.¹ However, we have found that the acoustic waves generated on the periphery of the casing perpendicular to the sensor plane do not contribute to the measured PA signal. The consideration of the average pressure on the sensor foil in positions C or E shows that only the magnitude of high-frequency oscillations with the wavelength considerably smaller than the sensor foil diameter will be suppressed. In the plastic samples under investigation, the wavelength of the primary PA pulses was larger than the sensor diameter, so the signal should not be attenuated. The calculations of the sound velocity in the experiments with the detector in C and E positions showed a good agreement with the data in Table I when we used the distance between the laser beam focus and the nearest border of the PVF₂ sensor film.

Another factor to be mentioned is the wall shape of the industrial plastic wares. We have tested the influence of the sample wall curvature on the intensity and propagation time of the PA signals. It was found that the bending of the samples at the curvature radii on the order of 20 mm and the angles up to 90° did not noticeably change the sound velocity and the PA signal intensity measured with the detector in positions C and E. Sound velocity measurements were also carried out using different directions of the acoustic wave propagation. However, we did not find any noticeable anisotropic effects related to the orientation of polymer molecules in the tested samples. In addition, normal colored paper labels attached to the tested plastic samples did not affect the measured velocity or the amplitude of PA signal either.

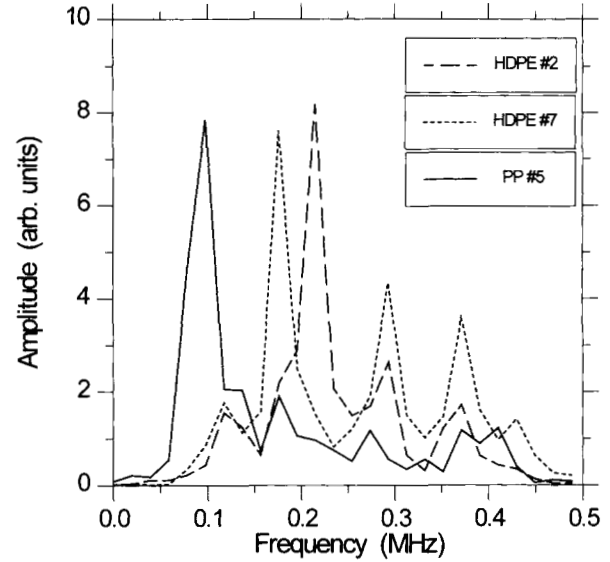
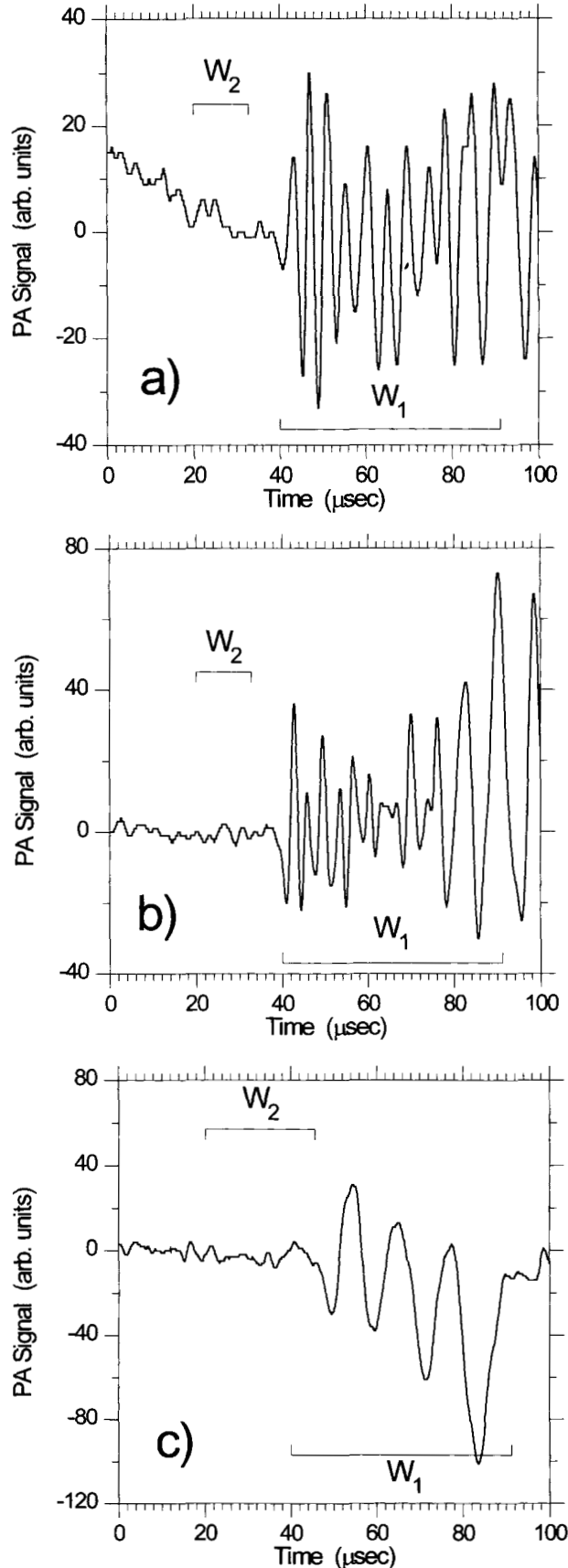


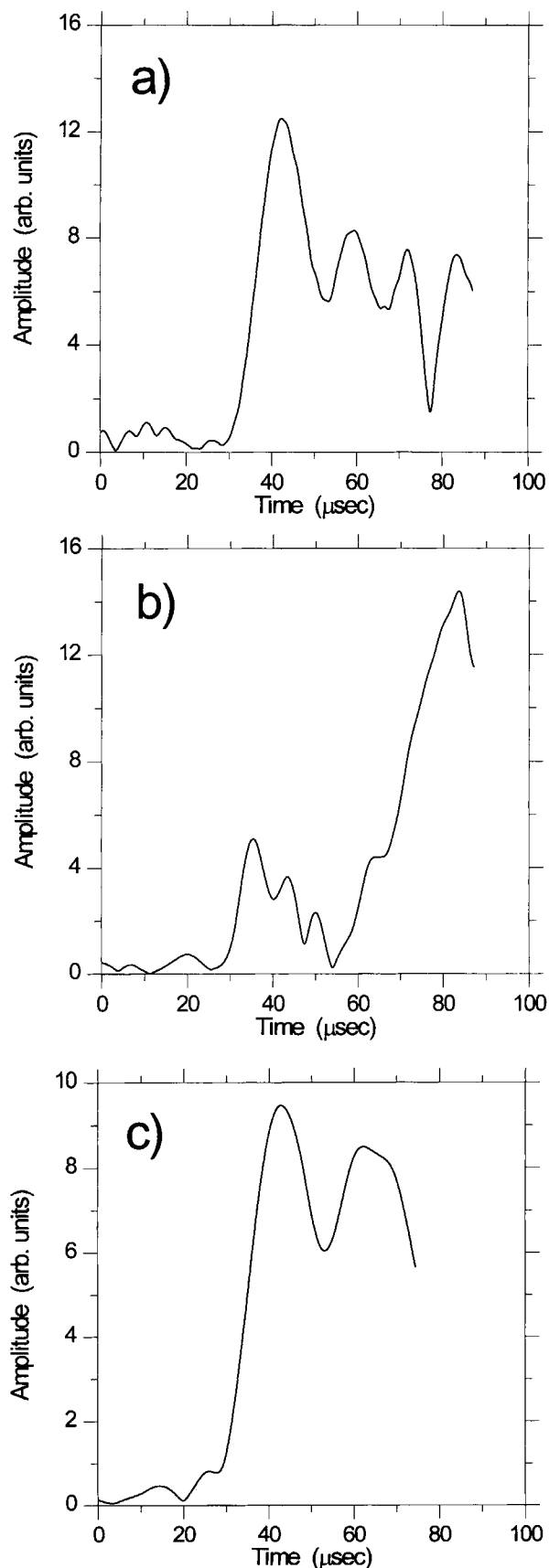
Figure 5 The frequency responses of the PA signals.

Frequency Analysis of PA Signals

Besides sound velocity determinations, we tried to use the longer time scale PA signal for the plastics testing. It has been shown that the analysis of transient signals provides significant information regarding resonant modes in the PA cell assembly.⁶

Figure 4 shows the transient structures of the PA signals for the samples under investigation. The Fourier analysis of these data presented in Figure 5 has been carried out using the following technique. A fixed Welch window⁷ indicated as W_1 in Figures 4 (a-c), was applied to the beginning of the PA signal. The Fourier transform of this weighed signal was divided by the Fourier transform of the detector time response, and the square root of the resulting filtered power spectrum, representing a frequency response of the tested samples, is plotted in Figure 5. This signal analysis removes the distortions caused by the sensor system and shows the spectrum of frequencies in the transient structures. The filtered Fourier transforms show that definite frequencies contribute to the PA signal of the samples under investigation. The main feature exhibited in spectra of samples HDPE #2 and HDPE #7 is the presence of high-frequency components absent in the spectra of sample PP #5. A comparison of Figure

Figure 4 Time domain PA signals for samples (a) HDPE #2, (b) HDPE #7, and (c) PP #5. The fixed windows W_1 were used to calculate Fourier transforms. The moving windows W_2 were used to calculate "time profiles" for the most prominent frequency components.



4 (a-c) and 5 shows that the initial part of the PA signal of sample PP #5 has the most prominent frequency component at 98 kHz, whereas the sample HDPE #7 has the most intense frequency at 175 kHz and sample HDPE #2 at 216 kHz. The differences in these frequency characteristics can be explained not only by different material compositions, but also should be influenced by different wall thicknesses of these samples. In order to monitor the time-dependent effects related to the propagation of the acoustic waves, we have calculated "time profiles" for the most intense frequency components. A narrower moving Welch window, W_2 , was scanned along a PA signal, and the amplitude at a chosen frequency was plotted as a function of the window position on the time scale. As shown in Figure 6 (a-c), the amplitudes reach the maximum values when the scanning window is at the position of the primary PA signal, and are attenuated with time. The oscillations are probably due to the limited number of data points used for these Fourier transforms. These plots enable us to evaluate the travelling time of the acoustic wave having the corresponding frequency. We expect that these features can be used for the characterization of the dispersion properties of the samples and for obtaining additional parameters in the testing of industrial plastics, especially in the case when some different plastics have overlapping ranges of sound velocities.

PA Measurements on Commercial Plastic Containers

Testing commercial plastic containers, we had to increase the laser pulse energy to 85% of its nominal value to obtain a good signal-to-noise ratio. Thus prolonged PA measurements were not possible with the greased sensitizer. Nevertheless, it was possible to obtain PA signals. The sound velocities determined using these samples coincide well with the data in Table I. However, due to the more complex shape of these objects, the determination of the distance between the focus point and detector position was less precise than with the rectangular samples. In particular, when the excitation and detection points were separated by an edge of the container, this led to a systematic error, increasing the determined sound velocity by 1-4%. So the most pref-

Figure 6 The "time profiles" for the frequency components (a) at 216 kHz; sample HDPE #2; (b) at 175 kHz, sample HDPE #7; and (c) at 98 kHz, sample PP #5.

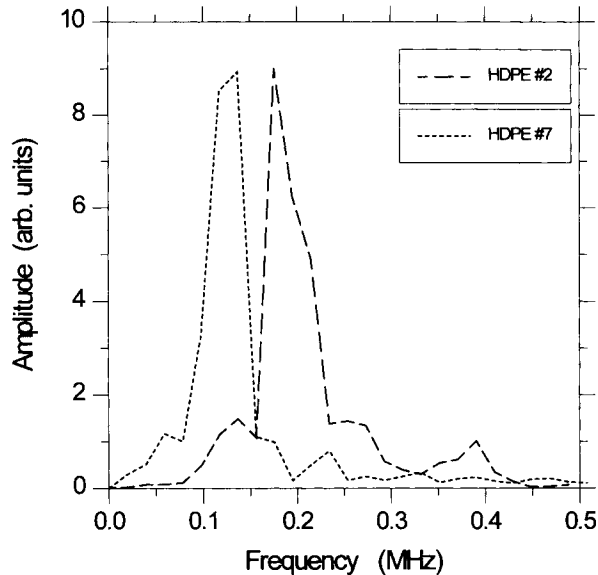


Figure 7 The frequency responses of the PA signals for the containers composed of HDPE #2 and HDPE #7 plastics.

erable experimental arrangements require that both excitation and detection occur on the same surface of the sample.

The sample shape should influence the transient structure of the PA signal and the frequency spectrum. This is illustrated by the frequency domain presentation of the beginning parts of the PA signal for the containers composed of HDPE #2 and HDPE #7 plastics, as shown in Figure 7. The main frequency components presented in this plot are shifted by approximately 45 kHz to lower frequencies compared to Figure 5. This difference is related to different test sample geometry. The data obtained demonstrate the feasibility of distinguishing these real samples on the basis of sound velocities, in particular combining these data with the frequency analysis as an additional source of information.

CONCLUSIONS

Despite the limited range of consumer plastics tested in this study, we have demonstrated that the time-resolved, pulsed laser, wavelength independent, photosensitized acoustic technique can be applied for the testing of industrial plastics. To characterize plastic wares, sound velocities can be determined as well as the frequency response. The application of a sensitizer removes the problems related to the light absorption by the tested sample. The sensitizers preserve the sample surface from ablation and make the PA testing nondestructive. Further testing and designs on a conveyer device integrated with the sensor will be required before a pilot scale project.

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