Acoustic emission and e.s.r. studies of polymers under stress

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A nearly noise-free apparatus for the stressing of polymers is described. It has been used, in conjunction with a sensitive piezo-electric transducer and associated apparatus for the generation, detection and collection of acoustic emissions, from stressed polymers. It is shown that detectable levels of acoustic energy are released from several polymers and composites, and that the distribution of acoustic events varies with material examined. Parallel experiments have been carried out in which free radicals are generated by stressing bulk polymer in the cavity of an e.s.r. spectrometer. There is some correlation between stress and both acoustic emissions and free radical generation.

Keywords Polymers; spectrometry; stress; electron spin resonance; acoustic emission; free radical

INTRODUCTION

An acoustic emission is a transient elastic wave generated by the rapid release of energy within a material. It is often associated with local redistribution of material which is, in most cases, the initial indication of the impending failure.

Acoustic emission techniques can be used to monitor rapid-energy release events as large as the advancement of a subcritical crack and as small as material readjustment due to movements of about 50 dislocations[1]. Acoustic emissions in strained metals are caused by the motion of dislocations in crystal lattice and phase transitions during plastic deformation[2]. For polymers a slightly more than linear increase of acoustic activity with increasing strain and stress has been reported by Grabec and Peterlin[3]. They also observed a close correlation of acoustic bursts with craze initiation and growth. Both Zhurkov[4] and Peterlin[5] have reported the production of free radicals during crack formation in films and fibres.

We have embarked on a long term study of acoustic emissions from polymers under stress, with two major objectives in mind:

(i) to investigate whether the pattern of acoustic signals from a particular sample may be used analytically to characterize the sample and/or to enable predictions to be made about its mechanical performance;

(ii) to discover the origins of the acoustic signal.

In particular, we seek to apply new mathematical techniques of signal analysis and pattern recognition to establish relationships between acoustic emission, mechanical performance and other data. In addition the samples are being examined by a variety of spectroscopic and microscopic techniques and mechanical testing.

In this first paper we describe the experimental arrangements for the detection of acoustic emissions from polymers under stress and parallel e.s.r. experiments, together with the preliminary results obtained.

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EXPERIMENTAL

Samples

The samples examined were prepared in the laboratories of ICI, Welwyn Garden City. They consisted of five unmodified homopolymers, four modified samples and one copolymer. Samples were provided as ASTM dumbells, sheets or discs as shown in the table below. Sheets and discs were cut into dumbells before stressing.

Instrumentation and experimental procedure

The apparatus required for acoustic emission studies of polymers under stress consists of a stressor, an acoustic emission transducer, an amplifier and a recording system.

Acoustic tensile apparatus

A purpose built 'noiseless stressor' to be used for the tensile acoustic emission measurements was designed by Mr M. J. Dowzell and built by Mr L. P. Parsavell, both of the Laboratory Apparatus Section I.C.I. Petrochemicals and Plastics Division, Welwyn Garden City (*Figure 1*). The layout is shown in *Figure 2*.

The apparatus was specifically designed to ensure minimal mechanical noise transfer, between moving parts. Air bearings are incorporated in all mobile parts to remove metal-to-metal contact and hence frictional noise.

The sample is stressed by a pneumatically loaded piston and cylinder, supplied by a servo-driven regulator valve. The rate of loading is variable via a gear box upon the servo-motor. Stress is increased at a constant rate, no attempt being made to limit sample extension.

The load can be monitored by a full bridge strain gauge system incorporated between the lower clamp and lower air bearing.

A special 'Purair' filter system is used on the input compressed air line to remove any particles or liquid from the mains supply.

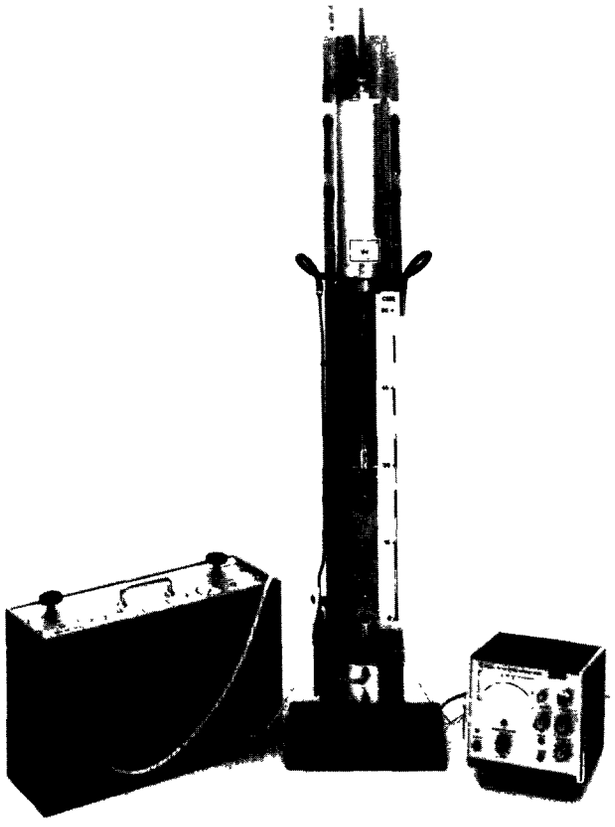

Figure 1 Photograph of the apparatus.

The airline is divided and fed to two regulators; the bearing line, 0–60 psi, and the load cylinder, 0–60 psi. In addition there is an extra filter at the output to the mains air supply to trap the greater part of the fluid in the compressed air supply and to conserve the filters. All filters are self-venting.

The machine is of robust construction for stability and is mounted upon a bench by four locating bolts through the base. A sandwich of 'teco' sound insulation pad and wood is placed between the bench and the machine base to decrease sound transmission to the machine frame. The loading cylinder is of adjustable height so a variety of sample lengths can be catered for. The loading cylinder has a 10 inch stroke, so that 100% extension of the sample is possible.

Although the exhausts for the air-bearing have suppressors on them they still emit a detectable noise. Consequently, further sound-proofing is provided by a 'Perspex' cabinet, which encloses the clamp area but leaves the bearing outside. The loading piston shaft passes freely through the top and there are holes at the side to accommodate electrical cables. The cabinet is obviously not airtight but a significant level of airborne noise reduction has been achieved.

Clamping systems. Two types of clamps have been used on the tensile machine. The first is based on the design described by Dunegan[6]. The sample is held in position by two hooks. The hooks themselves had a section removed from the curved portion to accommodate the sample. A pin passing through a hole in the sample and resting on the hook held the sample firm during subsequent loading. The hooks were interfaced to the tensile machine shaft by a set of connecting wires which were designed to minimise noise transfer from the machine to the sample.

The hooks were specifically designed to eliminate the necessity of gripping the sample and hence avoiding the possibility of sample slippage. However problems arose in the pins passing through the sample when loading. The pinholes enlarged and often fracture occurred there. Problems also occurred with the connecting wires interfacing the clamps. They were prone to fracture. The hooks were therefore abandoned in favour of a more conventional jaw-type design.

The grip is applied by tightening a bolt which feeds through both jaws. The jaws are attached to the stressor by a noise attenuation device described by Wood[7]. This serves the same purpose as the wires in the previous design. The device is basically a coupling consisting of a sandwich of five interfaces bolted together. Alternate interfaces are of steel and 'Teco' pad to ensure maximum acoustic missmatch and hence greatest attentuation of sound transferred from machine to sample.

With this type of clamping mechanism there is a danger that sample slippage occurs introducing frictional noise as a source or error into the acoustic measurements. However this did not appear to be the case. Any noise from slippage that did occur must have been below the general noise level.

Extension measurements. Sample extension measurements were made by a rack and pinion, the rack being attached to the mobile clamp and the pinion to a potentiometer shaft. The extension was recorded as a voltage, and converted to length by a calibration curve. Most of the samples were stressed at loading rates between 2–10 Kg min^{-1}.

Detection of acoustic signal. The power of the acoustic emission signal was monitored using the method described by Hatano[8] which is based on measurements of the rate of production of acoustic emission energy.

The acoustic signal is detected by a piezoelectric transducer, (Dunegan Research Corporation S140). The acoustic signal thus converted into electrical signal is then amplified and filtered (100–300 kHz) to remove extraneous noise. Root mean square (RMS) acoustic emission power measurements are made by placing a resistance in parallel with the transducer, the acoustic emission power is related to the energy dissipated over the resistance by Joule's Law:

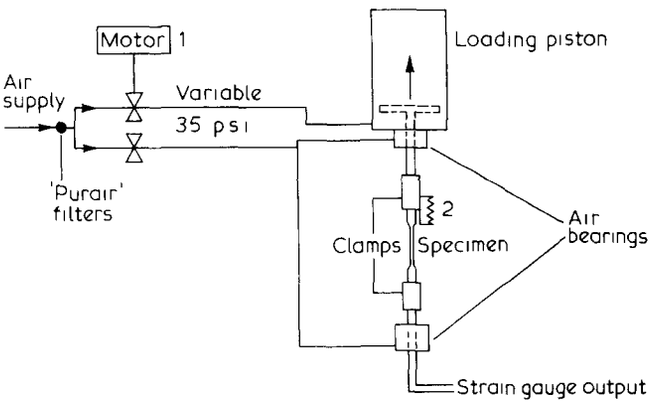

Figure 2 Diagram of the noiseless stressor. 1, Motor drives air supply valve to ensure constant loading rate. Also has variable gear box so that loading rate can be changed. 2, Rack connects to wheel of potentiometer for extension measurements

Table 1 Summary of acoustic results

Sample	Form in which sample was examined	Total number of samples examined	Number of samples having the number of signals indicated				Average power ($\times 10^{-8}$ J s^{-1})
			Zero signals	1–9 signals	10–19 signals	20 or more signals	
Nylon-6,6	Injection moulded ASTM bar	28	7	15	6	0	0.0617
'Diakon'	Injection moulded disc	7	2	1	0	4	0.0822
'Diakon' + 30% rubber	Injection moulded disc	7	2	3	2	0	0.1224
'Diakon' + 60% rubber	Injection moulded disc	7	3	4	0	0	0.0107
Polypropylene	Injection moulded ASTM bar	30	10	14	4	2	0.3866
PTFE	Sintered sheet	29	6	21	2	0	0.7418
PVC + stabilizer	Compression moulded sheet	32	2	23	2	5	0.1912
PVC	Compression moulded sheet	6	0	2	3	1	–
Propylene/ethylene copolymer	Injection moulded ASTM bar	20	9	11	0	0	0.0822

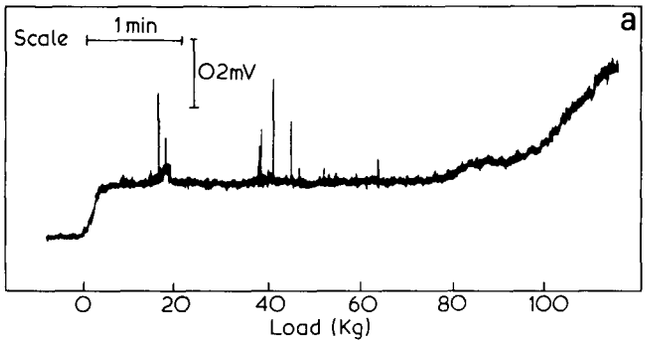

Figure 3a Acoustic Emission Trace from a narrowed nylon-6,6 sample. Loading rate = 21.132 kg min^{-1}; sensitivity: 1 cm = 0.2 mV; maximum load = 112 kg

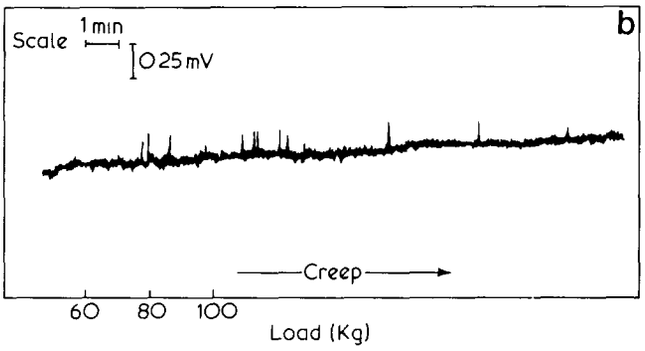

Figure 3b Acoustic emission trace from a nylon sample cut from a sheet. Loading rate = 10.182 kg min^{-1}, sensitivity: 1 cm = 0.25 mV; maximum load = 112 kg

$$P = V^2/R$$

where P is the power, V is the RMS voltage and R is the value of the resistance, which in these experiments was 19 ohms. The amplifier output is then passed through an RMS to d.c. converter, (Analog Devices type 442J I.C. Chip). The system has a lower frequency limit of 10 KHz with a minimum averaging constant of 1.5mS. A d.c. voltage of RMS acoustic emission power was obtained as output and plotted upon a potentiometric recorder (see *Table 1*).

E.s.r. measurements

Specimens were cut into 1 cm strips and necked by milling to enable failure to be monitored within the spectrometer cavity. All samples were tested in air at room temperature. Samples were clamped in the cavity and dead-weight loaded, a spectrum being recorded upon each new addition of load. A background spectrum was recorded for each sample before loading commenced. Samples were also strained on an Instron Universal testing machine and then conveyed to the spectrometer where spectra were recorded. The spectrometer used in this study was a Varian E4.

RESULTS

Unmodified nylon-6,6

Acoustic. No acoustic emissions were observed from standard dumbell samples of nylon-6,6. The samples (3.2 mm thick) did not fracture; so they were reduced in width or notched. A few signals were observed on occasions from narrowed samples (*Figure 3a*). Most notched samples gave at least one acoustic emission before fracture.

Samples that were cut from sheets (1.6 mm thick) of nylon-6,6 were seen to produce acoustic emissions on the majority of the runs (*Figure 3b*). The signals were quite weak however.

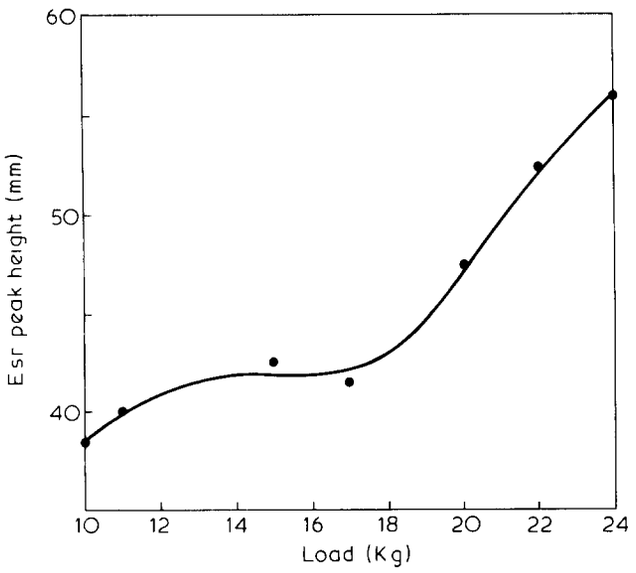

Figure 4 Graph of intensity of e.s.r. signal from nylon under load

E.s.r. Most of the e.s.r. work was carried out on nylon samples. Specimens were made from three different sources. The first specimens were cut from compression moulded sheet. Samples dead-weight loaded in the cavity gave a singlet spectrum corresponding to a peroxy radical. If it were possible to further load the sample the intensity of the signal increased, *Figure 4*. A sample was left unclamped in the cavity to determine the decay rate of the radical spectrum. This was found to be small over a period of over 1 h. It was therefore considered that radical decay did not severely affect the results.

In addition to this some samples were stressed on an Instron universal testing machine through various degrees of extension. All spectra taken after stressing showed no apparent change from the background spectra taken of the unloaded samples.

Specimens cut from injection moulded ASTM dumbells were dead-weight loaded in the cavity. Background spectra taken showed multiplet peaks indicating that radicals were already present in the samples. This was possibly due to the fact that the samples were filed to the correct width. The results are difficult to interpret. However, shape and intensity of the e.s.r. signals did change upon loading samples to fracture. One sample, unlike the others, did not give an initial background signal, nor detectable level of free radicals on fracture.

Other specimens were cut from injection moulded discs. These samples were dead-weight loaded in the cavity with no free radicals being detected. Samples were also strained on an Instron Universal testing machine to various stages of draw through to fracture; these also produced negative results. A sample that was ground, using a file was found to have a singlet peroxy radical peak.

Unmodified 'Diakon'

Acoustic. No acoustic emissions were recorded from 'Diakon' samples more than 15 mm wide. The samples were not fractured and seemed not to extend. Acoustic emissions were, however, observed from narrower samples. The number of signals appeared to increase with decreasing width of sample. *Figure 5* shows one of the traces obtained from a 'Diakon' sample.

E.s.r. Samples were loaded in the cavity to brittle fracture. An initial concentration of peroxy radicals was detected in one sample. The intensity of the signal increased upon loading the sample. Another sample was loaded to fracture without any free radicals being detected.

Polypropylene

Acoustic. Standard ASTM dumbells of polypropylene occasionally produced acoustic emissions during loading and also under constant load. Most of the signals, although significant in number, were quite weak. One sample monitored under a constant load of 112 Kg gave spectacular results (*Figure 6a*).

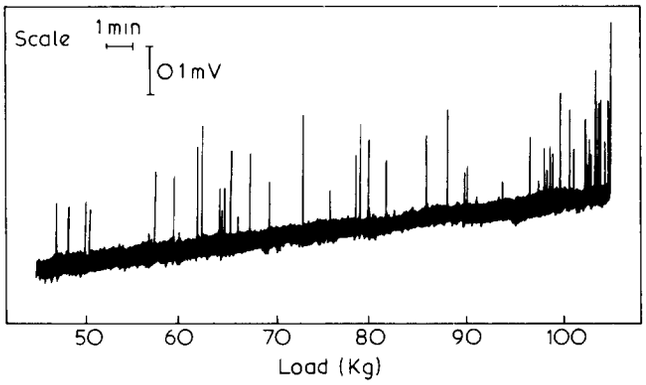

Figure 5 Acoustic emission trace from 'Diakon'. Loading rate = 2.478 kg min^{-1}, sensitivity: 1 cm = 0.1 mV. Fractured at 105.4 kg

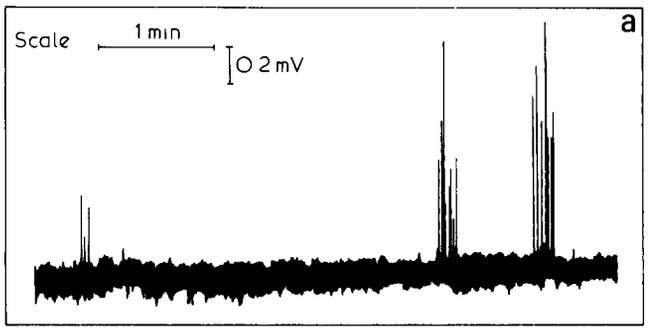

Figure 6a Acoustic emission trace from polypropylene monitored at a constant load of 112 kg. Sensitivity: 1 cm = 0.2 mV

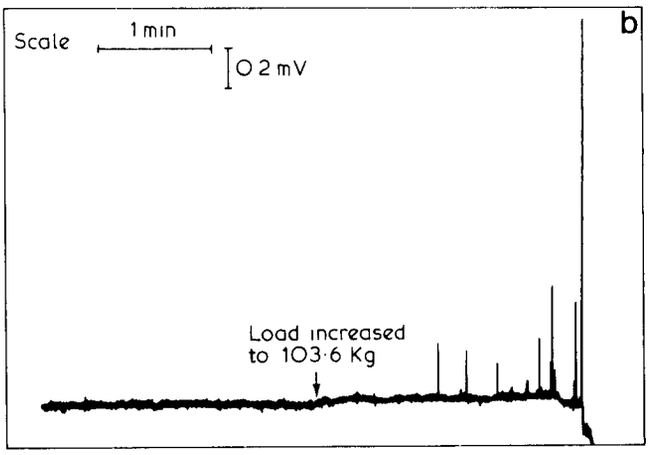

Figure 6b Acoustic emission trace from a narrowed propylene sample. The load was manually reduced from 103.6 to 98 kg immediately after stress-whitening and increased back to 103.6 kg after some time. The emissions were observed at 103.6 kg

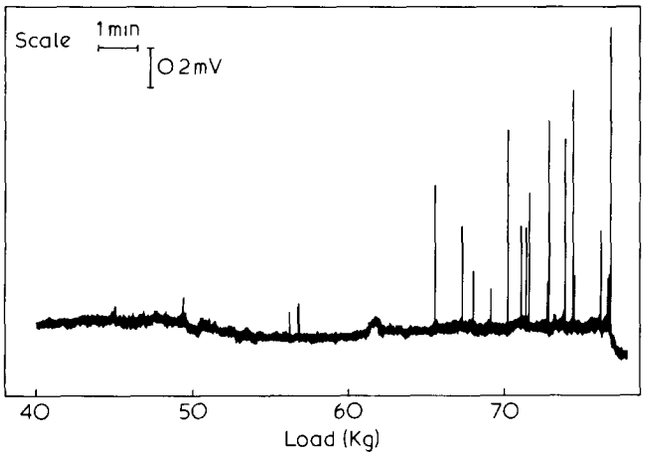

Figure 7 Acoustic emission trace from PTFE. Loading rate = 2.423 kg min^{-1}, sensitivity: 1 cm = 0.2 mV, fractured at 77 kg

One major event was observed just before fracture for most narrow dumbells. This observation led to the speculation that more acoustic emission signals would be recorded if the load could be controlled near fracture. To test this, a narrow sample was stressed until stress whitening occurred. The load was then reduced from 103.6 kg to 98.0 kg manually and left at this load for about 10 min. On returning the load to 103.6 kg, it was observed that several acoustic emission signals were emitted (*Figure 6b*). The disadvantage of such a procedure is that manual control of the load is not uniform and cannot be reproduced accurately.

Notched polypropylene samples occasionally produced some acoustic emission signals. Even in the cases in which events were not observed during the loading process, one major event was observed just before fracture.

E.s.r. All samples had a brittle fracture in the cavity with little or no apparent draw. In none were free radicals detected.

Polytetrafluoroethylene

Acoustic. The acoustic emissions observed from PTFE were few but very strong, relative to the other samples. *Figure 7* shows one of the traces obtained from this polymer.

The sample elongated to more than 100% of its original length before it fractured.

A few runs carried out on PTFE using a fine recording pen showed up some activity on a smaller scale in the narrowing and broadening of the trace. In most cases this broadening followed the emission of very strong signals and is presumably the result of numerous acoustic emissions of very low intensity.

E.s.r. Samples were loaded in the cavity with ductile extension. It was not possible to fracture samples as they extended to the constraints of the apparatus without fracturing. Free radicals were detected in some of the samples as peroxy singlets. The concentration was observed to increase with the addition of load. However, because of the fact that the sample was creeping, the active volume within the cavity was decreasing all the time.

Unstabilized PVC

Acoustic. Standard dumbells and notched samples of unstabilized PVC gave acoustic emissions with a reasonably similar general pattern but with variations in the number of emissions from sample to sample. In contrast to notched samples, the dumbell samples were remarkably quiet (*Figure 8*). This is probably due to substantially higher forces exerted in the region around the notch tip than those in the other regions of the sample. This leads to plastic deformation at the notch tip taking a relatively long time before the sample fractures. This is in contrast to the dumbell samples in which fracture generally follows immediately after necking.

Stabilized PVC

Acoustic. The generation of signals followed a generally reproducible pattern although the number of signals observed varied from sample to sample. On few occasions the emissions appeared as bursts of activity (*Figure 9*). All the signals were emitted after stress-whitening had started. The average rate of emission and the average signal intensity were seen to increase towards fracture. The samples had elongated by an amount averaging 3.7% of their original length by the time of fracture.

A few samples of stabilized PVC were monitored using a fine recording pen. The narrowing and broadening of the trace was even more pronounced than that observed in PTFE.

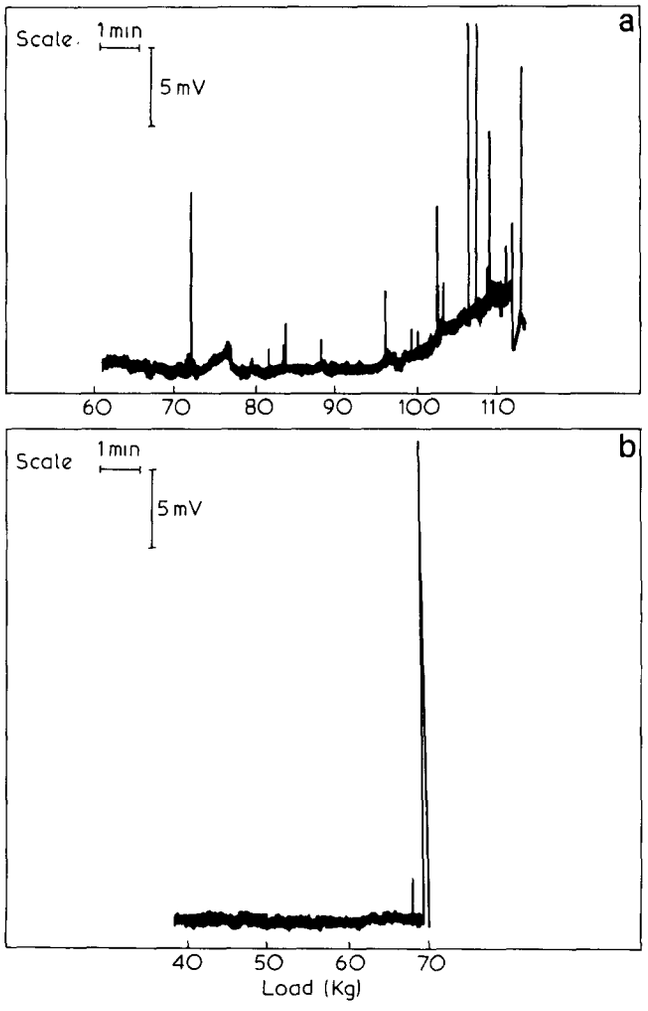

Figure 8 Acoustic emission trace unstabilized PVC. (a) Notched Sample. Sensitivity: 1 cm = 5 mV, fractured at 112 kg; (b) Dumbell. Sensitivity: 1 cm = 5 mV, fractured at 70 kg

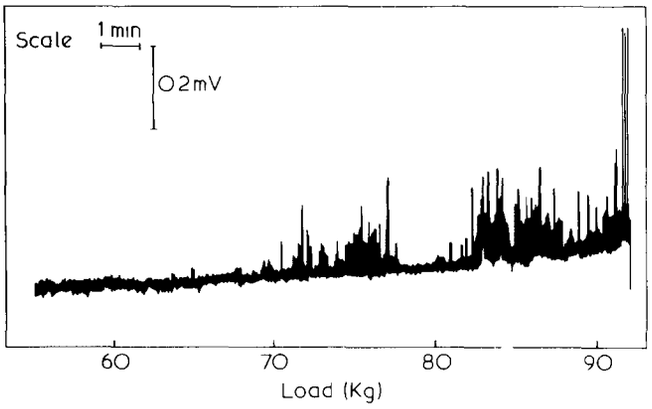

Figure 9 Acoustic emission trace from PVC with Stabilizer. Loading rate = 2.355 psi, sensitivity: 1 cm = 0.2 mV, fractured at 92.4 kg

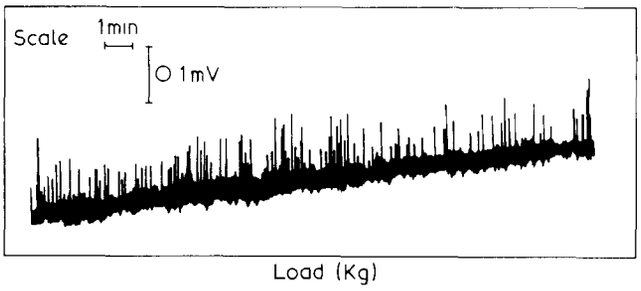

Figure 10 Acoustic emission trace from fibre-glass filled nylon-6,6 under no applied load. Sensitivity: 1 cm = 0.1 mV

E.s.r. Samples were dead-weight loaded to brittle fracture in the cavity with little or no apparent draw and no appearance of free radicals. A further set of samples were taken and drawn on an Instron Universal testing machine and then allowed to relax as they were taken to the laboratory where their e.s.r. spectra were recorded. This process was repeated until the sample fractured. All of this class of sample yielded free radicals only after necking and the concentration of radicals increased with further extension of the sample.

Glass-filled nylon-6,6

Acoustic. This polymer is nylon-6,6 to which 33% glass fibre has been added. The sample emits acoustic signals immediately on clamping in the stressor even with no load applied (*Figure 10*). An unclamped sample does not emit acoustic signals.

The sample produced acoustic emissions in sufficient numbers to study the following aspects:

(a) the time-based change in the number of signals emitted by a clamped sample with no applied load;

(b) the relationship between the load and the number of signals emitted for different loading rates;

(c) the relationship between the signal intensity and the load for different loading rates.

The histogram (*Figure 11*) shows that the number of signals emitted decreases exponentially with time for a clamped sample with no applied load.

The relationship between the number of signals emitted and the load is shown in *Figure 12*. It is clear that the number of signals emitted increases exponentially with increasing load. Changes in the loading rate do not seem to produce any major effect on the results.

Before application of the load, the sample was left on the stressor for 24 h, to allow the signals to decay to levels below the detection limits. The load was then applied. The number of acoustic emissions below 45 kg are very few, but above this they increase with increasing load. Changes in the loading rate do not seem to produce any marked effects on the results, for the range used in this study.

Signal intensity (power) with respect to load for different loading rates was obtained by plotting the power of the strongest signal at a given load. It would have been preferable to obtain an integral at a given load but the facilities for doing so were not then available. The results are broadly similar to those shown in *Figure 12*, but the scatter makes the deduction of the relationship between the load and the intensity inconclusive. Changing the loading rate does not seem to have any effect on the intensity of the signal for the range examined in this study.

The glass filled nylon-6,6 showed unusual acoustic activity. Samples reclamped on the stressor a few days after then had been loaded to 112 kg produced acoustic emissions even before the applications of the load. The emissions were allowed to decay to levels below detection before reloading. As the load was applied, acoustic emissions, less numerous and weaker than before, were observed. They were also seen to increase in number and intensity as the load was increased.

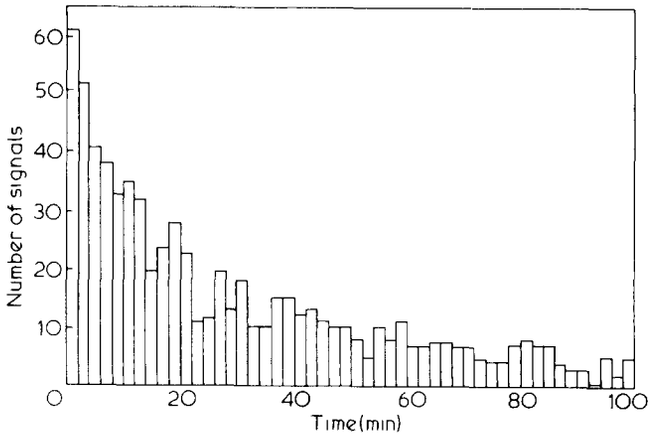

Figure 11 Frequency *versus* time histogram for signals from fibre-glass filled nylon-6,6 under no applied load

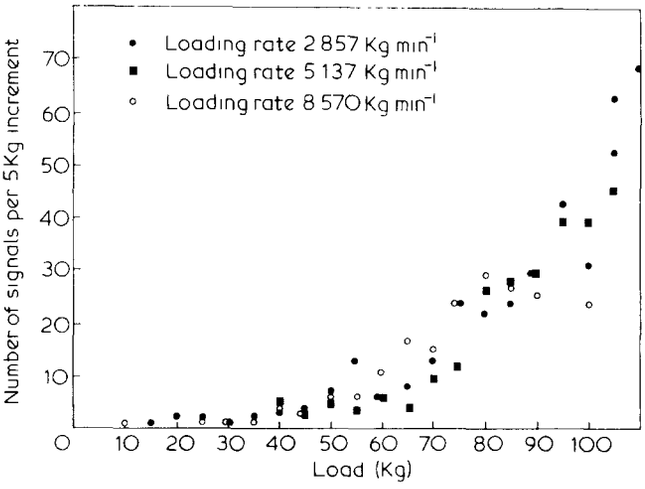

Figure 12 Number of signals *versus* load for different loading rates on fibre-glass filled nylon-6,6

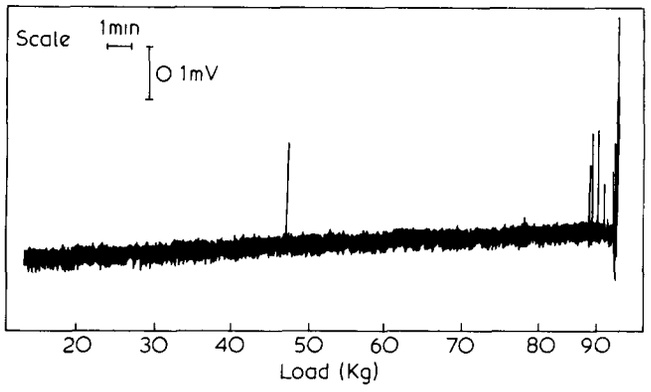

Figure 13 Acoustic emission trace from Diakon + 30% rubber. Loading rate = 2.976 kg min^{-1}, sensitivity: 1 cm = 0.1 mV. Fractured at 92.4 kg

Modified 'Diakon'

Acoustic. Two other samples of modified 'Diakon' were examined, one containing 30% and the other 60% rubber.

The sample with 30% rubber produced acoustic emissions on most of the runs attempted. The emissions appeared in the region of maximum extension rate just before fracture (*Figure 13*). All the acoustic emissions were observed after stress whitening had started. The 60% rubber sample, however, gave very few emissions. In the runs in which signals were observed only one had more than one signal. Stress whitening was observed in all the samples even though no signals were seen.

Propylene–ethylene copolymer

Acoustic. The majority of the several standard dumbell samples, examined during loading and under various constant loads between 84 and 112 kg, gave no acoustic emissions. A few signals were observed from one of these samples. However, a greater number of notched propylene–ethylene copolymer samples gave acoustic emission signals.

DISCUSSION

Table 1 summarizes the acoustic results obtained in this study. It is clearly seen that different samples display different acoustic emission activity. The modified and unmodified samples show differences pertaining to changes in ductility. The results show that more ductile samples are less acoustically active; the signal intensity of 60% rubber diakon being notably low. Although there is a significant fall in the number of signals observed due to increasing ductility we certainly are able to record signals from ductile materials as opposed to Peterlin who asserted that signals from ductile materials were not strong enough to be differentiated from the background noise. Indeed, PTFE produced the strongest of the signals observed in this study. It is, of course, of high crystallinity and this may be a significant factor.

The nylon sample with 33% glass gave signals about ten times greater than those of unmodified nylon. This behaviour is in accord with Peterlin's observations[2].

The copolymer introduces a more ductile phase in polypropylene and it is therefore consistent that the polypropylene produced relatively more, and substantially stronger, acoustic emission signals than the propylene–ethylene copolymer.

The variation in the number of acoustic emissions generated in each batch of samples is illustrated in *Table 1*. From the results obtained so far, it would appear from columns 4–7 that the distribution varies from material to material but there is significant within batch variation. Notching increases the number of emissions for a given sample.

During the experiments it has been noted that there is a degree of comparability between the acoustic and e.s.r. results in that samples which are acoustically active also yield e.s.r. signals and *vice versa*. Within batches there appear to be related changes in the e.s.r. and acoustic emission signals and mechanical fracture patterns, the latter being indicated by the extent of stress whitening or crazing.

At this stage such observations are purely qualitative, but they provide a working hypothesis that there is an association between mechanical and structural factors, and acoustic emission patterns and e.s.r. spectra. Before any firm associations can be established, however, it is necessary to obtain more results, and to subject them to a rigorous mathematical analysis, such as cluster analysis. Work is well advanced along these lines. Additionally, the individual signals are being analysed to obtain information which may help to establish the origins of acoustic emissions.

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