Identification and characterization of reclaimed and recycled polymers by ultrasound attenuation

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Abstract

Ultrasound attenuation analysis has been demonstrated as a cheap, reliable method of identifying and characterizing polymeric materials and components, which can assist in the separation and reclamation of thermoplastics from polymer waste streams. Material–component broad band ultrasonic attenuation measurement and the measurement of the time of flight of an ultrasonic pulse, in either pulse echo or pulse through-transmission mode, can be combined to attain a signature of the material under investigation. The HL (Hull–Langton) signature is independent of component dimensions and hence is a powerful tool for the identification of components of complex shape where access to all surfaces may be restricted. The results presented demonstrate the ability of the technique to identify a range of different polymers, including reinforced materials.

1. Introduction

1.1. The waste problem

Thermoplastic waste is widely perceived to be a major environmental problem. The volume of waste materials continues to rise in step with the consumption of plastic materials, which was in excess of 33 million tonnes in the EC in 1992. Attention has focused on the economic treatment and disposal of waste materials from both commercial and domestic products, including packaging, white goods, scrapped automotive parts and textiles [1–3].

There are more than 50 generic polymer types, each produced in up to 50 different grades, including co-polymers specifically formulated for their applications, by more than 40 manufacturers. Hence there are about 100 000 polymer variants in circulation which could potentially enter the waste stream. However, the vast majority of the 13 million tonnes of plastics which entered the waste stream in Western Europe in 1992 comprised just seven generic types, with over half being polyolefins. Around 93% of the total polymers in the waste stream are made up from about 14% of the variants. Some rationalization will occur in the future, resulting in a reduction in the number of variants. However, this in itself is unlikely to make recycling of

polymer waste any easier. Increase in the consumption of thermoplastics and their resultant entry into the waste stream, even at a conservative 3% growth rate per annum across the range, will mean that by the year 2000 it will be necessary to deal with about 19 million tonnes of polymer waste.

Reclamation of plastic components and recycling of polymeric materials are of increasing interest to the industrial sector, including materials suppliers, waste collectors and separators, materials processors, product users and processing equipment suppliers. However, with the inherent limitations in current identification and separation technology, it is inevitable that a relatively high percentage of recycled materials will contain "contaminants".

Small amounts of contaminants can render reclaimed polymers unsuitable for reuse. For example, it is imperative that reclaimed polethylene terephthalate (PET) from consumer drink containers does not contain poly(vinyl chloride) (PVC) as a contaminant in amounts greater than 100 ppm, because the significant differences in processing temperatures between the two materials can result in the formation of low molecular weight degradation products. Reclamation of plastics from automotive components has similar problems: residual amounts (less than 2%) of high density polyethylene (HDPE) in polypropylene (PP) for example can result in a serious reduction in tensile strength from 35 to

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26 MPa (about −25%) and in flexural modulus from 1.5 to 1.2 GPa (about −20%), whilst HDPE contaminated with PP suffers a marked reduction in impact properties from 0.15 to 0.098 kJ m⁻¹ (about −35%).

1.2. Current ideology

In the UK most plastic waste (approximately 90%) is buried in landfill sites, where it is hoped that the inert nature of plastics will have no long-term harmful effects. Increasing cost of landfill in the future could preclude this approach. In Germany the cost of landfill is about £150 per tonne, whilst in the UK the cost is relatively low at about £8 per tonne. However, this situation could change rapidly with new EC legislation.

Incineration with energy recovery has been postulated as an alternative way of dealing with the waste problem [1, 4]. This approach, however, is viewed by many as both the waste of a diminishing natural resource and environmentally unfriendly owing to the potential impact of gas emissions [5]. Direct reclamation is arguably the best approach to retaining the many benefits of plastic whilst minimizing the impact associated with waste disposal. Recycling takes place on a significant scale within the UK and is a major element in the EC waste management strategy.

1.3. The need for identification

Increasing use of a wider range of thermoplastics and polymer blends with additives has made the indentification and separation of waste materials and components a difficult, expensive, labour-intensive task. Moreover, at present little knowledge exists regarding the effects of recycling, in particular multiple recycle–processing stages, on the properties of polymeric materials.

2. Identification techniques

2.1. Currently available systems

A number of techniques have been developed to assist in identification of plastic waste, including moulded-in codes [6], X-ray spectroscopy [7] and Fourier transform IR spectroscopy [8]. However, none of these methods of approach has proved to be either completely satisfactory or acceptable to a wide proportion of the industrial waste management sector.

2.2. Ultrasound attenuation analysis and polymer identification

Ultrasonic attenuation offers a fast, reliable, inherently safe approach which has considerable potential for providing the best all-round method of characterization of polymer waste both on-line and off-line. The approach adopted precludes the need to measure component–material dimensions and is based on the use of attenuation analyses for medical diagnostics as developed by Langton et al. [9, 10]. Thomas et al. [11] have demonstrated the potential of using ultrasonic velocity and selective attenuation analysis to monitor details of the polymer state during processing. Polymer characterization using ultrasonic velocity analysis to predict molecular orientation and crystallinity in injection-moulded HDPE plates has been attempted by Nobuhiko et al. [12, 13]. However, their approach suffers from two major limitations: firstly, accurate measurement of small changes in ultrasonic velocity necessitates very accurate measurements of component dimensions; secondly, no attempt was made to nullify the effects of residual stresses on compressive or shear wave velocities. Such effects can be significant [14, 15], particularly surface residual stresses.

The novel technique developed by Hull and Langton (HL) [16–19] combines measurements of broad band ultrasonic attenuation (BUA) and through-transit time into a specific signature (the HL index) that does not require accurate measurement of component dimensions. Hence the approach is easily applicable to complex shapes. In addition, granulated and flake polymers (reclaimed "fluff") as well as solid components can be scanned. Moreover, since materials are scanned in bulk, the effects of residual stress are less important.

2.3. HL ultrasound analysis

At any given test frequency, if A (dB) is the measured ultrasound attenuation, then

$$\alpha = \frac{A}{d}$$

where α (dB mm⁻¹) is the attenuation coefficient and d (mm) is the distance traversed through a polymeric material by an ultrasonic pulse. The measured time of flight of an ultrasonic pulse, t (s), is given by

$$t = \frac{d}{V}$$

where V (mm s⁻¹) is the velocity of sound for either compressive or shear waves in a polymer. Hence for any given polymer under test a signature S (dB s⁻¹) can be obtained where

$$S = \alpha V = \frac{A}{d}\frac{d}{t} = \frac{A}{t}$$

The overall analysis can be improved upon by taking measurements using both V_c (compression wave velocity) and V_s (shear wave velocity) and scanning attenuation over a range of frequencies (broad band ultrasonic attenuation analysis).

The HL index (dB MHz^{-1} s^{-1}) is obtained from the regression slope of the attenuation *vs.* broad band frequency profile of any material under test, divided by the through-transit time:

$$HL\ index = \frac{A}{f}\frac{1}{t} = \frac{C}{t}$$

where C (dB MHz^{-1}) is the attenuation *vs.* frequency regression slope. Hence the need to measure component dimensions is obviated.

2.4. Broad band ultrasound attenuation

To determine the BUA of a material, it is necessary to compare the amplitude of an ultrasound signal over the chosen frequency range through a reference material, *e.g.* degassed water, and compare this with an amplitude spectrum obtained after propagating through the measured material. It is then possible to plot attenuation (α) as a function of frequency (f) and express the BUA index as the regression slope.

The variation in linearity about this regression may also be utilized as a measurement parameter. The non-linearity may be expressed as the percentage ratio of the deviation in the regression slope divided by the mean value for the regression slope. Work to date suggests that a significant cause of this non-linearity is a complex interaction between the excitation of the ultrasonic wave and the molecular structure of the material. For example, semicrystalline PE demonstrates a highly linear relationship, whereas fully crystalline PP demonstrates a high degree of non-linearity.

3. Experimental technique

The approach adopted employs a digital ultrasonic analyser coupled to either one or two ultrasonic transducers for broad band frequency pulse echo–through-transmission analysis. A schematic diagram of a typical set-up is shown in Fig. 1. Analysis of the ultrasonic properties of a specimen–component is facilitated by an integral digital computer using customized system software.
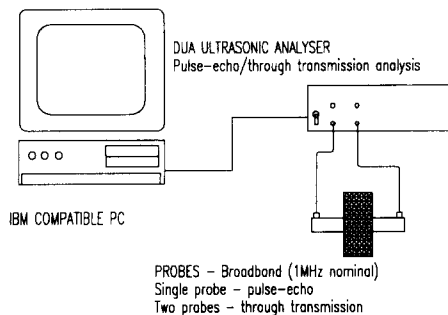

PROBES — Broadband (1MHz nominal)
Single probe — pulse–echo
Two probes — through transmission

Fig. 1. Schematic diagram of ultrasonic identification equipment.

TABLE 1. HL indices and non-linearity values for a range of polymeric materials

Material	HL index (dB MHz^{-1} s^{-1})×10^6	Non-linearity (±%)
LDPE	1.003	1
HDPE	0.656	4
Nylon 66	0.465	25
EPR[a]	0.212	6
Perspex	0.284	10
Urethane foam	2.33	9
ABS[b]	0.312	10

[a]EPR, ethylene propylene rubber.
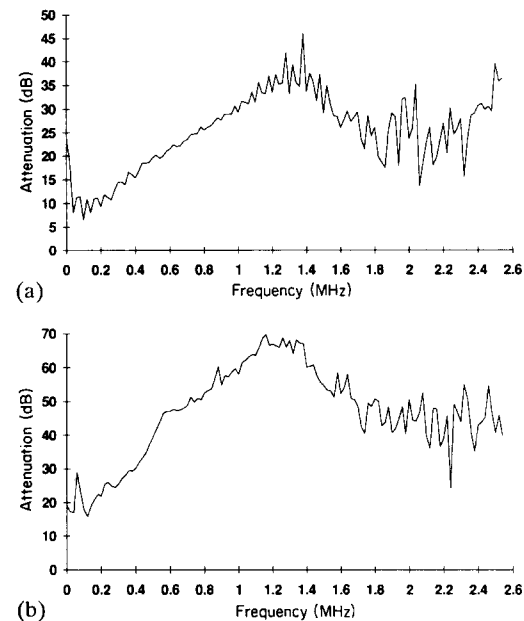[b]ABS, acrylonitrile butadiene styrene.

Fig. 2. Attenuation *vs.* frequency traces for (a) a PE block and (b) a PP block.

A specific HL index or signature is obtained which may be compared against a known database for polymer identification (Table 1). It is possible to identify homopolymers, copolymers and polymer blends [18, 19].

4. Results

The capability of the approach adopted by Hull and Langton can be readily demonstrated with the following examples.

(1) *Attenuation traces* of HDPE and PP illustrated in Fig. 2 and *regression slopes* illustrated in Fig. 3 indicate that PP exhibits a much greater deviation from the regression slope than does HDPE.

(2) PP samples of *various thicknesses* between 10 and 80 mm have been analysed. The attenuation *vs.* frequency traces (Fig. 4(a)) at different sample thicknesses
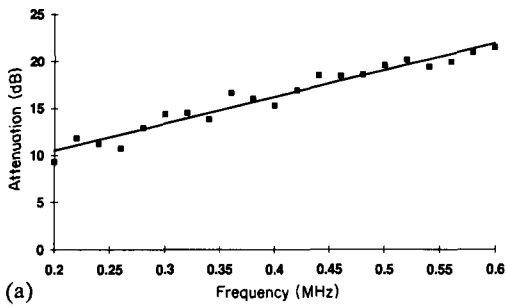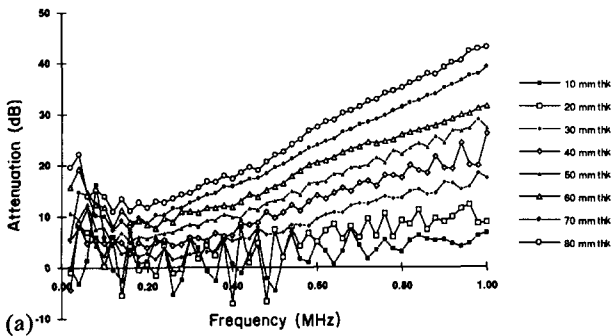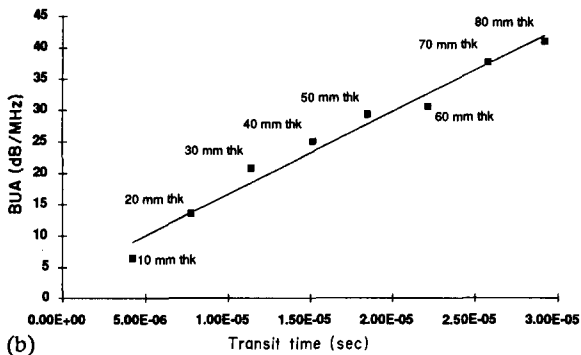
(a)
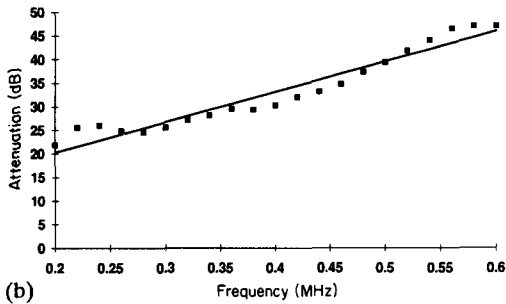
(b)

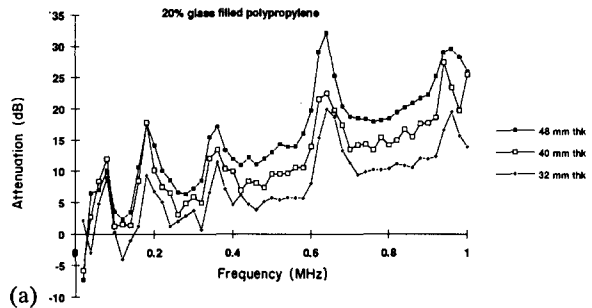Fig. 3. Regression slope fitted to the (a) PE and (b) PP traces.

(a)

(b)

Fig. 4. (a) Attenuation *vs.* frequency and (b) BUA *vs.* transit time for varying thickness of PP block.

(a)

(b)

(c)

Fig. 5. Attenuation *vs.* frequency for (a) varying thickness of glass-filled PP, (b) varying thickness of talc-filled PP and (c) unfilled, glass-filled and talc-filled PP.

(3) An initial survey of the ultrasound characteristics of polymers modified by *reinforcing fillers* has indicated that the effects of fillers on attenuation are significant and hence may allow modified polymers to be readily identified. Figures 5(a) and 5(b) show typical profiles obtained during a study of 20% glass-filled and 20% talc-filled PP specimens. In each case characteristic peaks are evident which are not apparent when testing unmodified material. Available evidence suggests that the peaks appear to relate to the type of filler used (Fig. 5(c)). However, filler orientation, filler shape (axial ratio) and filler dispersion are parameters that could also affect attenuation behaviour. These parameters are currently under investigation.
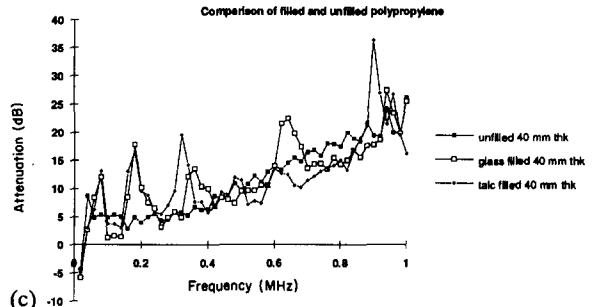
indicate significant fluctuation for thin samples due to reverberation of the ultrasonic pulse within the sample. Stable results may be obtained by employing shorter, higher frequency ultrasound signals. The regression between BUA and transit time (Fig. 4(b)) illustrates little variability, thus validating the concept of the HL Index.

5. Conclusions

In the light of this work it is possible to draw the following conclusions.

(1) Ultrasound attenuation analysis is a reliable method of identifying polymeric materials and components and possesses the potential to be developed into a cheap but powerful method of identifying recyclate in the polymer waste reclamation industry.

(2) The HL technique is superior to current methods, and since the approach adopted is both non-destructive and does not rely on thickness measurements, it is inherently more suitable for on-line quality control testing of products with complex shapes.

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