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OF COMMERCIAL POLYMERS

MECHANICAL PROPERTIES OF RIGID POLYVINYL CHLORIDE, EFFECT OF FILLERS

Prepared for publication by
J.C. CHAUFFOUREAUX
Solway & Cie, Brussels,
Belgium

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MECHANICAL PROPERTIES OF RIGID POLYVINYL CHLORIDE, EFFECT OF FILLERS

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Solvay & Cie - Brussels

Abstract - The paper summarizes the work done by the IUPAC working party "Structure and Properties of Commercial Polymers" on the effect of mineral fillers on the mechanical and dynamic mechanical properties of rigid PVC. Two grades of calcium carbonate (0,07 μm and 2,4 μm) were added separately, at two different concentrations (10 and 20 %), in the same basic composition for extrusion of rigid PVC. The five powder compounds obtained were processed using the same thermomechanical conditions.
It was studied which influence concentration, particle size and agglomerates not destroyed during processing have on :

- the impact strength of unnotched (tensile impact and ball drop test) and notched (prestressed samples and Charpy test) specimens,
- the tensile properties and tensile creep of unnotched specimens,
- the static and dynamic fatigue of notched and unnotched specimens.

The results show that, although the fillers have no influence on the β peak of the PVC, they modify all the other mechanical properties :

- the rigidity is increased ; this effect is most marked with the coarse filler and at the higher concentration,
- the yield and the drawing stresses are lowered : this decrease is most significant with the fine filler and at higher concentration,
- fillers can have an effect on the initiation of cracks, especially when agglomerates are present ; on the other hand, they increase the minimum energy needed to propagate a brittle fracture,
- tensile creep results are in good agreement with tensile and mechanical dynamic test data as far as rigidity is concerned ; fillers increase the non-linearity of creep.

Fatigue measurements also show the effect of the fillers on initiation and propagation of the failure.
Owing to their action on the mechanism of propagation of failure, the fillers can improve the resistance of PVC to brittle fracture. On the other hand, they can make crack initiation easier, especially when agglomerates are formed during processing. If the uniform dispersion of the fine filler in the composite seems to be more difficult to reach than is the case for the coarse one (2,4 μm), its effect on the propagation of a brittle fracture seems to be higher.

INTRODUCTION

Previous work on the mechanical properties of rigid PVC (1 - 5) have shown that the behaviour of this raw material from linear deformations up to break is controlled by its molecular structure and by the density and shape of the defects induced during processing. In particular, the transition between tough and brittle modes of rupture in tensile and impact tests has been associated with the freezing of the molecular relaxation mode β.
The structural heterogeneities induced by the processing of PVC or by a second phase dispersed in the matrix, change the local stress distribution in the material. Dependent upon their constitution, shape, dimensions and compatibility with PVC, these heterogeneities can be :

- either zones of concentration of stresses which will locally initiate fractures and decrease the impact resistance of the product,
- or zones of energy dispersion which will increase the minimum energy needed for the propagation of the fracture and improve the impact resistance of the PVC.

The aim of the study undertaken by the Working Party has been to characterize the influence of structural defects, induced by mineral fillers ($CaCO_3$) dispersed in the PVC matrix, on the mechanical and dynamic mechanical properties of rigid PVC. The influence of the dimensions of the filler particles on the rupture of PVC was specifically investigated in several test procedures : tensile, impact, ball-drop, static and dynamic fatigue tests, and tensile creep.
The participants in this part of the study of the mechanical properties of rigid PVC were : ICI, Montedison, Solvay & Cie, TNO (Delft), Technical University of Prague.

PREPARATION AND CHARACTERIZATION OF THE SHEETS AND TEST PIECES

Preparation

Five grades of rigid PVC sheets were extruded with a four-screw extruder Anger A4 80-84 provided with a 300 mm Johnson flat die. The extruded sheets were polished with an Olier calander. All the powder compounds selected for the extrusion have the same common basis of composition : Solvic 227 (suspension PVC - viscosity index 105 {test method ISO R 174/61}) containing lead stabilizers and lubricants ; they differ only in the quality and amount of filler present. The concentrations in fillers are given in pourcents of the total weight of polymer.

Grade n°1 : **unfilled**
Grade n°2 : filled with 10 % of coated $CaCO_3$ - mean particle size 0,07 µm-filler A
Grade n°3 : filled with 20 % of filler A
Grade n°4 : filled with 10 % of coated $CaCO_3$ - mean particle size 2,4 µm-filler B
Grade n°5 : filled with 20 % of filler B.

The powder compounds were mixed in a two speed Henschel 150 mixer.

The extruded sheets were annealed at 100°C for 2 hours and cooled at a rate of 8°C per hour. ISO R 527 type I test pieces were prepared by means of a Tensilkut machine running at 20.000 rpm. All test pieces were cut parallel to the extrusion direction. This prevents slight transverse irregularities in thickness from affecting the geometry of the deformation zone.

Characterization of the sheets and test pieces

Thickness and aspect. The thickness was measured by a dial gauge micrometer (accuracy ± 0,01 mm). The resultats are given in Tables 1A and 1B.

The thickness tolerances are reasonable. Two additional comments must be made :

- the shoulders of the test pieces are sometimes not symmetrically opposed, displacements up to 2 mm were recorded
- grades 2 and 3 show defects on surface due to "clumping" of filler.

TABLE 1A. Thickness of the sheets

Grade	Material type	Nominal thickness (mm)	Mean thickness (mm)	Standard deviation (mm)	Minimum value (mm)	Maximum value (mm)
1	unfilled	1	1,10	0,024	1,03	1,15
2	10% fine filler A	1	1,04	0,033	0,98	1,09
3	20% " " A	1	0,99	0,032	0,92	1,05
4	10% coarse " B	1	1,02	0,049	0,93	1,11
5	20% " " B	1	1,07	0,063	0,92	1,14

TABLE 1B. Thickness of the test pieces ISO R 527 type 1

Grade	Material type	Nominal thickness (mm)	Mean thickness (mm)	Standard deviation (mm)	Minimum value (mm)	Maximum value (mm)
1	unfilled	1	1,00	0,030	0,93	1,06
2	10% fine filler A	1	1,05	0,034	0,98	1,12
3	20% " " A	1	0,99	0,026	0,91	1,04
4	10% coarse " B	1	1,00	0,049	0,91	1,14
5	20% " " B	1	1,02	0,059	0,89	1,11

Structure. The structure of the five grades of sheet has been observed with an optical interference microscope (Plate 1). The dispersion of the filler is homogeneous, but in grades 2 and 3, agglomerates can be detected. As their dimensions can reach several tens of microns, their influence on the mechanical properties of the sheet must be taken into account.

PLATE 1. Magnification 870 X

Fig. 1. Unfilled PVC

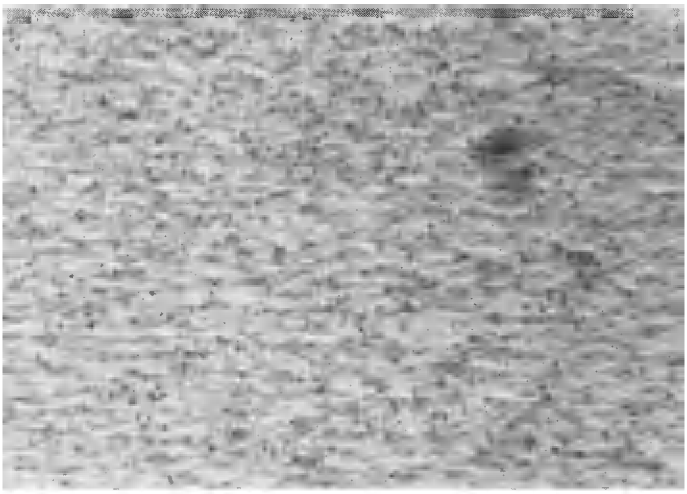


Fig. 2. Filled PVC with 10 % fine $CaCO_3$

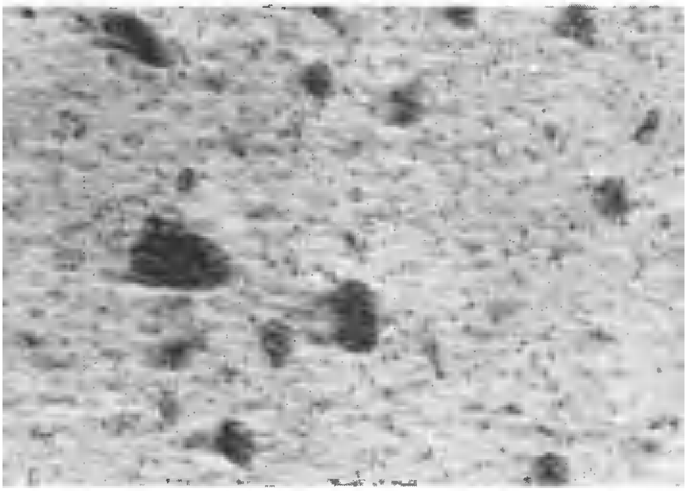


Fig. 3. Filled PVC with 20 % fine $CaCO_3$

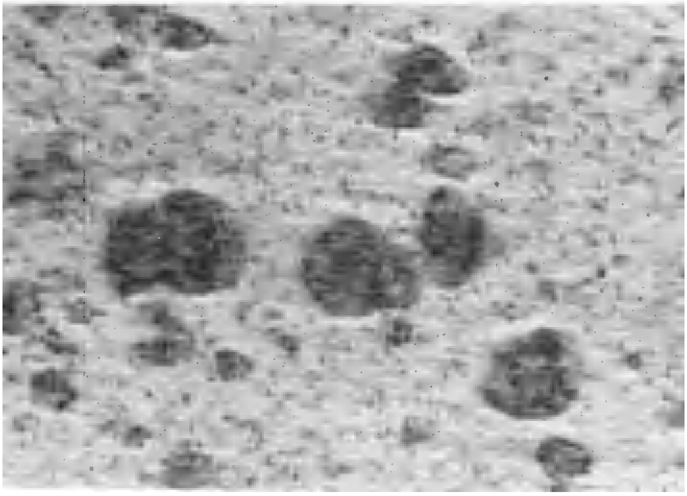


PLATE 1. Magnification 870 X

Fig. 4. Filled PVC with 10 % coarse $CaCO_3$

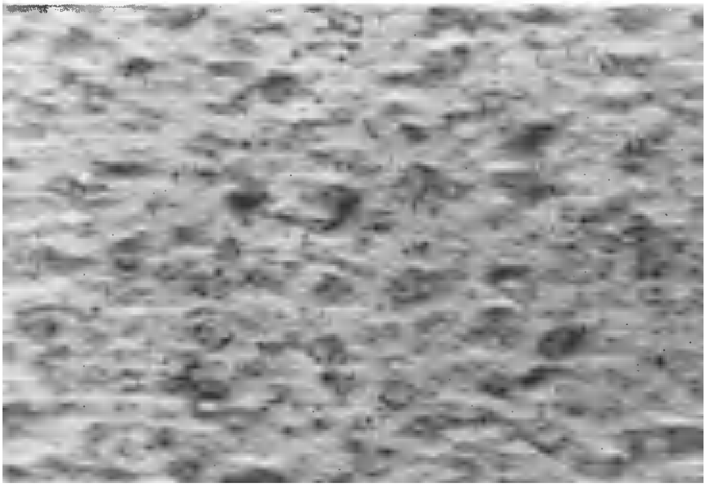


Fig. 5. Filled PVC with 20 % coarse $CaCO_3$

Density. The density of the materials was determined at 23°C by the immersion technique (in water) ; dimensions of the specimens : 20 x 40 mm x thickness of the sheet. The accuracy is $\pm 3 \times 10^{-4}$. The results of the measurements are given in Table 2.

TABLE 2. Densities of the materials

PVC grade	Density Experimental data (g/cm^3)	Calculated density (g/cm^3)
1	1,4263	-
2	1,4752	1,4880
3	1,5326	1,5441
4	1,4746	1,4880
5	1,5308	1,5441

If one tries to calculate the densities of materials 2 to 5 from the density of material 1 (which is different from that of pure PVC because of the presence of lead stabilizer and lubricants) and from that of $CaCO_3$ (calcite) = 2,711 g/cm^3, higher densities than those experimentally obtained are found.

The discrepancy can probably be related to an increase of the porosity of the filled grades of PVC. Small cavities can be created locally at the bondaries of the filler particles or inside agglomerates.

Effect of fillers on Tg. The glass transition temperature Tg was determined by means of a Differential Scanning Calorimeter DSC-1B Perkin Elmer. The PVC samples were tested at a heating rate à 8°C/min (1st run) and after a standard thermal history (5 min at 100°C, cooling down to 40°C at -8°C/min) were reheated at 8°C/min (2nd run). The results are given in Table 3 ; they show that the filler, at least up to the weight fraction here considered, does not affect Tg. This is in good agreement with the data reported by Schwarzl on polyurethane rubber filled with NaCl (6). A systematic difference of about 3°C occurs between the two runs.

TABLE 3. Glass transition temperature

Material	Tg (1st run) (°C)	Tg (2nd run) (°C)
1	83	80
2	82	79
3	82	79
4	82	80
5	82	79

Shrinkage. The dimensional stability of the five grades of PVC has been tested at 100, 120, 140 and 160°C during the tensile experiments. The measured shrinkages are given in Table 4. The significant shrinkage observed at high temperature was induced by stretching the extruded sheets at high temperature between the flat die and the calender.

TABLE 4. Shrinkage (%)

Temp. (°C) PVC	100	120	140	160
1	2.4	3.0	7.6	16.1
2	1.7	3.4	5.1	11.5
3	1.3	2.1	4.8	9.6
4	1.9	3.9	4.9	10.3
5	1.1	2.3	4.0	9.1

DYNAMIC MECHANICAL PROPERTIES

Shear modulus and damping factor tan δ by free torsional vibrations

The results obtained are given in Fig. 1-5 ; they are in good agreement for the shear modulus and for the localization of Tg. Some disagreement appears in the values found for tan δ and for the localization of the β transition ; these can be accounted for by the slight difference in the frequencies of vibration selected by the participants ; 1 Hz by TNO ; 3 to 1 Hz by Montedison and 8 to 2 Hz by Solvay & Cie.

The values of the modulus G' found by the participants show the influence of the filler on rigidity. No influence of the dimensions of the filler on shear modulus can be detected at 10 %. At 20 % it seems that the coarse filler increases the rigidity more than does the fine one. The ratio between the shear modulus of the filled and the unfilled materials appears to be constant in the temperature range investigated (Table 5).

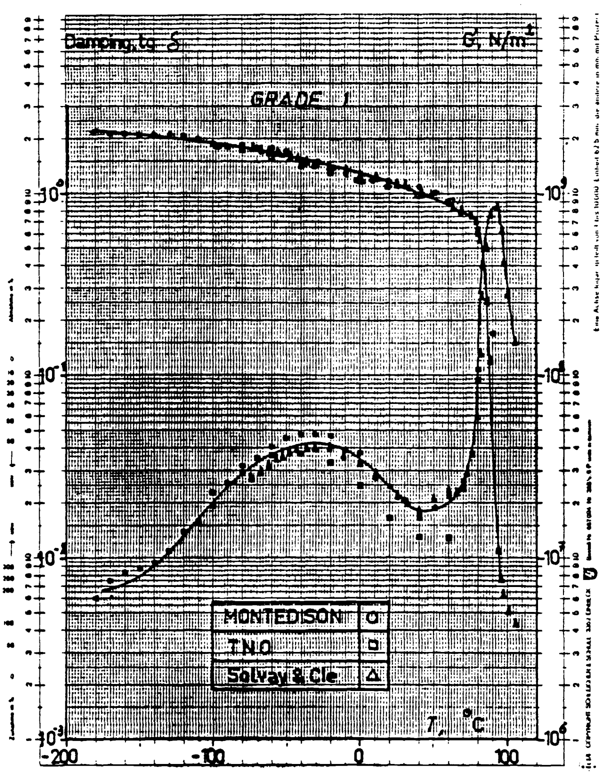


Fig. 1. Dynamic mechanical properties - damping and shear modulus - Grade 1

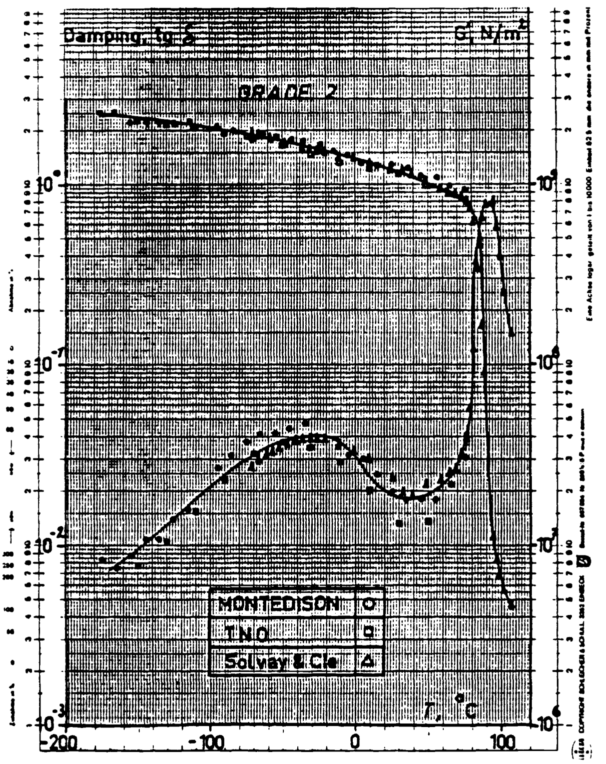


Fig. 2. Dynamic mechanical properties - damping and shear modulus - Grade 2

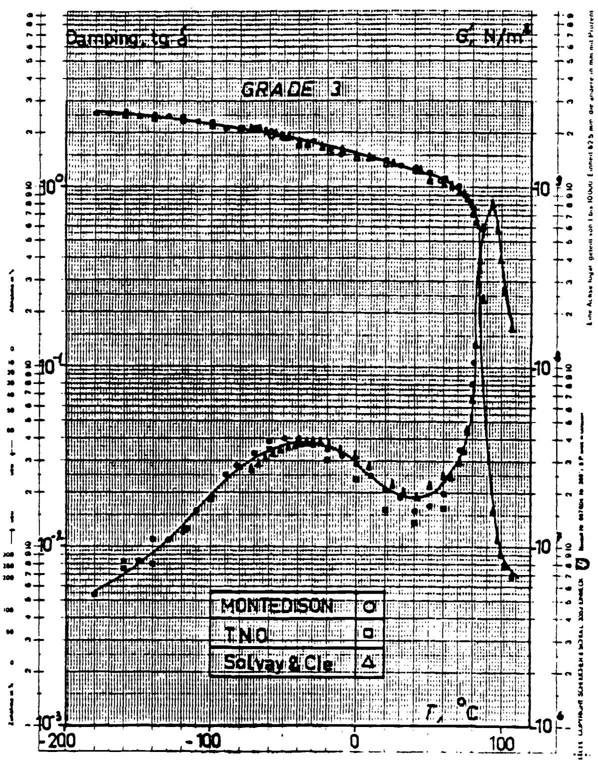


Fig. 3. Dynamic mechanical properties - damping and shear modulus - Grade 3

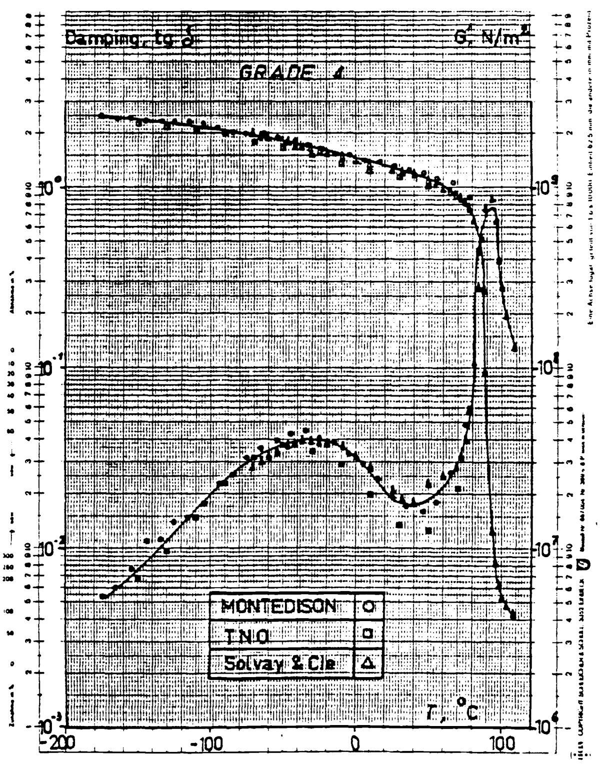


Fig. 4. Dynamic mechanical properties - damping and shear modulus - Grade 4

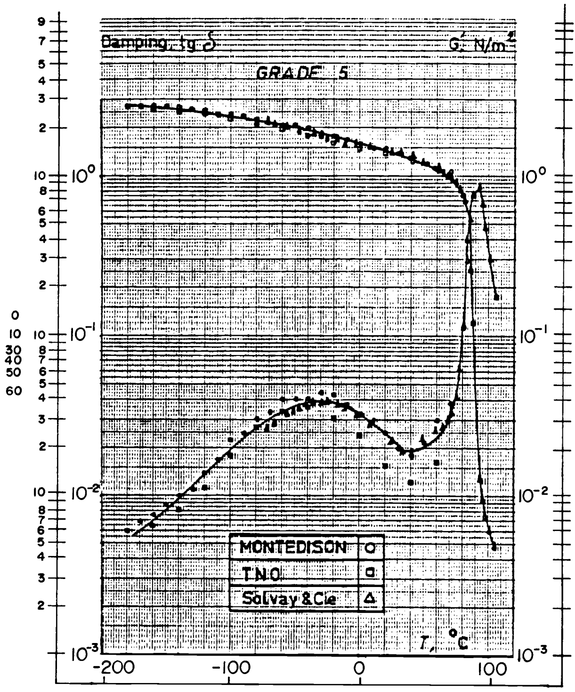


Fig. 5. Dynamical mechanical properties - damping and shear modulus - Grade 5

TABLE 5. $\frac{G' \text{ filled}}{G' \text{ unfilled}}$

PVC \ T (°K)	173	223	273	323
2	1.08	1.07	1.08	1.08
3	1.20	1.19	1.20	1.22
4	1.09	1.09	1.09	1.11
5	1.23	1.24	1.24	1.23

<u>Young's modulus and damping in flexural vibration</u>

Young's modulus and the damping factor tan δ were measured in flexure at frequencies of 100 and 1000 Hz at room temperature.

TNO and Solvay used the same kind of apparatus for this measurement. The specimen, a bar with a rectangular cross-section, is suspended vertically. It is clamped at the upper end, and excited electromagnetically with the aid of a small magnet glued to its lower end. The vibration amplitude is measured by means of a capacitive transducer located near the clamp. TNO utilized a home-made device, Solvay a Brüel & Kjaer apparatus.

The results obtained in the two laboratories are in good agreement for tan δ. They are given in Fig. 6 for E' and in Table 6. The Young's moduli measured by Solvay are systematically lower than the results of TNO.

TABLE 6. Young's modulus and tan δ*

PVC	E' (100 Hz) 10^9 N/m²		E' (1000 Hz) 10^9 N/m²		tan δ (100 Hz) 10^{-2}		tan δ (1000 Hz) 10^{-2}	
	TNO	Solvay	TNO	Solvay	TNO	Solvay	TNO	Solvay
1	3.56	3.48	3.82	3.72	3.42	3.3	4.63	4.7
2	4.05	3.67	4.34	3.82	3.58	3.4	4.75	4.9
3	4.47	4.01	4.77	4.28	3.42	3.35	4.43	4.5
4	4.32	3.81	4.59	4.00	3.26	3.3	4.63	4.7
5	4.77	4.35	5.07	4.47	3.36	3.4	4.60	4.5

* TNO : 20°C ; Solvay : 23°C

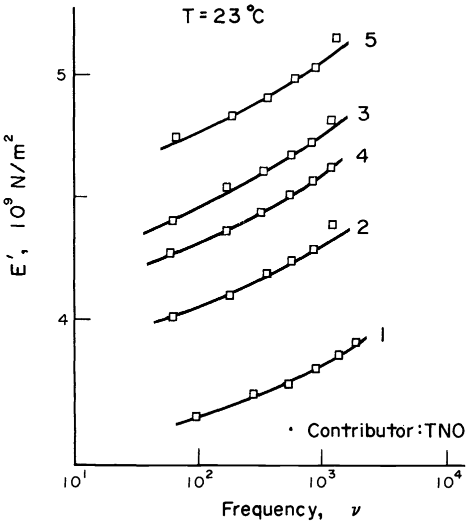


Fig. 6. Flexural vibration - Young's modulus

No systematic influence of the fillers on the damping factor can be detected. On the other hand, the modulus increases with the concentration of filler and with its dimensions. That increase of the shear and the Young's moduli with filler content is in agreement with the expectations of the composite materials theories (7).

MECHANICAL PROPERTIES

Tensile properties

Tensile properties have been measured by four participants : TNO, University of Prague, ICI and Montedison. The test pieces were machined in the longitudinal direction. Some measurements made by TNO in the transverse direction show slight anisotropy of the sheets produced by the stretching at high temperature during processing. Information about the apparatus and test conditions used by each laboratory is given in Table 7.

TABLE 7. Tensile properties - test conditions and equipment

Contributor	Apparatus	Test piece	Temperature (°C)	$\dot{\varepsilon}$ (s^{-1})	Measurements
TNO (Delft)	Instron universal testing intrument	ISO R 527 type I	20 to 160	7.6 10^{-3}	σ_y, σ_D (20°C) σ_b, ε_b
ICI	idem	ISO R 527 type I	23, -20	1.7 10^{-3} and 1.7 10^{-1}	"
University of Prague	?		-80 to +80	3.33 10^{-3}	σ_y, σ_D, ε_b
Montedison	Instron TTCM home-made device for high speed testing	ISO R 527 " "	23 " "	3.4 10^{-3} 3.4 10^{-2} 1.7	σ_y, σ_D, ε_b

Yield stress. The comparison between results obtained at -20°C and +23°C at 1.7 10^{-3}, 1.7 10^{-1} and 1.7 s^{-1} given below, shows that the yield stress, σ_y increases by about 45 % with a decrease of 43°C and by about 40 % when the strain rate is decreased by 1000.

TABLE 8. Unfilled PVC : influence of temperature and strain rate on the yield stress

T (°C)	$\dot{\varepsilon}$ (s^{-1})	σ_y (MN/m^2)
- 20	1.7 10^{-3}	85.4
+ 23	1.7 10^{-3}	58.7
+ 23	1.7 10^{-1}	70.9
+ 23	1.7	82.3

About 12°C has the same influence on the yield stress as a factor 10 in strain rate. All the measurements performed at 1.7, 3.3 and 7.6 10^{-3} s^{-1} can thus, in first approximation, be put together and compared. Indeed, the variation of strain rate around the mean value, a factor 2, is equivalent to less than 4°C. The argument made below Tg can also be extended above Tg for the rupture stress. However, it can not be applied to the elongation at break. The values of the strain rate have been selected in the tough-tough transition zone, where the variation of this property versus the strain rate is important. The results obtained by the contributors are given in Fig. 7 and Table 9 as function of temperature. Inclusion of filler in all cases reduces σ_y. As regards the type of filler, at the 10 % level no real differences were observed and the decrase in σ_y amounted to be between 0 and 11 %, depending on temperature. At the 20 % level, however, the fine filler (0,07 µm) was seen to depress σ_y more than the coarse filler (2,4 µm). It can also be seen that increase in filler content from 10 to 20 %, pro rata, produced a bigger reduction in σ_y than shown by the inclusion of 10 %. Generally the effect is larger than the reduction in concentration of PVC in the sheets caused by the filler (9 % and 17 %).

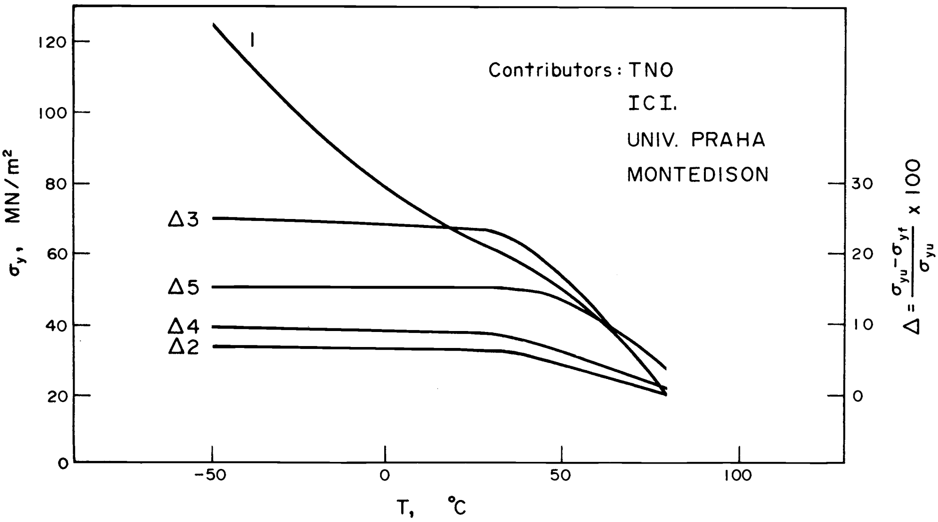


Fig. 7. Tensile properties of rigid PVC - Yield stress

TABLE 9. Decrease of σ_y by the fillers

$$\frac{\sigma_y \text{ unfilled} - \sigma_y \text{ filled}}{\sigma_y \text{ unfilled}} \times 100$$

PVC	-50°C	-20°C	20°C	23°C	40°C	60°C	80°C
2	1	7	4	6	9	< 0	0
3	25	24	19	21	23	12	0
4	9	9	5	7	12	0	2
5	15	14	13	14	18	2	4

Except grade 3, at temperatures up to 40°C, the decrease of σ_y by the filler cannot be correctly calculated by means of simple equations presented for the composite materials (8)

$$\sigma_{yf} = \sigma_{yu} (1 - 1,21\, \emptyset^{2/3})$$

where σ_{yf} is the yield stress of the filled PVC
σ_{yu} is the yield stress of the unfilled PVC
$\emptyset$ is the volume fraction of the filler.

Taking 0.048 and 0.092 as the volume fractions of the fillers in the PVC filled with 10 and 20 % of $CaCO_3$, that calculation predicts reduction factors of 0,16 and 0,25 for the yield stresses of the filled materials.

Drawing stress. The drawing stress is the stress level in the plateau region of the strain/stress curve which occurs after yield. The values obtained at -20, 20 and 23°C are given in Table 10.

TABLE 10. Drawing stress σ_D (MN/m^2)

PVC	-20°C, 1.7 10^{-3} s^{-1}	20°C, 7.6 10^{-3} s^{-1}	23°C, 1.7 10^{-3} s^{-1}
1	72.3	53.0	47.7
2	65.4	50.5	44.7
3	necking rupture	44.6	necking rupture
4	65.7	50.9	45.1
5	62.8	47.6	42.4

σ_D follows a similar pattern to that exhibited by σ_y, with the exception of grade 3 (20 % fine filler) in which necking rupture occurs sometimes. This behaviour must be connected with the effect of the agglomerates on rupture. The phenomenon of necking rupture persists in all grades at 1.7 10^{-1} s^{-1} strain rate. It is probably a result of neck instability, under non isothermal test conditions, with temperature increasing. The ratio of σ_y/σ_D can be used as a measure of the propensity of a material to cold draw.

TABLE 11. $\frac{\sigma_y}{\sigma_D}$

PVC	-20°C 1.7 10^{-3} s^{-1}	20°C 7.6 10^{-3} s^{-1}	23°C 1.7 10^{-3} s^{-1}	23°C 3.4 10^{-3} s^{-1}
1	1,18	1,24	1,23	1,26
2	1,18	1,21	1,23	1,25
3	-	1,20	-	-
4	1,16	1,22	1,22	1,22
5	1,13	1,20	1,18	1,21

The fillers have only a slight effect on the ratio σ_y/σ_D. A decrease of temperature from 23°C down to -20°C also reduces slightly the propensity of the PVC to cold draw. In conclusion, the presence of filler does not seem to have any dramatic effect on this early part of post yield behaviour, its influence only becoming apparent at the fracture stage.

Breaking stress. Incorporation of filler in the formulation leads to a decrease in the breaking stress σ_b with respect to the unfilled grade as shown in the next Table and in Fig. 8.

TABLE 12. $\frac{\sigma_b \text{ unfilled} - \sigma_b \text{ filled}}{\sigma_b \text{ unfilled}} \times 100$

PVC	-50°C	-20°C	20°C	23°C	40°C	60°C	80°C	120°C	140°C	160°C
2	5	11	12	0	15	12	9	22	1	3
3	25	17	26	11	34	31	34	32	20	17
4	12	8	2	0	7	2	11	16	15	12
5	18	15	11	11	16	10	17	23	14	12

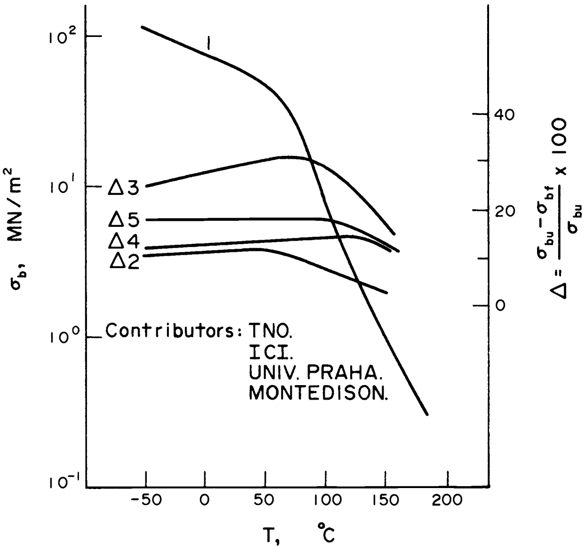


Fig. 8. Tensile properties of rigid PVC - Breaking stress

The conclusions which can be inferred from the breaking stresses are similar to those developed above on yielding and drawing stresses.

Elongation at break. The results obtained by the contributors are given in Fig. 9. Incorporation of the coarse filler and of 10 % of fine filler leads to a small decrease in elongation at break. The fine filler at 20 % strongly reduces the elongation at break below the glass transition temperature. Above Tg, no difference can be detected between the two grades of filler. As for the drawing stress, the tensile impact strength and the ball drop energy at break which will be discussed in the next sections, the adverse effect of the fine grade of $CaCO_3$ is probably caused by the agglomerates of fine particles detected.

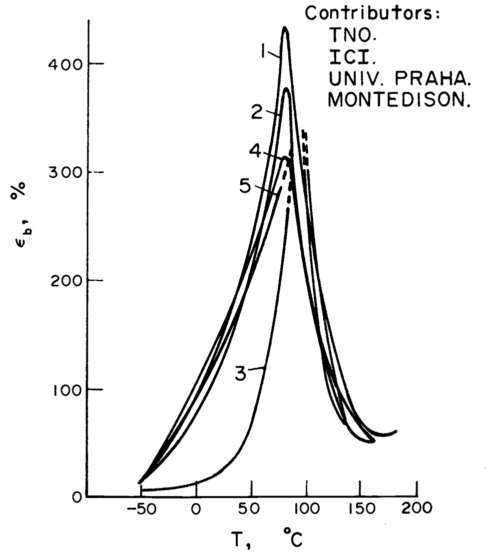


Fig. 9. Tensile properties of rigid PVC - Elongation to break

Tensile impact and ball drop tests

Tensile impact tests at room temperature have been performed by TNO and Solvay. TNO used a Zwick and Co Impact Tester type 5101 with a 1.500 J hammer. Solvay used a Frank device with 750 and 1.500 J hammers. Both laboratories worked according to DIN 53448. The results obtained are given below (Table 13) and on Fig. 10.

TABLE 13. Tensile impact strength

PVC	TNO		SOLVAY	
	T.I.S. (kJ/m^2)	Standard deviation (kJ/m^2)	T.I.S. (kJ/m^2)	Standard deviation (kJ/m^2)
1	704	61	680	90
2	277	77	388	188
3	141	55	150	24
4	717	92	703	151
5	635	104	619	132

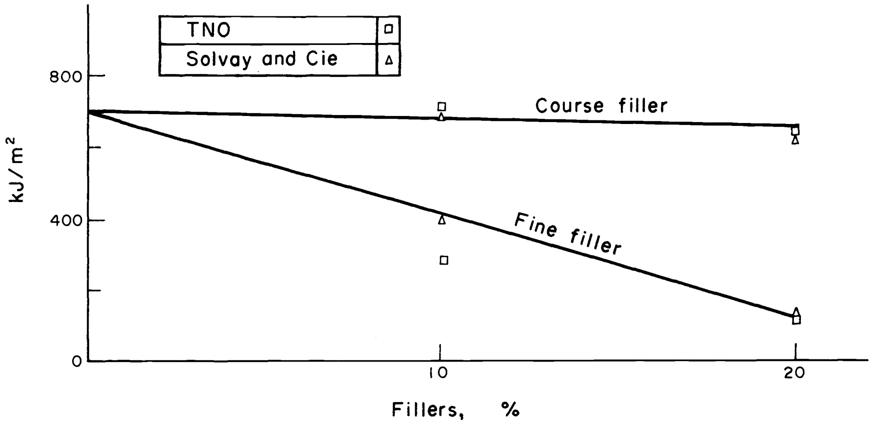
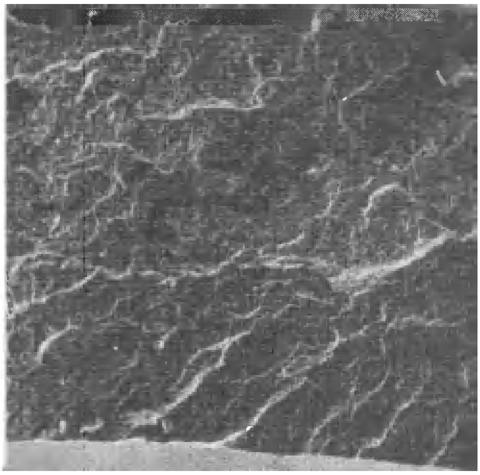


Fig. 10. Tensile impact strength

The results are in good agreement. Up to 20 %, the coarse filler does not reduce the impact strength of PVC very much. The small increase of standard deviation is probably connected with the heterogeneity of the products. The large decrease of tensile impact strength observed with the fine filler is surely due to heterogeneity in the distribution of filler. Stress concentration loci are not uniformly distributed into the specimen (Plate 1). Plates 2A and 2B show the fracture surfaces of the test pieces observed with a scanning electron microscope. The filler through its effect on the stress distribution and the propagation of the fracture, modifies the surface appearance (Photography 1 and others). When the rupture strength decreases, the volume of PVC deformed is reduced (Photographs 2 and 3) but there is no basic modification of the rupture process. At a high magnification photographs 7 and 8 taken in the propagation zone of the cracks, show that all the ruptures are tough.

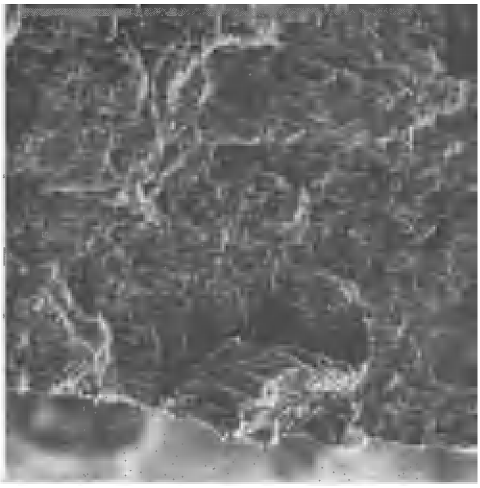
PLATE 2A. Tensile impact-fracture aspect - Scanning Electron Microscopy

Phot. 1. Unfilled PVC
(Magnification : x 100)



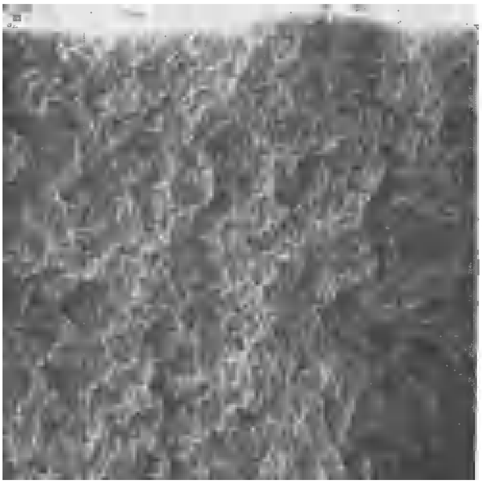
Phot. 2 : 10 % fine filler
Brittle fracture
(Magnification : x 100)

Phot. 3. 10 % fine filler
Tough fracture
(Magnification : x 100)



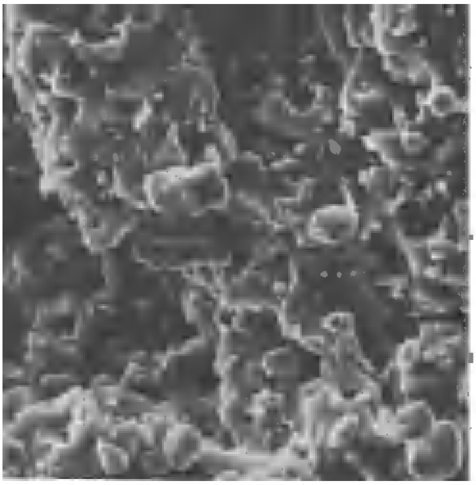
Phot. 4. 20 % fine filler
(Magnification : x 100)

PLATE 2B. Tensile impact-fracture aspect - Scanning Electron Microscopy

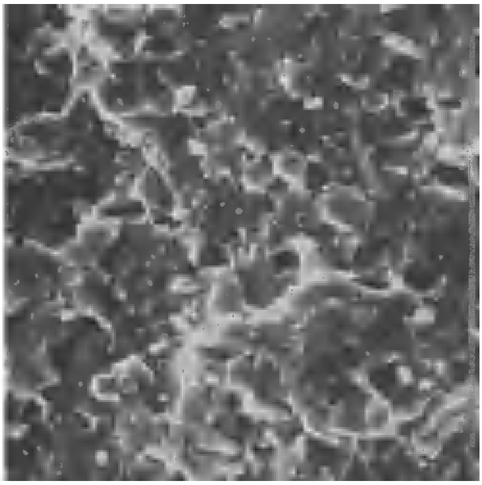


Phot. 5. 10 % coarse filler
(Magnification : x 100)

Phot. 6. 20 % coarse filler
(Magnification : x 100)



Phot. 7. 20 % coarse filler
Brittle fracture
(Magnification : x 2000)



Phot. 8. 20 % coarse filler
Tough fracture
(Magnification : x 2000)

The size difference between the two fillers does not modify the rupture process. The large variations recorded in the tensile impact strengths between the two qualities of filler and, for the same quality, between test pieces, are produced by bigger agglomerates (up to about 30 µm). These conclusions are corroborated by the results of ball drop experiments made by Montedison (Table 14) at room temperature.
Disk-shaped (Ø = 100 mm) specimens are hydraulically clamped into the specimen supporting head by means of an annular clamp whose internal diameter is 60 mm. The dart head, equipped with strain gauges, is hemispherically shaped (Ø = 20 mm). Test conditions are :

- drop height : 1 m
- dart weight : 6 kg
- impact speed : 4,43 m/s.

Table 14 reports the medium values of the maximum specific load P (i.e. load/thickness), the deflection at break f, and the specific energy U determined on the five PVC grades. Minimum and maximum values obtained for these quantities have also been reported.

TABLE 14. Ball drop test

Material	Filler	P (kN m^{-1})	f (mm)	U (kJ m^{-1})
1	-	2474 (2422-2612)	15.95 (13.29-17.10)	25.33 (20.72-29.48)
2	Fine 10 %	1480 (644-1816)	6.10 (3.31-7.50)	4.38 (1.01-6.80)
3	Fine 20 %	927 (587-1125)	4.31 (3.41-5.09)	2.08 (1.00-2.92)
4	Coarse 10 %	2532 (1425-2570)	13.18 (4.86-15.73)	21.20 (3.98-24.92)
5	Coarse 20 %	2413 (2240-2473)	13.12 (11.52-14.62)	17.73 (14.30-20.63)

Minimum and maximum values reported in brackets.

A visual observation of the broken specimens shows that the fracture mechanism is different for the various samples. PVC 1 fails by yielding and necking ; samples 2 and 3 fail in an apparent brittle way ; however a small yielded area is evident at the centre of the broken specimens. The failure behaviour of samples 4 and 5 is tough but the propagation of necking is hindered. The sheets which have the larger concentration of agglomerates, have the lower ball-drop test energy at break. The large scatter of results for PVC 4 (10 % coarse filler) is also related to the non uniform dispersion of the filler. Those results can be put together with tensile data. Though the strain rate is different in both experiments, the decrease of the impact strength and the energy at break can be explained by the reduction of the elongation at break brought by the bad dispersion of the fine filler.

Impact strength on prestressed samples

This test (1) assesses the brittleness treshold of a material submitted to a notched impact test of low energy. The depth of the notch made by the blade which completes the hammer, is large compared with the size of the structural defects or heterogeneities of the PVC. The test measures the prestress level in the test piece necessary to propagate the brittle rupture in the whole material. The results obtained are given in Table 15.

Prestress level at break (MN/m^2)	Filler			
	0 %	10 %	20 %	
	13,5	20,8	20,3	Fine CaCO$_3$
		18,6	22,9	Coarse CaCO$_3$

In the range of concentration used, the fillers increase the minimum value of energy needed to propagate the crack. The agglomerates do not influence the prestress level at break and the two fillers have the same influence on the result of the test.

Fracture mechanics

The apparent critical "stress-intensity factor" $K_{I,c}$ has been determined at 23°C according to the DEN (Double Edge Notch) geometry by Montedison. Strip shaped specimens have been obtained from ISO R 527 specimens. The width W was about 9.3 mm, the depth a/2 of each notch was about 1.5 mm. Sharp notches have been obtained by means of a razor blade which was used only one time ; the depth of the notch was controlled by means of a micrometric device. Experiments have been carried out by means of an autographic tensile impact apparatus ; the impact speed was 0.51 m/s ; 10 specimens have been used for any material. The results are given in Table 16.

TABLE 16. Dependence of $K_{I,c}$ on filler dimensions and content

Material	Filler	$K_{I,c}$ (MN $m^{-3/2}$)
1	-	2.30 (2.20 - 2.36)
2	Fine 10 %	2.65 (2.56 - 2.76)
3	Fine 20 %	2.68 (2.53 - 2.80)
4	Coarse 10 %	2.53 (2.46 - 2.61)
5	Coarse 20 %	2.56 (2.49 - 2.68)

Minimum and maximum values reported in brackets

The resistance of the materials apparently increases, by increasing the content of filler, and the improvement is higher for the fine filler. The type of fracture can be classified as "brittle" from the recorded curves but a microscopic inspection of the fracture surfaces showed that there was in any case a plastic deformation at the tip of the notch and that its area increased by increasing the filler concentration. This means that some material yielded at the tip of the notch and as a consequence the radius curvature of the notch increased and the overall stress profile changed. Formally, no definitive conclusions can be given about the influence of the filler on the intrinsic resistance against the propagation of the crack because the purely elastic model on which the fracture-mechanics experiments is based does not more hold. Nevertheless, the apparent resistance to crack propagation, which add the plastic deformation energies to the intrinsic resistance against the propagation of a crack increases when fillers are mixed with PVC. The effect of the fine grade looks to be higher than that of the coarse one.

Charpy notched impact strength

To confirm the influence of the fillers on the propagation of failure in rigid PVC, the Charpy impact strengths of the unfilled and filled grades of PVC were measured by Solvay at room temperature on notched test pieces, according to German standard DIN 53453. New sheets were prepared for these measurements. The test pieces were milled with a Tensilkut machine from 4 mm thick sheets prepared by milling on a two roll open mixer at 190°C and pressed at 195°C. No filler agglomerates bigger than 1 µm can be detected in the pressed sheets. The results obtained are given in Table 17.

TABLE 17. Charpy impact strength on notched specimen

PVC	Charpy impact strength (kJ/m^2)	Standard deviation (kJ/m^2)
1	6,5	0,43
2	13	1,4
3	36	8,5
4	8,7	0,67
5	9,6	0,47

The results are in good agreement with the impact strength prestressed samples for grades 1, 2 and 4, and tensile impact data obtained with notched specimens. They show an increase in the apparent resistance of the specimen to the propagation of cracks. The improvement given by 20 % of filler seems to be greater than that obtained with 10 %. As no agglomerates appear in the test pieces, the results can be directly correlated with the quality of the filler. The fine grade seems to give a better improvement of cracks propagation resistance than the coarse one ; the effect is particularly well marked at 20 %.

Tensile Creep

Creep in tension was measured by TNO using an apparatus constructed "in house". Before measurement, the specimens were thermally pretreated as follows : 1/2 h at 95°C, cooled in 1/4 h to 23°C, kept for 23 hours at the measuring temperature, cooled slowly to below 0°C, stored until use below 0°C ; heated to the measuring temperature and kept for 1 hour at the measuring temperature before the beginning of the experiment.
The results obtained at 60°C are given in Fig. 11 and 12.

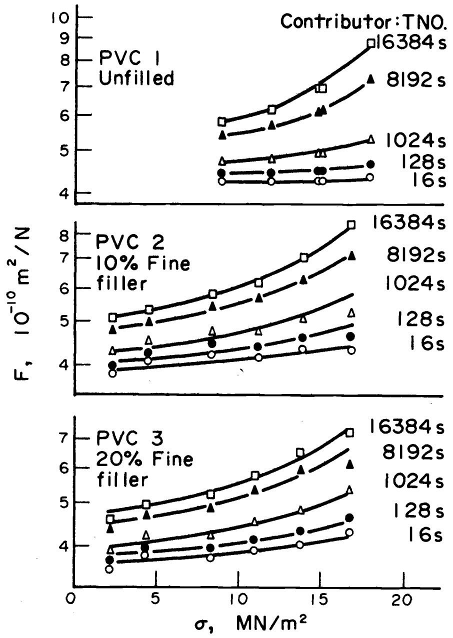


Fig. 11. Tensile creep of rigid PVC at 60°C.

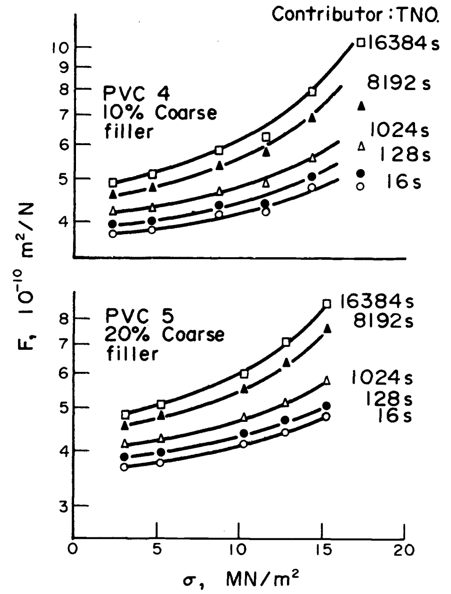


Fig. 12. Tensile creep of rigid PVC at 60°C

For each creep time measured, the compliance is plotted as a function of stress for the 5 PVC grades. The behaviour of the materials is not linear and some scatter occurs. Up to a stress of about 14 MN/m^2, the deviation can be as large as 5 % ; this is probably due to individual variations between the specimens. The non linearity increases in the sequence PVC unfilled, PVC filled with fin $CaCO_3$, PVC filled with coarse $CaCO_3$. At longer creep times, the non linearity is more pronounced than at shorter creep times. The logarithmic slope of the creep curves is about the same for PVCs 2 through 5 and increases with increasing stress level. These results are in good agreement with the dynamic modulus and tensile data reported. At short times and low stresses, the fillers have a stiffening effect. When stress or time are increased, plastic deformations take place earlier for filled materials than for the unfilled one.

Fatigue properties

Static fatigue. Static measurements were performed by I.C.I. on apparatus it had developped, with the five PVC grades at 23°C, 50 % r.h. Measurements on notched specimens were added for the unfilled PVC (grade 1) and the PVC filled with 20 % of coarse $CaCO_3$ (grade 3). The results obtained are given in Fig. 13 for the unnotched specimens. The stresses have been precalculated to give a failure time between a few seconds and about 10^7 seconds.

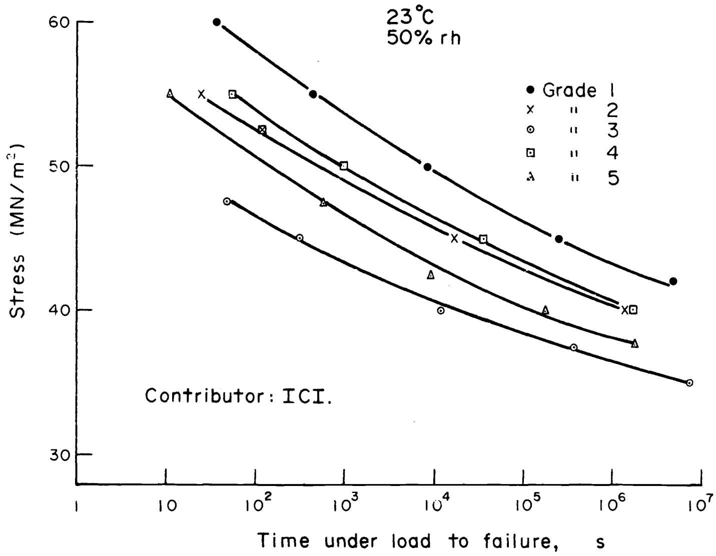


Fig. 13. Mechanical properties of rigid PVC - Static fatigue

Under continuously applied load conditions, all materials exhibit static fatigue. Failures in all grades are ductile, by necking rupture. At times up to about 10^7 seconds, there is no indication of any ductile-brittle transition. However, the addition of filler generally reduced the natural propensity of PVC to cold draw, since the neck does not stabilize. The reduction of yield stress by the fillers, observed during the tensile experiments, is maintained similar for all grades. Fine filler decreases the failure time more than does coarse filler. To check on the possible existence of a ductile-brittle transition at 23°C, the behaviour of specimens containing two notches was studied. Two notch tips radii, r, equal to 250 and 10 µm were used. The results are given in Fig. 14. In spite of the high elastic stress concentration factors produced in the material close to the notches (4.2 for r = 250 µm), no brittle failure occurs. Because of the ductility of the materials, fracture is essentially dominated by the yield stress.

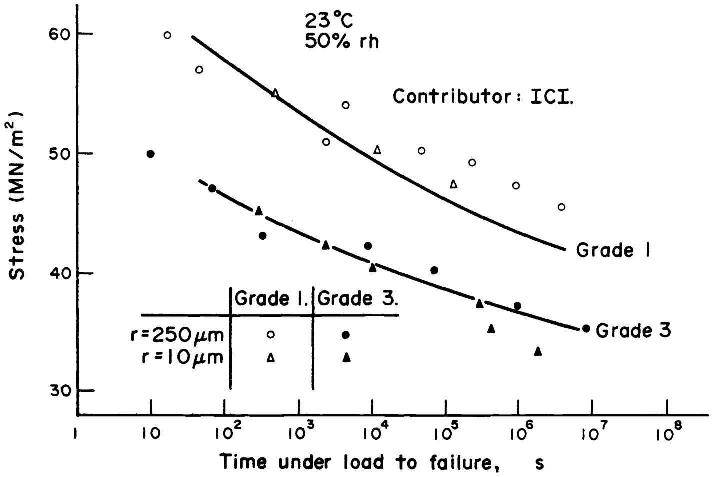


Fig. 14. Mechanical properties of rigid PVC - Static fatigue - Notched specimen

Except for two measurements obtained with grade 3 at a failure time longer than 4.10^5 seconds, the results obtained with the 10 µm radius notches are similar to those found with the unnotched test pieces. If we assume that the notched test pieces cannot produce a higher fatigue resistance than an unnotched specimen at the same stress level, all the results obtained with the notched test pieces follow the same behaviour as that found for the unnotched test pieces.

Intermittent loading and dynamic fatigue. Intermittent loading experiments were carried out by I.C.I. A pneumatically operated arm connected to a non-linear dashpot (9) controlled the weight pan and ensured rapid but smooth loading on the apparatus used for static fatigue measurements. The cycle period was set by a pair of "clock switches" so that the "on load" and "off load" periods could be varied. For this program, the cycle chosen was 10 s "on load", 10 s "off load" (50 mHz) and unnotched specimens were tested. For the dynamic fatigue experiments the frequency schedule was 2.5 Hz. Both, notched (10 µm notch tip radius) and unnotched test pieces, cut from sheets of grades 1 and 3, were tested in dynamic fatigue. The results obtained are given on Fig. 15 and 16 for the unnotched specimens and on Fig. 17 for notched ones. They are compared with the data of the static fatigue measurements.

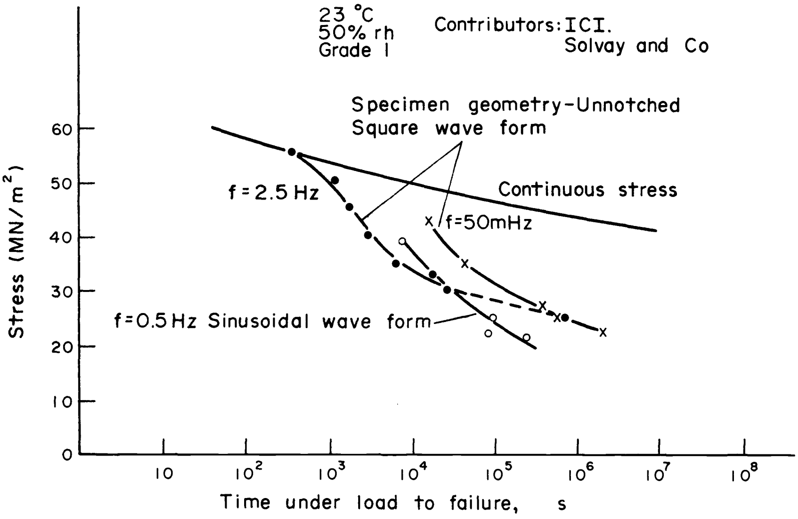


Fig. 15. Mechanical properties of rigid PVC - Dynamic fatigue

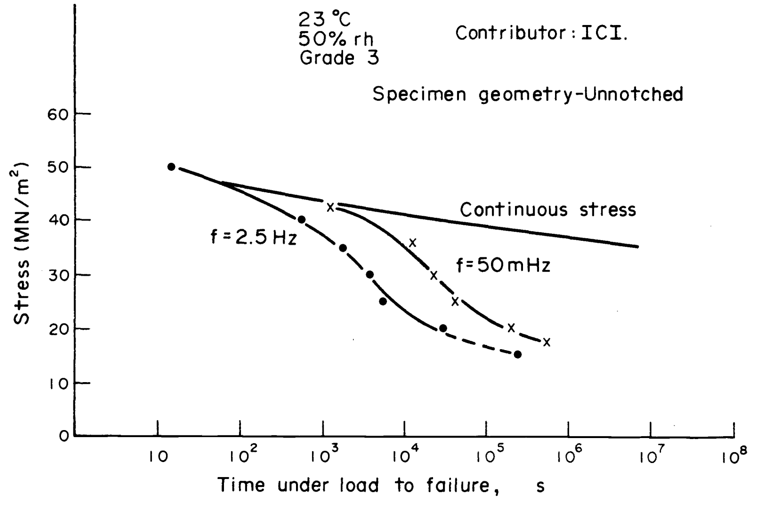


Fig. 16. Mechanical properties of rigid PVC - Dynamic fatigue

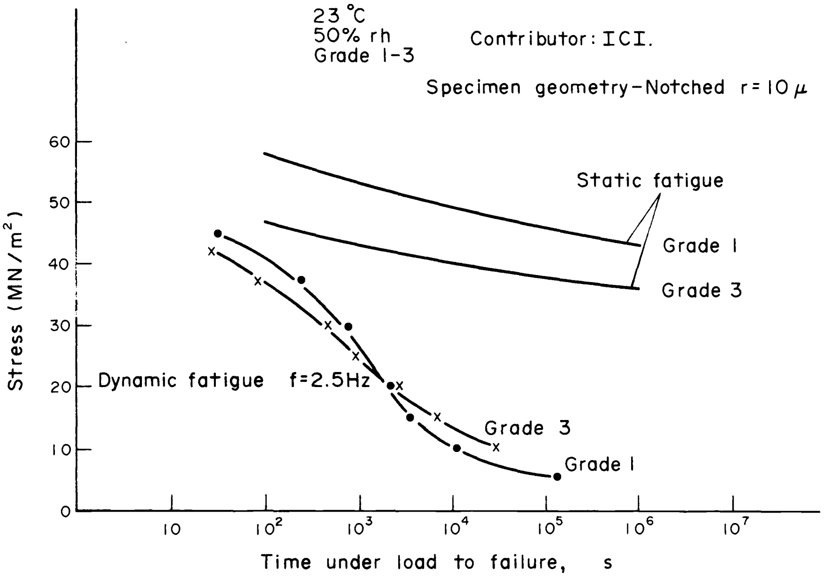


Fig. 17. Mechanical properties of rigid PVC - Dynamic fatigue

Solvay also performed dynamic fatigue measurements at 0.5 Hz with a self made apparatus. In this case, the waveform of the loading was sinusoïdal. PVC grades 1, 2 and 4 were tested. The results are given on Fig. 15 for the unfilled PVC. They are compared with the ICI results obtained at 50 mHz with the five grades of PVC on Fig. 18.

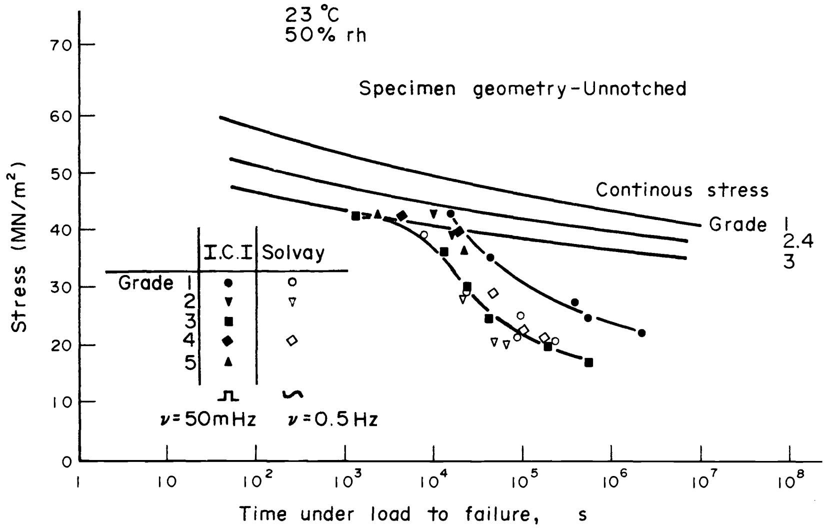


Fig. 18. Mechanical properties of rigid PVC - Dynamic fatique

For both grades 1 and 3, the results obtained at 50 mHz and 2.5 mHz with a square weveform, show that the effect of increase in frequency is to reduce the actual load bearing life time at stresses in excess of 25 MN/m^2 for grade 1 and 15 MN/m^2 for grade 3 (Fig. 15 and 16). However, as the applied stress is reduced below theses values, fatigue resistance becomes less stress sensitive and the effect of frequency largely disappears. The results obtained at 0.5 Hz with a sinusoïdal waveform do not show the strong decrease in stress sensitivity (grade 1 - Fig. 15). Except at high stress levels and short failure times, all the PVCs show a dynamic fatigue effect (fig. 18). Intermittent loading or dynamic fatigue reduces the actual load support lifetimes considerably from that which the material would withstand if continuously loaded at the same stress. The difference between filled and unfilled materials is not so well established with the sinusoïdal waveform. The results obtained in intermittent loading experiments can be interpreted by a fracture mechanics analysis. Values for the parameters of fracture toughness (K_I) and material inherent flow size (2C) are given in the next Table.

TABLE 18. Fracture mechanics parameters

Material	K_1 ($MN/m^{3/2}$)	2C (μm)
PVC 1	0,35	110
PVC 3	0,49	600

Since the stress to produce fracture σ_F in a material is related to the parameter K_I and 2C by an equation of the form

$$\sigma_F = f\left(\frac{K_1}{\sqrt{2C}}\right)$$

then the respective importance of the individual contributions by K_I and 2C can be appreciated. The values obtained show that the filler increased the fracture toughness. Although it is dangerous to ascribe physical significance to the concept of inherent flaw size (2C), it is interesting to note that the coated precipitated calcium carbonate (Ø = 0.07 μm) markedly increases flaw size from 110 up to 600 μm. This could come about as the result of either severe agglomeration and or poor adhesion between filler and the PVC matrix. The behaviour of the notched specimens is quite different. The geometry of the notch is so severe that the energy component requires to initiate a crack has been drastically reduced. Essentially, this behaviour reflects the resistance of the materials to crack propagation. As was found with the impact strength on prestressed specimen and the Charpy notched impact strength, the addition of 20 % of fine filler increases the resistance of grade 3 to crack propagation. This improvement arises probably as a result of a crack stopping mechanism associated with the filler particles. Comparison of Fig. 15, 16 and 18 reveals that the presence of filler dramatically reduces the fatigue resistance of PVC. This can be attributed to the easier crack initiation mentioned previously. As no considerable differences appeared in time-to-failure between unnotched and notched specimens (r = 10 and 250 μm) in static fatigue (Fig. 14) and as the four filled grades show approximatively the same decrease in failure time in dynamic fatigue tests (Fig. 18) ; the effect of crack initiator is probably more directly connected with the characteristics of the fillers than with the agglomerates. This effect can be associated with the influence of the fillers on the yield stress in tensile measurements.

CONCLUSIONS

The analysis made by the Working Party defines the effect of the fillers and their dispersion on the mechanical properties of rigid PVC ; especially on rigidity, initiation and propagation of cracks, creep and fatigue. Fillers increase the rigidity of PVC. The effect is more marked at 20 % and with the coarse filler than at 10 % or with the fine grade. The damping factor in the glass region is not affected by the filler quality or concentration. Dynamic and tensile data are confirmed by the results of tensile creep measurements ; the fillers decrease the compliance at short creep time and at low stress levels. Yield and drawing stresses are reduced by the fillers. This effect is higher for the fine grade than for the coarse one. In tensile creep measurements, the results obtained at short creep time and at low stress levels are reversed at long times and high stress levels. The non-linearity of the compliance-stress relation, at a given creep time, becomes thus more pronounced with fillers ; the coarse grade beeing more active than the fine one. Independently of its particle structure, the filler decreases the energy required to initiate a crack. That effect becomes very important when agglomerates are present in the composite. When its dispersion in the bulk is correct, the filler does not influence the crack initiation very much at a concentration of 10 %. Nevertheless, as the finer filler depresses the yield and drawing stresses more than the coarse one does, it is more than likely that its effect on crack initiation is higher. This behaviour is probably connected with the number of particles distributed in the bulk and with the surface properties of the filler. Impact strength on prestressed specimens and on Charpy notched test pieces and dynamic fatigue test on notched specimens are related to the propagation of cracks in the PVC. The geometry of the notch is made in such a way that it always initiates the fracture so that the effect of structural defects, such as agglomerates, on rupture becomes negligible. As a plastic deformation always precedes the formation of the crack in the filled PVCs, it is not possible to define the intrinsic resistance against the propagation of the rupture. Nevertheless, the results obtained show that the fillers increase the apparent minimum energy required to propagate a crack in PVC : i.e. the sum of the plastic deformation and propagation energies. The effect is especially clear for the Charpy measurements. It seems to be increased with the concentration of the filler and to be higher with the fine $CaCO_3$ than with the coarser one.

Static and dynamic fatigues give results which are in good agreement with impact, tensile and creep tests. Even at high stresses, the time to failure is reduced by the filler and the minimum energy level required to propagate the crack is increased. The frequency effect on rupture time becomes less well marked at a low stress level. Owing to their action on the mechanism of propagation of failure, the fillers can improve the resistance of PVC to fracture. On the other hand, they can make crack initiation easier, especially if agglomerates are formed during processing. The uniform dispersion of the fine filler in the composite seems to be more difficult to achieve than for the coarse one (2.4 μm) but its effect on the propagation of a brittle fracture seems to be higher.

REFERENCES

1. A. Gonze, Pure Appl. Chem. 18, 553-567 (1969)
2. A. Gonze and J.C. Chauffoureaux, Pure Appl. Chem. 35, 317-351 (1973)
3. H. Oberst and W. Retting, J. Macromol. Sci. Phys. B5 (3), 561-592 (Sept. 1971)
4. G. Ajroldi, T. Casiraghi, G. Vittadini and G. Carbuglio, Stress-strain Properties of PVC : Influence of the Processing Temperatures, Euromech 37, Naples (1972)
5. J. Zelinger and U. Heidingsfeld, Intern. J. Polymeric Mater. 1, 317-330 (1972)
6. F.R. Schwarzl, H.W. Bree, C.J. Nederveen, Proc. 4th Inter. Cong. Rheol. E.H. Lee ed., Interscience, New York (1965) Part 3. p. 241
7. E.H. Kerner, Proc. Phys. Soc. (London) 69B, 808 (1956), Composite Materials : Testing and Design
8. L. Nicolais, M. Narkis and R.E. Lowengood, ASTM, STP 497 (1972)
9. W.H. Mills and S. Turner, Machines for Materials and Environmental Testing, Paper 23, Joint I Mech. Eng./SEE Symposium, Manchester (Sept. 1965)