INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
MACROMOLECULAR DIVISION

A COLLABORATIVE STUDY OF THE DYNAMIC MECHANICAL AND IMPACT PROPERTIES OF POLYVINYL CHLORIDE

A Report of the IUPAC Working Party on The Relationship of Performance Characteristics to Basic Parameters of Polymers

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A COLLABORATIVE STUDY OF THE DYNAMIC MECHANICAL AND IMPACT PROPERTIES OF POLYVINYL CHLORIDE*

INTRODUCTION

The objective of this IUPAC Working Party, under the Chairmanship of J. W. Barrett, is to study the effect of molecular parameters of polymers on such functional properties as melt rheology and mechanical properties. Owing to the number of participants involved and the nature of the functional tests large quantities of the selected polymers are required and to satisfy the needs of the programme most of the work done by the Working Party has been with commercial materials.

The first agreed programme was concerned with determining the dynamic mechanical and impact properties of general purpose and toughened polystyrene and also rigid and toughened polyvinyl chloride (PVC). The work on the polystyrene was of particular value in comparing the results obtained in the participating laboratories. This work formed Part I of the present series. It was presented at the International Symposium on Macromolecular Chemistry held in Prague in 1965 and published in the *Journal of Polymer Science*, Part C, No. 16, pp. 3845–3864 (1968).

The present paper covers the collaborative work done with rigid and toughened PVC supplied by Solvay. This work was carried out by I. Franta, University of Prague; J. Heijboer, TNO, Delft; S. Baxter and T. T. Jones, Monsanto Chemicals Ltd., England; A. Rodeyns and A. Gonze, Solvay, Brussels and G. Pezzin, Padua University, Italy. All members used a torsion pendulum and in addition the TNO group used an apparatus for the study of resonance vibrations in flexure. Falling weight, Charpy and tensile impact strength measurements were also made in this study.

A further detailed mechanical study is currently being done using two of the polymers used in this programme. This further work, which will be more quantitative in nature, involves additional collaborators and the results will be published in a later report from the Working Party.

EXPERIMENTAL

Materials and equipment

Three materials were used:

No. 1—Rigid PVC (suspension PVC in a lead–cadmium stabilized formula).

* This report is No. II of the series prepared by the IUPAC Working party on 'The relationship of performance characteristics to basic parameters of polymers'. For report No. I *See* T. T. Jones, *J. Polymer Sci.*, Part C, No. 16, 3845–3864 (1968).

No. 2—The same PVC compound with 6 parts per hundred (pph) of chlorinated polyethylene (CPE) added.

No. 3—The same PVC compound with 12 pph of chlorinated PE added.

The specimens were cut from sheets which were compression moulded independently in each laboratory at temperatures ranging between 160 and 190 °C and under pressures ranging from 45 to 120 kg/cm^2. Moreover, the Solvay group used extruded strips for impact tests. *Table 1* gives the size and shape of specimens. *Tables 2* and *3* list the instruments used by the various laboratories.

Table 1. Size and shape of samples

	Dynamic mechanical tests (Dimensions in cm)	*Impact tests* (Dimensions in cm)
Monsanto	Bars of 5·72 × 0·63 × 0·051 cm and 5·72 × 0·63 × 0·165 cm	Discs: diam. 2·25 in. Thickness 0·060 in.
T.N.O.	Bars of 15 × 0·7 × 0·35 cm and bars of 5 × 0·65 × 0·051 and 0·165 for torsion tests Bars of 18·4 × 0·70 × 0·35 cm for flexture.	Dumbbell shaped specimens 0·32 × 0·13 cm in the reduced part for tensile impact test; 12·7 × 1·27 × 0·23 cm with notch for Charpy test.
Prof. Franta	Bars of 10 × 1 × 0·2 cm Clamping length: 8·0 cm	
Solvay	Bars of 8 × 1 × 0·028 cm Clamping length: 5·0 cm	Dumbbell shaped specimens 1·0 × 0·5 cm in the reduced part for tensile impact test. Thickness: 0·15 cm.
Dr. Pezzin	Bars of 10 × 1 × 0·1 cm Clamping length: 8 cm	

MEASUREMENTS

Dynamic mechanical properties

In every laboratory, the three PVC compounds were studied at various frequencies and temperatures as given in *Table 2*. The shear modulus and the mechanical damping factor were measured by means of a torsion pendulum; the TNO laboratory group also measured the Young's modulus E and the damping factor determined by flexural vibrations. A limited study of the effect of thickness of the specimens on shear modulus was also made by the TNO and Monsanto groups with samples No. 2 and No. 3; frequencies and thicknesses are given in *Figures 6* and *7*.

Impact properties

The aim of this section was to study the impact strength of the three PVC compounds over a large range of temperatures and at various shear rates or

Table 2. Apparatus for the dynamic mechanical measurements

Laboratory	*Name of type of instrument*	*Detecting and recording system*	*Method of use as defined in ISO Draft recommendation 533*	*Range of frequencies* (Hz)	*Range of Temp.* (°C)
Monsanto	Own construction after Nielsen	Variable condenser in tuned circuit. Pen recorder	Method B	0·2 to 2·0	−100 to +50 °C
T.N.O.	Nonius–T.N.O. Delft Torsion Pendulum with three moments of inertia.	Spark from one end of inertia bar to moving sensitive paper.	Method B	0·2 to 3·2	−160 to +70 °C
	Flexural vibration–own construction.			100 to 3·700	−80 to +40 °
Prof. Franta	Own construction after Nielson See K. H. Illers and H. Brenar in *Kolloid Z. 176* 110 (1961).	Sparking system	Method B	0·8 to 1·6 0·8 to 1·6	−104 to +65 °
Solvay	Zwick	Light beam reflected on to moving sensitive paper.	Method A	0·75 to 2	−65 to +20 °
Dr. Pezzin	Own construction	Variable condenser. Pen recorder.	Method B	0·1 to 3	−100 to +100 °

Table 3. Apparatus for impact tests

Laboratory	*Apparatus*	*Method*	*Measurements*
Monsanto	Falling weight test	BS 2782 Method 306 B	Temperature between −77 ° and +60 °C. Height of fall constant: 60, 96 cm. The weight of the striker is varied. 20 specimens for each temperature.
T.N.O.	Tensile impact test	T.N.O.	−190 °C and from −90 °C to +40 °C. Velocity of striker 3·3 m/s.
	Charpy notched impact	ASTM D 256 Method B	From −190 °C to +60 °C 6 tests for each value (in some cases only 2 or 4).
Solvay	Tensile impact test	Solvay	From −40 °C to +20 °C velocity: 2·7 m/s.

tensile speeds to see whether the results could be correlated with the non-destructive dynamic mechanical tests.

Both dynamic and impact tests are partially or completely governed by relaxation phenomena so that one can expect that an increase in frequency or shear rate will give rise to a corresponding variation of transition temperatures (cf. T. T. Jones *loc. cit.*)

Miscellaneous impact tests were performed on the three PVC compounds. *Table 3* recapitulates the kind of tests, ranges of temperature and velocities used.

RESULTS

Dynamic mechanical properties

Torsion pendulum experiments—The experimental results obtained in the five laboratories for shear modulus G and damping $tg\delta$ at a number of temperatures and frequencies were plotted against temperature for the three PVC's. Examples of the experimental results from the five laboratories are given in *Figures 1* and *2* for the PVC's No. 1 and 3 respectively at a frequency of about 1 cycle per second. The value of modulus and damping at 0·2, 0·5, 1·0 and 2·0 Hz have been determined from the experimental results by plotting the data as a function of frequency at constant temperatures. From these plots, interpolated values were obtained. The values obtained by workers at the TNO and Monsanto laboratories are given in *Figure 3* and *4* for the rigid and the toughened PVC respectively.

Flexural vibration experiments—At the TNO laboratory the dynamic mechanical properties were determined by means of a flexural test. From the graphs against frequency at a constant temperature the value of Young's modulus E and damping in flexure $tg\delta$, were read at 200, 1000 and 2000 Hz. These values are plotted in *Figure 5*, for rigid PVC and toughened PVC with 12 parts of CPE.

Determination of PVC secondary peak and of the CPE peak—*Tables 4* give the height and temperature of the PVC secondary peak and of the CPE peak at a number of frequencies for the three PVC's.

Calculation of apparent activation energies—The apparent activation energies can be calculated from the temperature shift of the damping peak vs. frequency.

The log of the frequency ν is plotted against the reciprocal of the absolute temperature of each peak. The apparent activation energies are calculated from the relation:

$$E = R.\ \ln \frac{\nu_2}{\nu_1} \Big/ \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The results of calculations obtained in the various laboratories are given in *Table 5.*

Effect of specimen thickness on shear molulus—This effect was studied by Monsanto and TNO laboratories after it had been recognized by Solvay

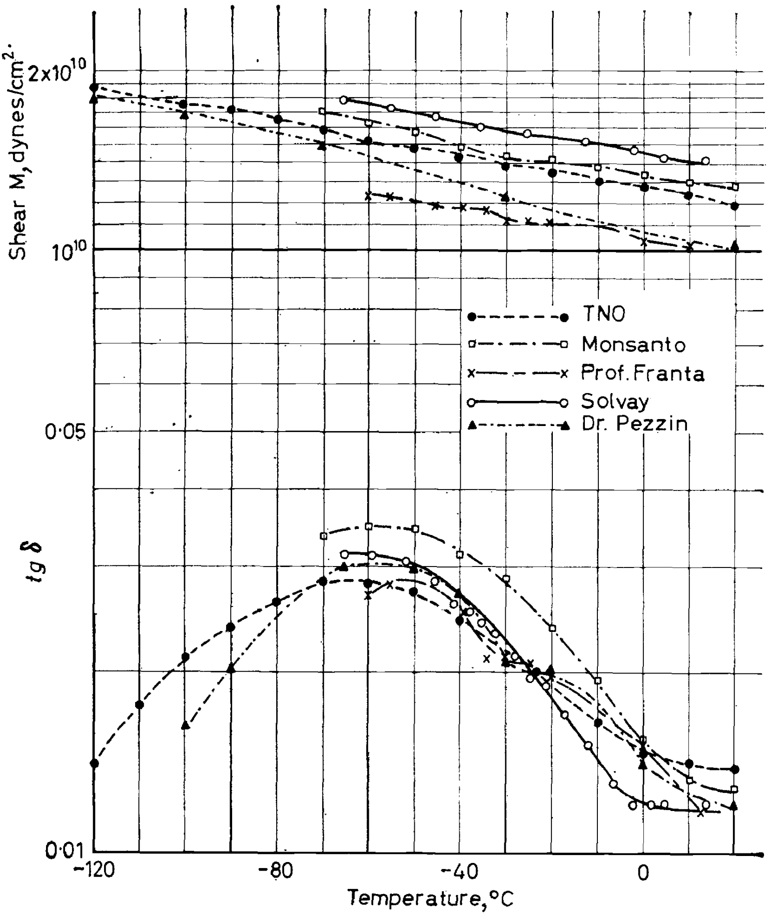

Figure 1. Rigid PVC

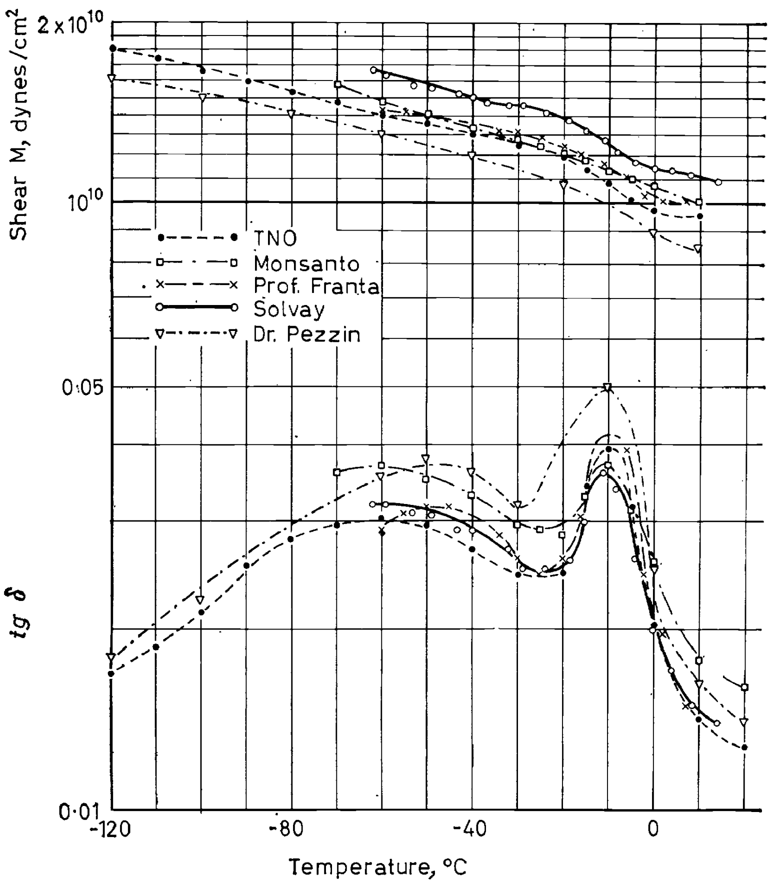

Figure 2. Rigid PVC + 12 parts CPE

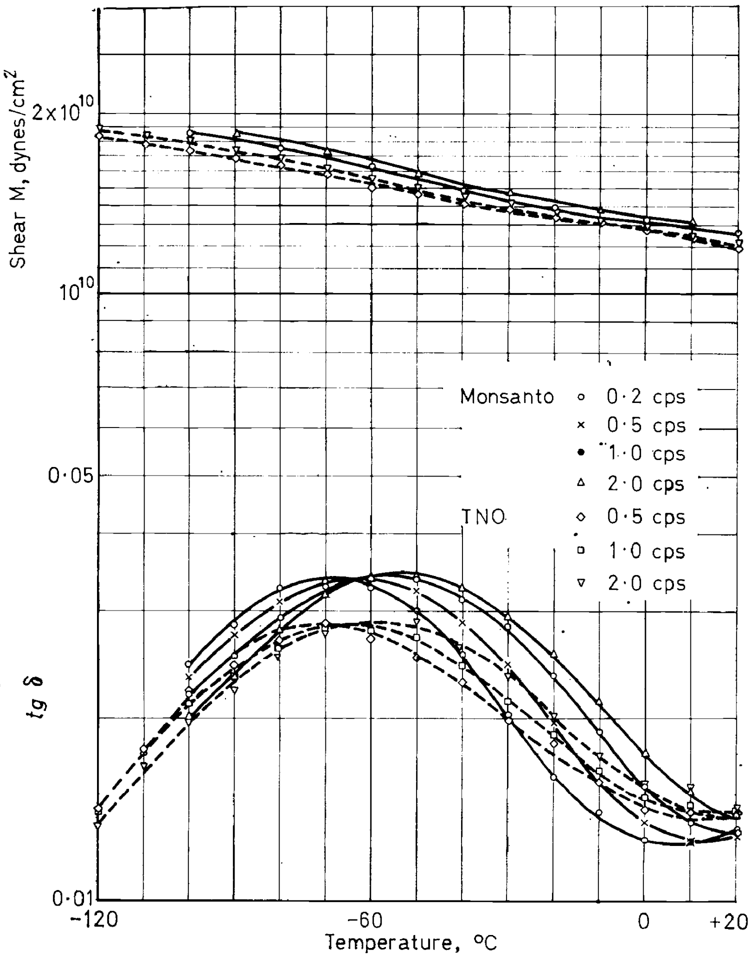

Figure 3. Rigid PVC

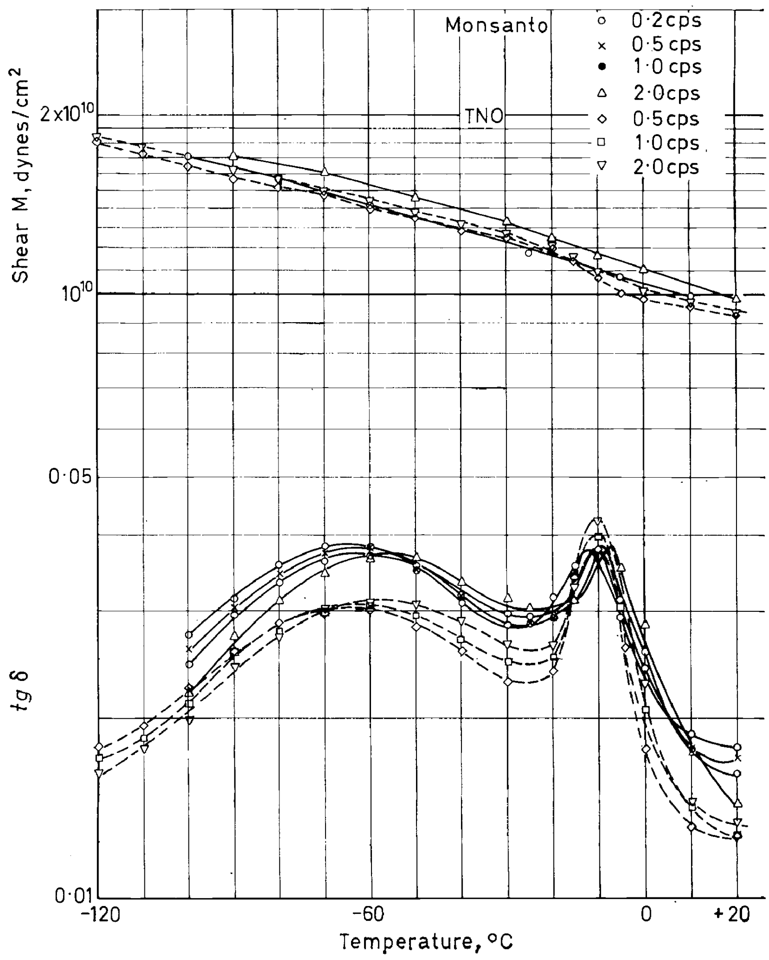

Figure 4. Rigid PVC + 12 parts CPE

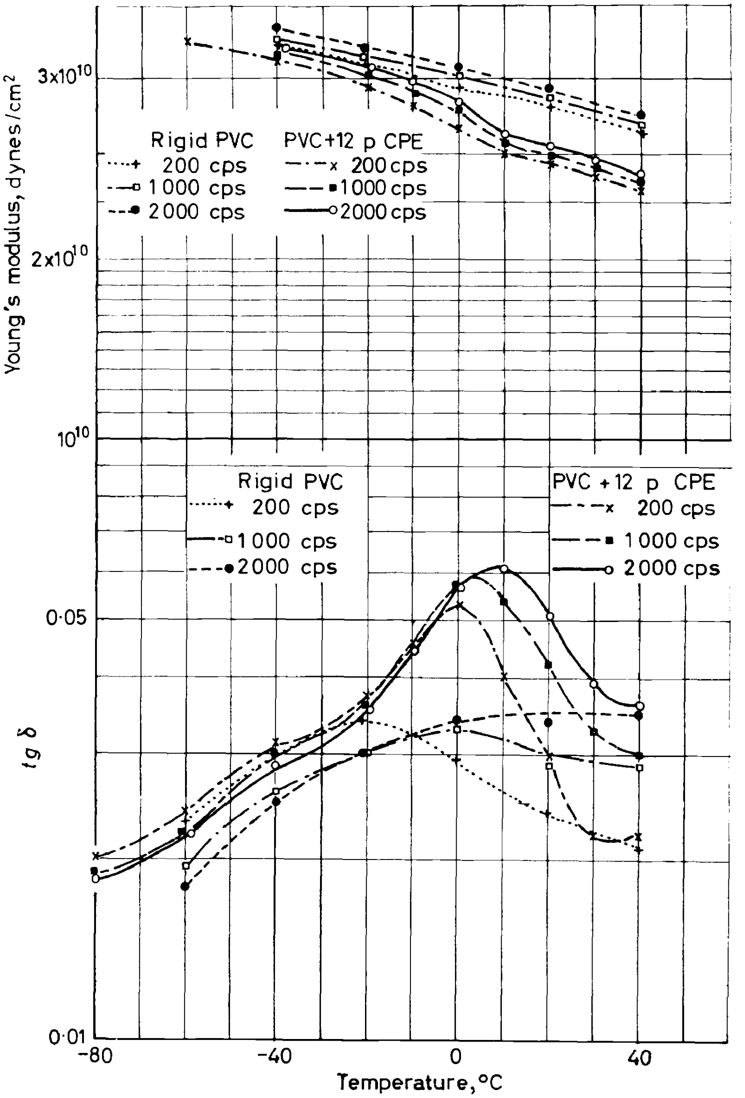

Figure 5. Young's modulus E and damping in flexture $tg\delta$ at constant frequencies—results of TNO

Table 4. Determination of PVC secondary peak and of the CPE peak

RESULTS FROM TNO

Material thickness (3·52 mm) / *Sample No.*	PVC *secondary peak* 0·5 Hz *height* (tan δ)	0·5 Hz *temp.* (°C)	1·0 Hz *height* (tan δ)	1·0 Hz *temp.* (°C)	2·0 Hz *height* (tan δ)	2·0 Hz *temp.* (°C)	200 Hz *height* (tan δ)	200 Hz *temp.* (°C)	1·000 Hz *height* (tan δ)	1·000 Hz *temp.* (°C)	2·000 Hz *height* (tan δ)	2·000 Hz *temp.* (°C)
1	0·028	−70	0·028	−65	0·029	−58	0·034	−21	0·034	+1	0·035	+10
2	0·031	−68	0·030	−65	0·032	−32						
3	0·030	−65	0·030	−60	0·031	−54						
					CPE *damping peak*							
2	0·028	−13	0·028	−12	0·031	−12						
3	0·040	−12	0·042	−11	0·042	−10	0·054	−1	0·058	+5	0·063	+7

RESULTS FROM MONSANTO

Material thickness (0·51 mm) / *Sample No.*	*Height and temperature of the PVC damping peak* 0·2 Hz *Peak Height* (tan δ)	0·2 Hz *Peak Temp.* (°C)	0·5 Hz *Peak Height* (tan δ)	0·5 Hz *Peak Temp.* (°C)	1·0 Hz *Peak Height* (tan δ)	1·0 Hz *Peak Temp.* (°C)	2·0 Hz *Peak Height* (tan δ)	2·0 Hz *Peak Temp.* (°C)
1	0·0336	−68·5	0·0339	−62	0·0344	−55·5	0·0349	−53·5
2	0·0332	−68·5	0·0339	−60·5	0·0354	−58·5	0·0356	−52·5
3	0·0388	−64·5	0·0383	−62·5	0·0371	−61·0	0·0370	−55·0
	Height and temperature of the CPE damping peak							
1	—	—	—	—	—	—	—	—
2	0·0217	−13·5	0·0248	−12·5	0·0268	−11·0	0·0283	−10·5
3	0·038	−11·5	0·038	−10·5	0·0381	− 9·1	0·0382	− 7·9

RESULTS FROM PROFESSOR FRANTA

Thickness (2 mm) / *Sample No.*	PVC *maximum* *Temp.* (°C)	PVC *maximum* *tg* δ	PVC *maximum* *f*−Hz	CPE *maximum* *Temp.* (°C)	CPE *maximum* *tg* δ	CPE *maximum* *f*−Hz
1	−55	0·028	1·64	—	—	—
2	−55	0·035	1·48	− 9	0·033	1·34
3	−50	0·031	1·42	− 6	0·039	1·26
1	−55	0·028	1·26	—	—	—
2	−55	0·031	1·30	−10	0·026	1·16
3	−55	0·031	1·14	−7	0·040	0·995

RESULTS FROM SOLVAY

	PVC *secondary peak* *Temperature* (°C)	PVC *secondary peak* *Peak height tg*δ	*Frequency* (Hz)
Sample 1 Thickness: 0·282 mm	−55 to −60	0·030	1·12
Sample 3	−55 to −60	0·032	1·08
	CPE *maximum*		
Sample 3 Thickness: 0·280 mm	−10·5°C	0·0355	1·30

Table 5. Apparent energy of activation (in kcal/mole)

Sample No.	PVC *peak* MCL *Low frequency region*	PVC *peak* TNO *Low frequency region*	PVC *peak* TNO *High frequency region*	CPE *peak* MCL *Low frequency region*	CPE *peak* TNO *High frequency region*
1	13	10	12	—	—
2	13	12	—	85	—
3	20	11	—	60	62

that their (Solvay) values of modulus were often higher than those obtained by the other laboratories (see *Figure 1*). *Figures 6* and *7* show some results for various frequencies and thicknesses.

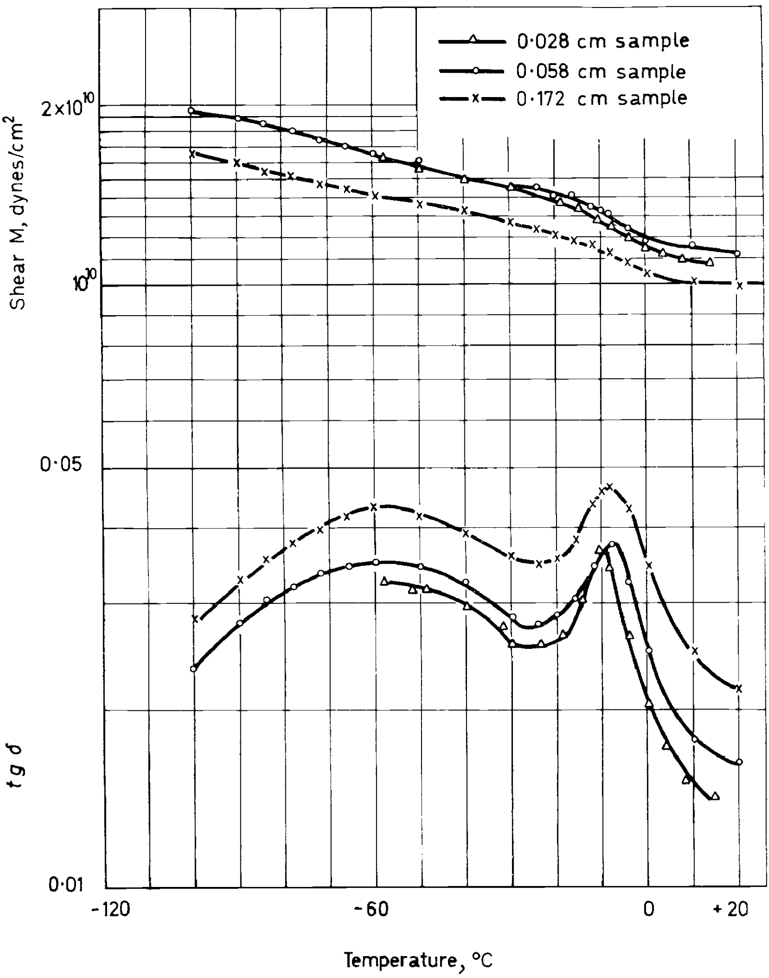

Figure 6. Influence of thickness on shear modulus and damping for the rigid PVC + 12 p CPE at a frequency of about 1 cycle/sec.—Monsanto and Solvay results.

Impact properties

The results from the falling weight impact test carried out by the Monsanto group are given in *Figure 8*. The tensile impact strength results from TNO and Solvay groups are plotted in *Figure 9* and the Charpy test results are represented in *Figure 10*.

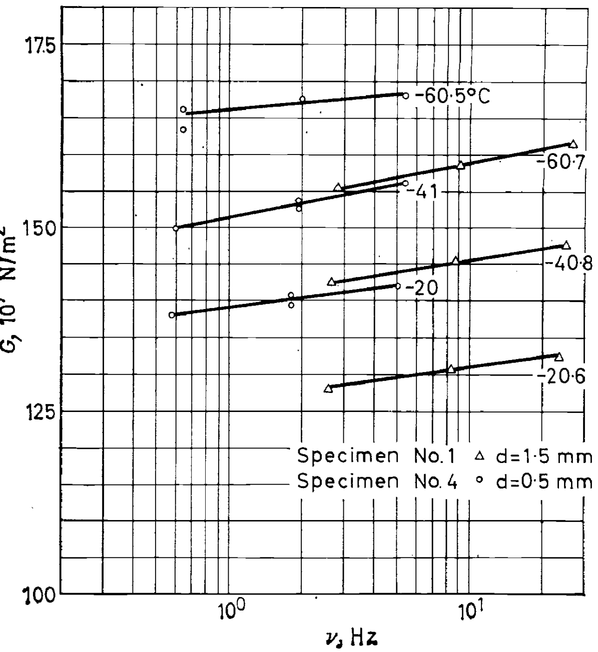

Figure 7. Shear modulus vs. frequency; influence of thickness—Results of TNO.

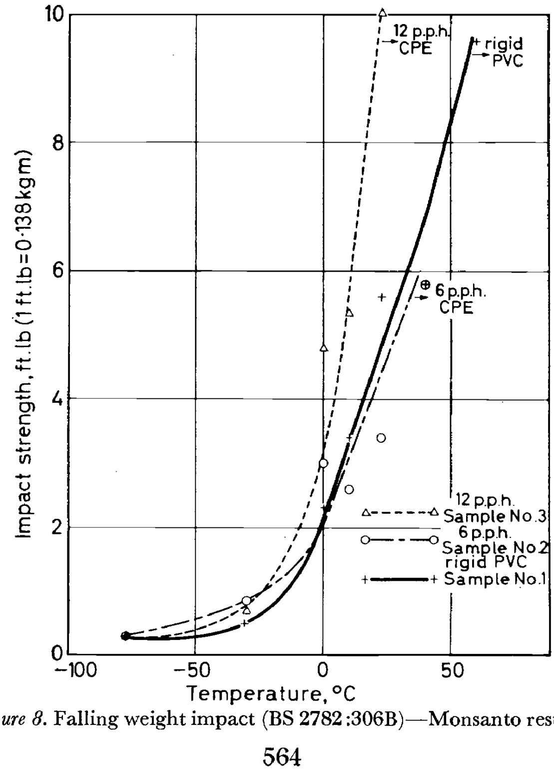

Figure 8. Falling weight impact (BS 2782:306B)—Monsanto results.

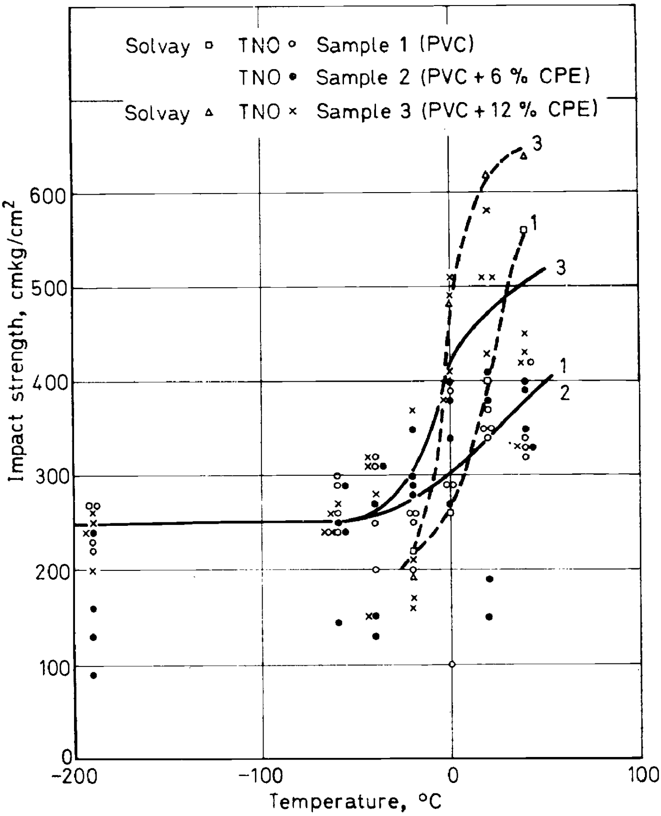

Figure 9. Tensile impact strength.

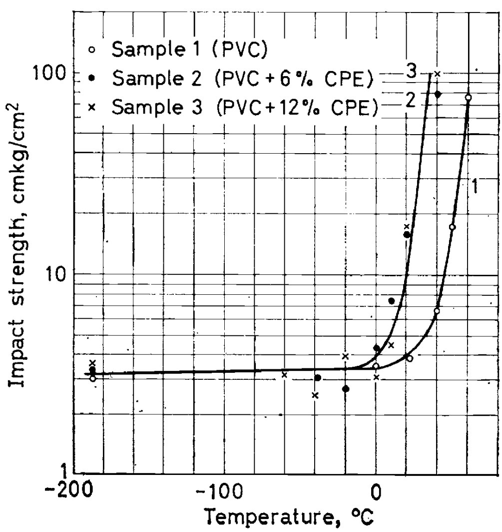

Figure 10. Charpy impact strength (notched)—TNO results.

DISCUSSION

Dynamic mechanical properties

It appears from *Figures 1* and *2* that each participant has obtained similar plots at slightly different frequencies and that the qualitative agreement is good. The plots are characterized by well known features. For a constant frequency the modulus falls with increasing temperature and steps in the curves can be observed. Associated with these steps we observe peaks in the mechanical damping vs. temperature curves. *Tables 4* summarizes this behaviour. For the rigid PVC a broad peak appears in the region −65 to −55 °C at 1 Hz. As the frequency increases the temperature of the peak increases but not necessarily its height. At 1000 Hz the damping peak is located at about 1 °C. For the toughened PVC a second, narrower peak appears at about −10 °C for 1 Hz. The height of this peak varies with the amount of CPE present. The greater is the amount of CPE, the greater is the loss of shear modulus. It is difficult to establish a marked effect of the CPE on the PVC peak. The first, broad peak is the PVC secondary peak. The second, narrow peak corresponds to the glass–rubber transition of the CPE additive.

The calculation of the apparent activation energies for the PVC secondary peak and for the CPE glass transition peak gives very different values. The energy is about 10–13 kcal/mole in the first case, 60 kcal/mole in the second. The difference between the apparent activation energies of the PVC secondary transition found by Monsanto in PVC samples No. 1 (13 kcal/mole) and No. 3 (20 kcal/mole) is not confirmed by the TNO results. It would probably be interesting to check those results to confirm the influence of a general tightening of the PVC structure in those portions where the chlorinated portion of the PE interacts with the PVC.

It seems, from the limited study which was made, that thickness influences the dynamic mechanical properties in that there is a slight increase in modulus and a decrease in damping when thickness is reduced, due most probably to surface orientation. These results do not agree with those obtained in the previous study of polystyrene.

Impact properties

The impact test results have given a very high degree of scatter. This is very likely due to the difficulty of preparing good moulded sheets. It is known that moulded sheets, which contain more defects than extruded sheets, are very sensitive to the impact tests. This scattering of results increases the difficulty of correlating them with dynamic mechanical properties. However, it seems from *Figures 8*, *9* and *10* that the well marked shift is observed of the brittle tough transition of toughened PVC compared with rigid PVC when using impact tests. The shift is about 20 °C. It is apparent that for the toughened PVC, in the tensile and falling weight impact tests, the transition temperature lies at about 0 °C. This transition temperature however, lies at about +20 °C in the Charpy test (notched). This difference of temperature shows clearly the influence of the rate of deformation on the impact transition temperature.

SUMMARY AND CONCLUSION

Dynamic mechanical and impact properties of three PVC materials have been studied at different temperatures by five collaborating laboratories.

While reasonable agreement has been reached for the dynamic mechanical properties, the impact tests varied widely in rate of elongation and specimen shape and size and correlation was not possible.

The importance of working with samples prepared in one laboratory is pointed out. Also the importance of using impact tests capable of yielding quantitative data on rate of strain is emphasized.

It is clear from this study that in order to correlate impact tests with dynamic mechanical properties it is advisable to use specimens prepared in one laboratory. In the case of the impact tests used it is essential to be able to make quantitative estimates of the rate of strain used as this influences the impact transition temperature.

FUTURE PROGRAMME

The further mechanical study, using PVC, is being done using extruded and compression moulded samples prepared by Solvay using polymers 1 and 3 as used in this investigation.