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Relating dynamic mechanical data to flexible PVC low temperature performance[1]

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Abstract

Flexible PVC is widely used in the medical industry in a wide variety of applications. In numerous instances, the material needs to sustain stresses at subambient temperatures. Dynamic mechanical analysis was correlated with product performance. It was found that the location of the T_g was the most important factor. However, impact studies indicated brittle-to-ductile transitions well below the T_g, most likely originating from sub-T_g secondary transitions. Further mapping of the product survival probability onto the impact spectrum allowed additional insights into the performance. Good agreement was also obtained with a method to predict the impact spectrum with DMA data.

Keywords: DMA; PVC; Impact performance

1. Introduction

Flexible PVC films and tubings of various types are often used in the medical industry. Plasticized PVC has frequently been the material of choice due to its wide formulation latitude, relative ease of processing, optical clarity for contamination inspections, and low cost. In numerous instances, these devices and delivery systems are subjected to the simultaneous conditions of subambient temperatures and mechanical stress. For example, near-freezing conditions can be expected during winter shipping. Blood components are frequently handled and centrifuge-processed at near 4°C. Certain drugs in premixed solutions are often stored and shipped frozen at about −20

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to −30°C to enhance chemical stability. Dry ice storage and transportation calls for temperatures of about −78°C, and in cryopreservation, liquid nitrogen at −196°C is commonly used. In each of these instances, a unique set of stresses are applied to the medical device under low temperatures. The ability of the packaging material to remain ductile and flexible in combination with product design and geometries at low temperatures to resist external stresses is the key to maintaining product integrity and the sterile barrier in packages [1].

Dynamic mechanical analysis captures the material responses to cyclic excitations over wide temperature and frequency ranges. Although the frequency and strain ranges tend to be rather low, compared to impact events, reasonable extrapolation can be used to generate useful predictions.

Impact testing, especially using instrumented recording systems, allows high speed stress/strain events to be captured and analysed over broad temperature ranges, and allows an intermediate stage analysis at both high speed and large strains.

In this article, we compare data generated by all three methods; product testing, dynamic mechanical analysis and instrumented impact testing, to gain understandings that allow reasonable predictions using rapid laboratory techniques without large experimental product studies. In this way, it is hoped that fundamental understanding can be achieved with broad applicabilities.

2. Experimental

Impact testing was carried out on a computer-controlled Dynatup instrumented impact tester with a 2-cm semi-spherical impact tup [2]. High-speed data aquisition, velocity sensing, temperature control, and data presentation were controlled by an Apple Macintoch computer with a National Instruments LabView instrument interface system. All samples were mounted on 15-cm-diameter aluminum testing frames. A special liquid nitrogen cooled environmental chamber capable to −150°C was used to condition the samples and hold the film holder during the impact event. Just prior to the experiment, an insulator gate to the chamber is first opened, allowing the traveling tup to penetrate the sample near the top of the chamber. The impact velocity was measured by the transit time of a 1.0-cm aluminum flag passing through an optical gate. Stress data from the instrumented tup is digitized by a high-speed analog–digital converter and transferred to the computer for impact energy and displacement calculations, and finally load versus displacement and impact energy versus displacement curves are plotted on a Hewlett Packard 7470 plotter. The overall schematic set up is shown in Fig. 1. In this series of experiments, impact velocity of about 3.3 m s^{-1} was used. Typical data are shown in Fig. 2.

Dynamic mechanical relaxation spectra were generated by a Seiko DMS-100 instrument using a Seiko 5500 controller. A typical temperature scanning rate of 3°C min^{-1} was used throughout this set of experiments. Multi-frequency data of 0.5, 1, 5, 10, 20, 50, and 100 Hz were collected during the temperature scan. A complete traversal of the specified frequencies took about 40 s. Thus a maximum temperature difference of 2°C could exist between the start and the end of a given frequency scan.

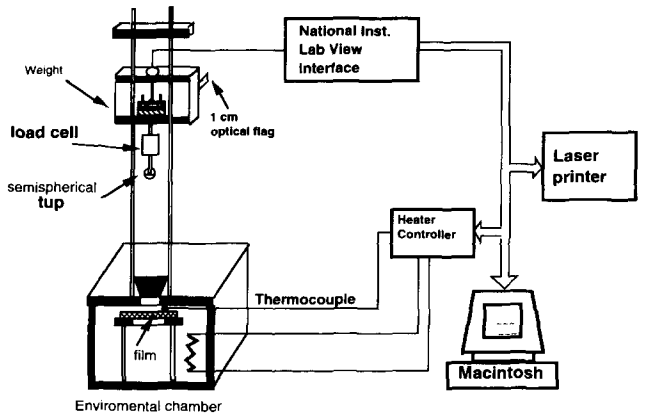

Fig. 1. Low-temperature impact testing setup.

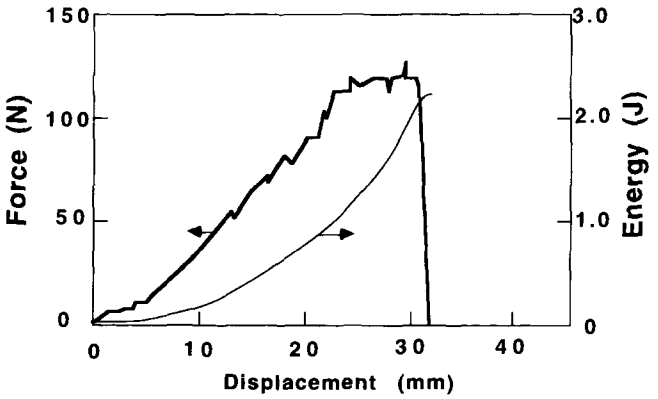

Fig. 2. Typical impact data.

Fracture surface morphologies was examined by a JEOL 35CF or a JEOL FE6300 field emission scanning electron microscopes after vacuum sputter coating with palladium to render the surfaces conductive. Fracture patterns were also documented by macrophotography with dark-field illumination.

Samples chosen for this study included flexible PVC samples labelled A, B, and C with di-ethylhexyl phthalate (DEHP), tri-ethylhexyl trimellitate (TEHTM), and citrate ester plasticizers of about 40% content, and T_g (tan δ, 1 Hz) of 8, -1, and -5°C respectively with thicknesses of about 350 microns, prepared on large-scale extrusion lines.

3. Results and discussion

From early studies by Schmieder and Wolf [3], it was known that the glass transitions of plasticized PVCs follow a predictiable functional relationship with the plasticizer type and content (Fig. 3).

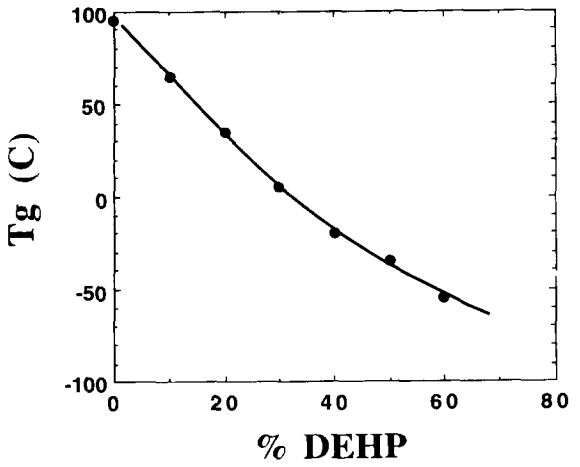

Fig. 3. PVC T_g vs. plasticizer content.

For a typical flexible sample of about 36% plasticizer content, the measured T_g is about 5°C at 1 Hz. This relatively high glass transition is expected to offer limited ductility at low temperatures. The 1 Hz dynamic mechanical loss spectrum for the samples are presented in Fig. 4. As expected, the higher content plasticizer samples had lower glass transition temperatures.

In the tan δ presentation, a narrow relaxation peak dominated over the entire temperature of measurement from about -130°C to about 120°C. Peak temperatures measured from E'' and tan δ at various frequencies are tabulated in Table 1. And from

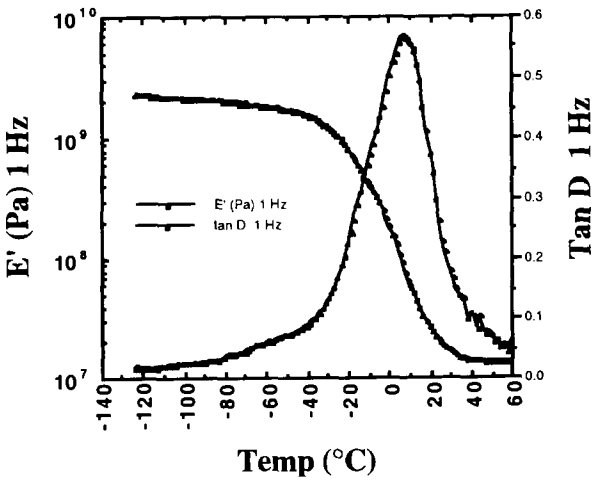

Fig. 4. 1 Hz tan δ spectra; samples A, B, C.

Table 1
Relaxation maxima locations (°C)

Sample	1 Hz	10 Hz	100 Hz
Tan δ			
A	8	15	24
B	−1	6	18
C	−5	2.5	14.1
E''			
A	−19	−14	−5
B	−29	−23	−14
C	−40	−33	−22

the frequency dependence of the E'' loss peak, activation enthalpy for the three samples are calculated (Fig. 5) and tabulated in Table 2.

It appears that there is a monotonic dependence of the activation enthalpy on the measured T_gs. This dependence could have arisen from the complete misibility between the dominant amorphous phase of PVC and the plasticizers.

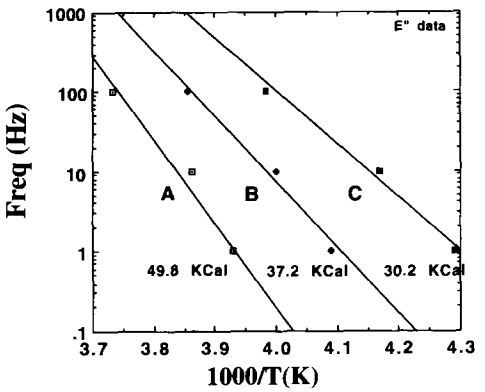

Fig. 5. Activation enthalpies from E''.

Table 2
Activation enthalpies (E'')

Sample	1 Hz E'' maxima °C	ΔH/kcal mol^{-1}
A	−19	30.2
B	−29	37.2
C	−40	49.8

3.1. Product performance

Fig. 6 presents the product failure rate in a standardized test conducted at −20°C as a function of the glass transition T_g. The data clearly indicate that the primary variable for the low-temperature performance of flexible PVC is the location of the glass transition temperature T_g. However, the data at a single temperature gave insufficient information to predict the temperature range over which the product is expected to survive. Therefore, film impact data over a wide temperature range are next examined.

For the DEHP sample, the impact energy versus temperature dependence indicated a brittle–ductile (B/D) transition at about −15°C; this is indicated as the first upturn in impact energy in Fig. 7. In most cases, the location of the B/D transition was also confirmed by the visual and scanning electron microscopic examination of the fracture surfaces. Typically, at temperatures below the B/D transition, jagged, glassy-brittle morphologies were observed, while above the transition, ductile, high elongation morphologies were seen. Separately, the ultimate displacements samples sustained before failure served as an independent confirmation of this transition. At about 5°C, a temperature significantly higher than the B/D transition, a second upturn was observed in the impact energy. This multiple or stepwise increase in impact energy was previously observed for multiphase materials [4]. However, recent data indicate that this is a very common phenomenon for polymers with prounced secondary transitions. Impact energies for the other two samples are shown in Figs. 8 and 9. For sample B and C, the B/D transition was observed at about −30 and −35°C respectively.

It is an apparent contradiction that the B/D transition located at a temperature lower than the 1 Hz glass transition can be attributed to the frequency dependence of the T_g process and a secondary relaxation process at about −80°C. The contribution to ductility from T_g is seen as the second upturn in the impact fracture energy starting at about 0–10°C. From the above data, it is evident that by choosing plasticizers with

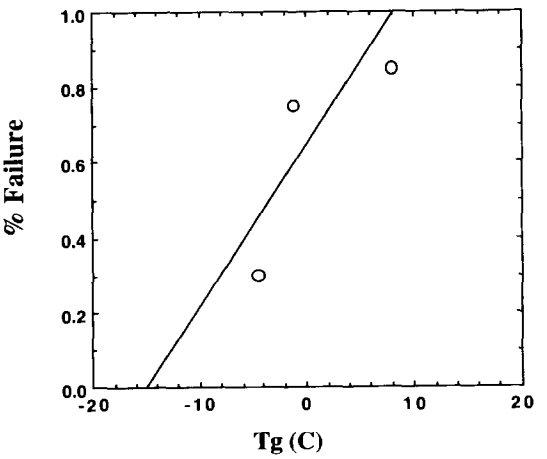

Fig. 6. −20°C product failure rates vs. T_g.

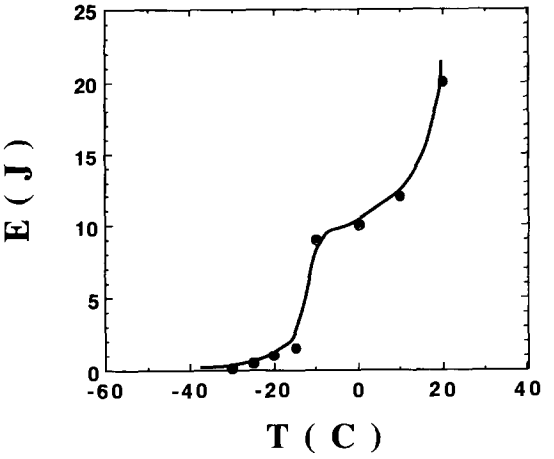

Fig. 7. Impact energy vs. temperature, sample A.

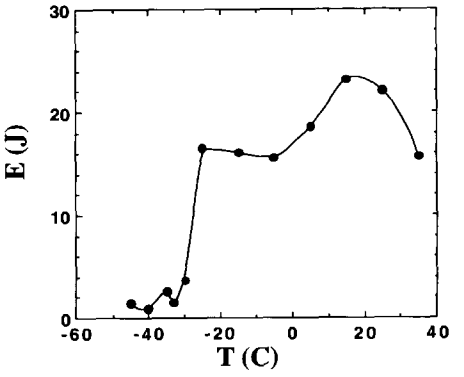

Fig. 8. Sample B: impact energy.

lower T_gs, or by increasing the plasticizer content, the B/D transition can be shifted to somewhat lower temperatures. However, for biomedical applications, this may come with accompanying losses in biocompatibility and mechanical strength.

For another product test, where temperature was varied as the independent variable, Fig. 10 depicts the failure rates for samples A, B and C. An interesting aspect of the low temperature product performance seen in Fig. 10 is that the failure process is not a sharp step-function of the temperature; rather, it is a statistical property having two end points located at: (a) the 100% point, at or below which all samples failed; and (b) the 0% point, above which all samples survive the test. The span between these two points was about 20–35°C.

A comparison with Fig. 7, for the film impact performance of sample A, indicates that the brittle ductile transition coincides with the 100% point, while the second

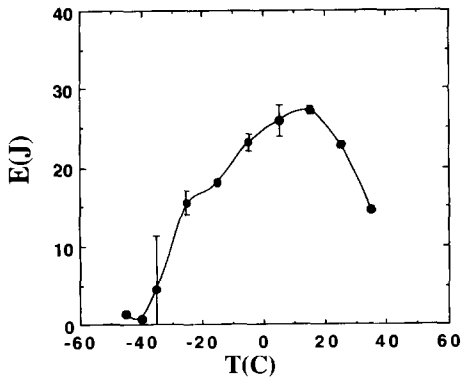

Fig. 9. Sample C: impact energy.

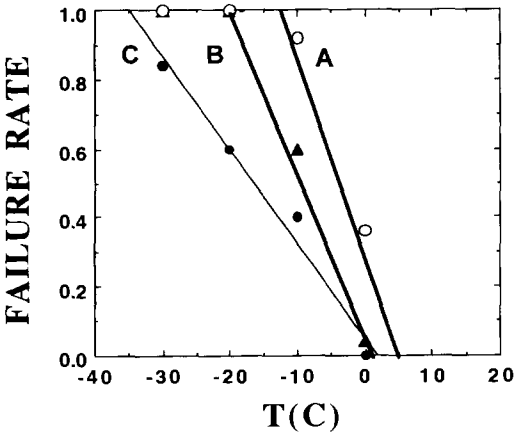

Fig. 10. Failure rates as function of temperature.

upturn in impact energy corresponds to the 0% point. From this correspondence, the mechanistic interpretation of our impact data becomes clear: that the B/D transition marks the temperature between certain failures and a greater than zero probability of survival. Evidently, in the temperature range between the B/D transition and the second (major) energy onset, one faces the following situation: although the film remains ductile when tested by itself, its fracture energy and ultimate elongation are still too low to protect the contents. Since in many cases the film contains frozen aqueous solutions, the well-known crack propagation from a composite brittle layer (ice) to an adhering ductile layer caused product failures. Therefore, to guarantee all product survivals, temperatures above the second, major onset in ductility are necessary. In this analysis, for the most complete predictions, other geometric and product-specific factors which could contribute to stress concentration effects must also be included.

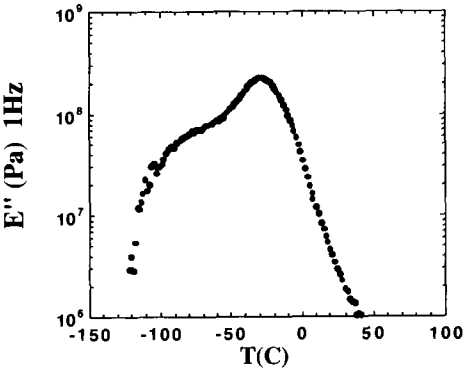

Fig. 11. E'' spectrum for sample B.

3.2. Dynamic mechanical analysis and impact prediction

The E'' spectrum differed considerably in appearance from the tan δ presentation. As an example, the 1-Hz E'' spectrum for sample B is shown in Fig. 11.

As well as the prominent T_g already mentioned, there are additional features worth discussing. First, in all cases a pronounced secondary relaxation was observed at about -80°C, a significantly lower temperature than the main glass transition. From earlier work by Diaz Calleja and others [5], it is believed that these relaxations originate on the main chain of PVC. Therefore, as a consequence, the observed B/D transitions are all lower than the T_g. In addition, the citrate-ester-plasticized sample had a significantly lower T_g at a similar plasticizer content with the TEHTM sample, indicating a more efficient plastization system.

Using a recently published technique [6] which allows a semi-quantitative calculation of the impact temperature function based on the E'' spectra extrapolated to moderately high frequencies, we calculated these theoretical predictions. Briefly, the E'' data at different temperatures were plotted on a frequency axis, linearly extrapolated to about 10 KHz from the available lower frequency data. Then an estimated impulse waveform covering the same frequency span is projected onto the E'' spectra and the overlap integral evaluated. The resulting "impulse dissipation" data, a measure of the material's ability to dissipate high frequency (impact) excitation, are plotted against the temperature to give a semi-quantitative prediction as a function of temperature.

The predicted impact function in terms of the B/D transition and the second onset for ductility were compared with experimental data and presented in Table 3.

It appears that a reasonably good prediction was achieved given the two very different modes of deformation of the samples. In typical DMA experiments, strains of less than 0.5% are used while the impact experiment involves very large strains to failure. For sample C, the predicted B/D transition was about 10°C too low. This may be caused, at least in part, by the temperature offset between the two experiments. In addition, the temperature dependence of the error appeared to indicate that the distribution of frequency components in the impulse function (arbitrarily chosen as

Table 3
Predicted vs. experimental impact performance of films

Sample	B/D/°C		2nd onset/°C	
	Predicted	Exp.	Predicted	Exp.
A	−15	−15	+5	+10
B	−25	−30	−8	−5
C	−45	−35	−15	−15

a 10 μs square wave) was not appropriate for the deep cryogenic temperatures. In other words, frequency components much higher than that of the 10 KHz cutoff are present, which when mapped onto the E'' function, would cause additional upward shifts in the temperature scale.

4. Summary

Three sets of experimental data: actual product performance, film impact, and dynamic mechanical analysis (DMA) over wide frequencies and temperatures, were generated to seek a basic understanding of the material/product performance. A good mechanistic relationship was obtained between the product performance and the film impact. With a slight error at low temperatures, the impact spectrum was predicted in turn from the DMA data. With further refinements, this method could reduce or simplify large sample requirements for product testing.

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