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Multistage wet grinding of talc: relation between physico-chemical parameters of the filler and mechanical properties of filled polypropylenes

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Three talc samples of different mineralogical composition were wet-ground with an increasing number of grinding cycles. On each sample the particle size analysis, X-ray diffraction spectra, infrared spectra and nitrogen adsorption isotherms were carried out. In parallel, three mechanical properties of talc-filled polypropylenes were determined. A statistical analysis based on normalized principal component analysis and multiple partial linear regression was then carried out in order to determine correlations between the physico-chemical parameters of the fillers and the mechanical properties of polypropylene composites. The results show that this approach is valid only if the samples are separated according to their mineralogical composition. On the basis of this first analysis, an "industrial" model based on easily obtainable parameters is proposed. It is very satisfactory for talc-rich samples. For more chloritic ores, some other parameters have to be measured to enhance the quality of the models. The approach proposed in the present study seems then very promising.

1. Introduction

Talc is widely used as a filler in the thermoplastics industry, especially as a reinforcing agent in polypropylene. The resulting composites are used for automotive and appliance applications. These materials have an agreeable surface aspect, a low mould shrinkage and are easy to process. The mechanical properties of the composites are also affected by the presence of talc particles. Predicting the mechanical property changes in a talc-filled polypropylene is a difficult task because a great number of parameters affect these characteristics [1]. Such parameters are for instance the filler volume weight fraction [2], the shape of the filler particles [3, 4], the particle size and distribution and the textural properties of the solid [5]. Some attempts have been made to develop semi-empirical equations for the prediction of some mechanical properties such as the flexural modulus or the Charpy impact strength [4]. Generally, only the relation between the filler volume/weight fraction or the nature of the filler and the mechanical properties has been successfully obtained [1, 4, 5]. The importance of surface treatment of the filler has also been demonstrated [3, 6].

In this study, we were mainly interested in deriving the relationships between the physico-chemical properties of talc samples and the mechanical properties of talc-filled polypropylenes for untreated fillers at a constant volume/weight fraction. The final goal is then to obtain simple predictive models.

2. Experimental procedure

2.1. Materials

Three samples, provided by Talcs de Luzenac SA, were used as crude material. One referred to as 00B is a very pure talc. Its mineralogical composition is approximately 98% talc and 2% of accessory minerals (chlorite and carbonates mainly). A second one referred to as 0083 is composed of 82% talc and 12% chlorite plus some accessory minerals such as carbonates or rutile [7]. The third one, referred to as 00C, is a chlorite-rich sample (55% chlorite, 43% talc) [7]. The starting materials are obtained by dry grinding and air classification in the plant of Talcs de Luzenac SA; the particle size distribution of all these samples is such that less than 1% of the particles are larger than 50 μm.

2.2. Grinding procedure

All the products were wet-ground in a Dynomill type KDL special (laboratory size) supplied by Willy A. Bachofen AG Maschinenfabrik, Basel [8, 9]. The solid

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concentration used for this study was 16% solid, i.e. 2000 g of solid and 10 l of water. Seven grinding cycles were performed on each starting material, i.e. 00B, talc 0083 and chlorite 00C. After each cycle a part of the pulp was sampled whereas the rest was ground again.

2.3. Analytical procedures and variable definition

2.3.1. Size distribution parameters

Particle size distributions were obtained by means of a Sedigraph 5000D without corrections for the non-sphericity of the particles. The curves were obtained on the dry samples. On the curves obtained *Dx* is the size of a fictitious grid through which *x*% of the particles are passing. The mean passing size *D50* was taken into account in the statistical analysis. Two other parameters commonly used by industrial laboratories were introduced as well: the settled density *Dt*, which is the density measured on a powder sample after a normalized tapping procedure, and the estimated shape factor *ESF*, used empirically as an indicator of the aspect ratio of particles, which is equal to $(D50/Dt)^{1/3}$.

2.3.2. X-ray parameters

X-Ray diffraction data were obtained on a Jobin Yvon X-ray diffractometer working by reflection and using the K_{α_1} radiation of copper. Coherent scattering domains were measured on oriented samples by using Scherrer's formula [10]. The measurements were carried out on the (0 0 2) (0.936 nm) and (0 0 6) reflections of talc and (0 0 2) (0.705 nm) and (0 0 4) reflexions of chlorite. This yields four parameters *CsdT2*, *CsdT6*, *CsdC2* and *CsdC4*.

2.3.3. Infrared parameters

Infrared spectra were recorded on a Bruker IFS 88 interferometer equipped with a diffuse reflectance attachment (Harrick Scientific Corp.). The mercury–cadmium telluride (MCT) detector was cooled down to 77 K. Preparation of the samples involved simply mixing 70 mg of the sample with 370 mg of KBr. The spectra were recorded after 200 scans and converted into absorbance units. A typical i.r. spectrum of a ground talc sample is presented in Fig. 1. It allows the definition of eight parameters represented in Fig. 1a, b and c; the six area parameters *3677, 3660, 3650, 3570, 3420, 1465* represent the area of the band at the designated wave number. The triplet 3677, 3660 and 3650 cm^{-1} indicates the amount of substitution in the octahedral layer of talc. Indeed, it has been shown [11] that these positions could be assigned to OH groups surrounded by three Mg atoms, two Mg atoms and one substituent (Fe or Ni depending on the sample) and one Mg and two substituents, respectively. The area of the bands at 3570 and 3420 cm^{-1} indicates the amount of chlorite in the sample whereas the band at 1465 cm^{-1} is related to the quantity of surface carbonates [9]. The parameter *S1050* is the slope of the band at 1050 cm^{-1} measured on its low-frequency side, whereas the parameter *Pos1000* is the position of the band at 1000 cm^{-1}. Both these parameters indicate the possible distortion of the tetrahedral layer with grinding.

2.3.4. Parameters obtained by gas adsorption

Nitrogen adsorption isotherms were obtained at 77 K on a quasi-equilibrium volumetric device previously described [12]. The adsorption data were first treated by the BET procedure [13]. It yielded two parameters, the BET surface area *SBET* and the *C* energetic constant, *CBET*. Through the use of the t-plot method [14], three more parameters were obtained: *Vmic*, the microporous volume present in the sample, *St0* the total surface area and *St1* the non-microporous surface area obtained by this method. The amount of lateral faces *SsL*, univocally related to the aspect ratio of the particles, was determined directly from the low-temperature adsorption isotherms as previously described [9, 12, 15].

2.3.5. Mechanical parameters of talc-filled polypropylenes

Talc-filled polypropylene granules were prepared in the laboratory of Talcs de Luzenac SA using the following procedure. Polypropylene and talc (40% filler) were dry-blended at room temperature after dehumidifying. The mechanical mixtures were introduced into a screw extruder at 230 °C. The strands of extrudate were cooled in water and later dried. They were finally chopped in a granulator. The products were then moulded at 240 °C at *CETRA* (Centre d'Etudes Techniques de la Region Aquitaine, Lacq, France) using an injection-moulding machine to obtain standard flexural bars. Three mechanical parameters were determined: (i) the flexural modulus called *Eflex* was determined on a Adamel–Lhomargy dynamometer with a crosshead speed of 2 mm min^{-1}; (ii) the impact strength called *Echoc* was determined using a Charpy pendulum on unnotched samples from impact tests at 23 °C with a relative humidity of 50%; and (iii) the heat distortion temperature *HDT*. Each sample was measured three times for error minimization.

2.4. Statistical analysis

The data were processed through statistical software called LED [16]. Two statistical methods were used: normalized principal component analysis [17] and multiple partial linear regression. As stated before, the main goal of this investigation was to derive possible correlations between application parameters of the filled plastics and characteristics of the mineral filler. Thus, in this paper, we will not study the evolution with grinding of the physico-chemical parameters measured on the different talc samples.

3. Results and discussion

3.1. Global analysis

Normalized principal component analysis was first carried out on the whole system, i.e. taking all the

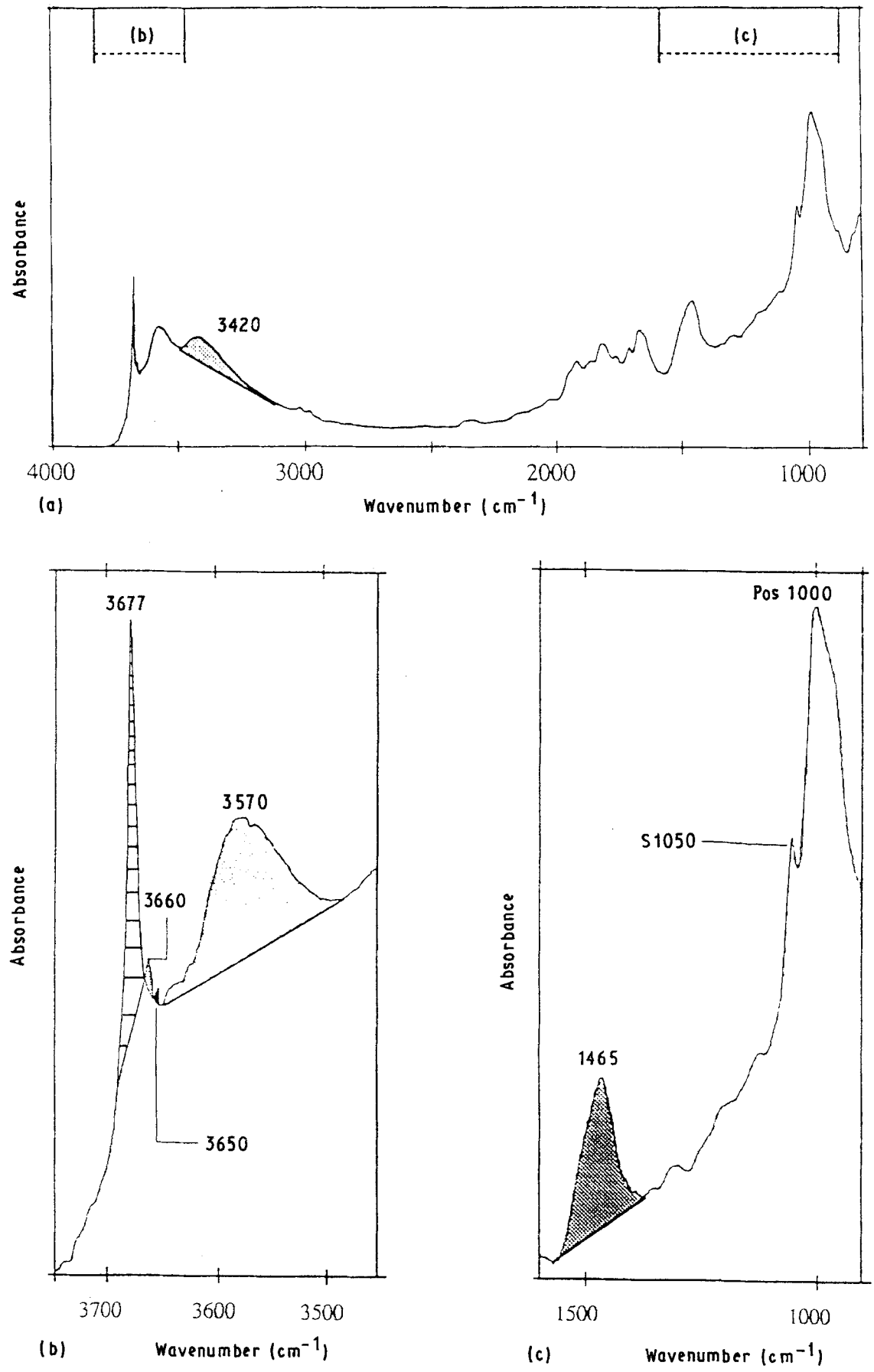


Figure 1 Typical diffuse reflectance FTIR spectrum of talc: definition of the different parameters used in the statistical analysis. (a) Wave numbers between 4000 and 800 cm^{-1}, (b) Wave numbers between 3800 and 3400 cm^{-1}, (c) Wave numbers between 1600 and 900 cm^{-1}.

samples and all the parameters. Analysis of the covariance distribution shows that 61% of the statistical information is spread along the two first factorial directions. Fig. 2 presents the projection of the different variables in the plane formed by the two first factorial axes. This diagram shows that the mechanical parameters of the polypropylenes are well explained. The flexural modulus *Eflex* and the heat

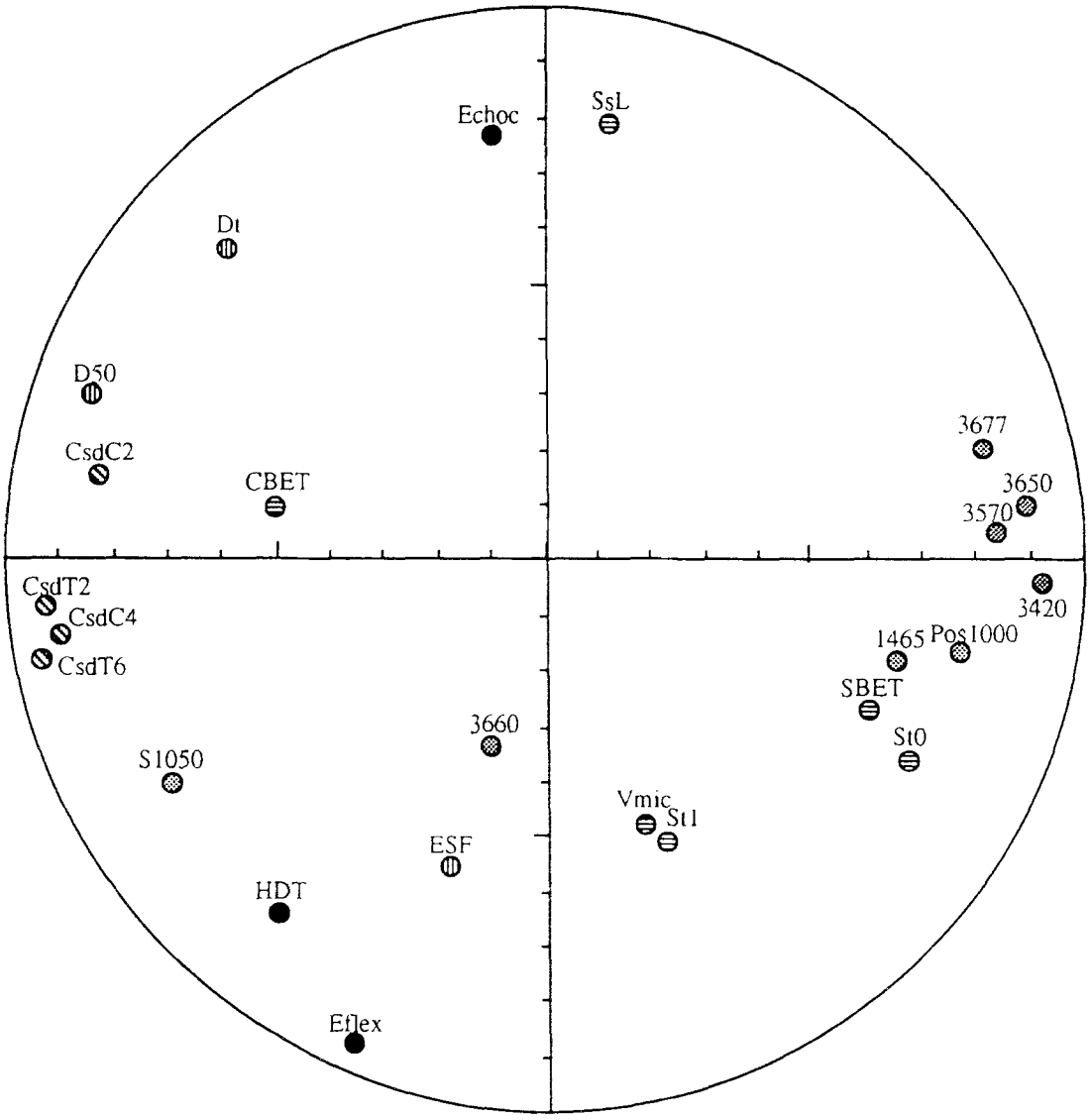


Figure 2 Normalized principal component analysis on the whole set of samples: projection of the variables in the plane formed by the two first factorial axes. (◍) Size distribution parameters, (⊘) X-ray parameters, (◉) infrared parameters, (⊜) parameters obtained by gas adsorption, (●) mechanical parameters of talc-filled polypropylenes.

distortion temperature *HDT* are normally correlated. They are also anticorrelated with the Charpy impact *Echoc*. *Eflex* and *HDT* are inversely correlated with the amount of lateral faces *SsL*. This means that particles with higher aspect ratios lead to better flexural and temperature distortion properties of the composites. This is a classical result for laminar fillers [4]. The Charpy modulus is correlated with the size of the particles, i.e. the smaller the particle size, the better the Charpy impact. This correlation has already been observed [5]. The best models obtained by multiple regression are as follows:

$$\begin{aligned} Eflex = & -7.65\,SsL - 23.3\,3570 - 1971\,Dt \\ & + 4.89\,CsdC4 + 7.21\,St1 - 14.6\,St0 \\ & + 32.6\,3420 + 16.4\,Pos1000 \\ & - 1303\,3650 - 2.20\,CsdT2 \\ & + 1.48\,CsdC2 - 11838 \end{aligned}$$

$R = 0.98$ with $R(Eflex, SsL) = -0.83$

$$\begin{aligned} Echoc = & -0.248\,St0 - 6.32\,S1050 - 0.85\,Pos1000 \\ & - 5.32\,Vmic + 0.21\,CsdT6 + 0.31\,1465 \\ & - 3.60\,ESF + 0.52\,St1 - 1.41\,D50 \\ & + 1.87\,3677 + 0.063\,CsdC2 + 0.20\,3420 \\ & - 0.019\,CsdT2 - 0.016\,SBET - 5.15\,3660 \\ & - 13.5\,Dt + 787 \end{aligned}$$

$R = 1.00$ with $R(Echoc, St0) = -0.60$

$$\begin{aligned} HDT = & -8.11\,3650 + 0.20\,3420 - 2.15\,3677 \\ & + 1.68\,S1050 + 0.09\,St1 + 0.05\,CsdC4 \\ & - 0.041\,CsdT6 + 98.97 \end{aligned}$$

$R = 0.92$

Though these models appear to be acceptable (good values of the correlation coefficient), the number of parameters introduced is much too high. This is probably due to implicit properties of the three starting

materials which are not described in the numerical characterization. In order to test this hypothesis, a projection of the samples in the plane formed by the two first factorial axes was carried out. The results of this analysis are presented in Fig. 3. It shows that the three series of samples are discriminated. It thus seems that it should be possible to obtain a much better model by treating each series separately.

3.2. Analysis by sample

3.2.1. Sample 00B

The results of normalized principal component analysis show that 76% of the statistical information is carried by the two first factorial axes. The projection of the parameters in the plane formed by these two axes is presented in Fig. 4. As in the previous analysis, the mechanical parameters of the polypropylenes are well explained. *HDT* and *Eflex* are correlated normally. They are also correlated inversely with the amount of lateral faces *SsL* and to a lesser extent with *Echoc*. This latter parameter is strongly correlated with the crystallinity parameters (coherent scattering domains of talc *CsdT2* and *CsdT6*, and chlorite,

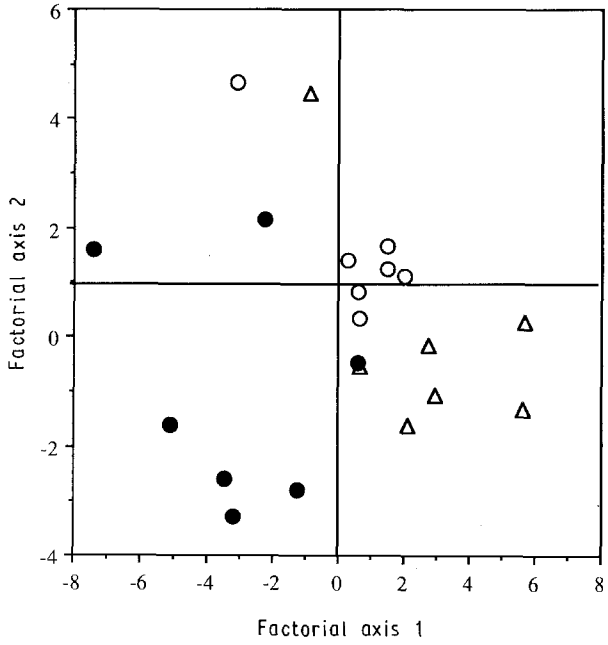


Figure 3 Normalized principal component analysis on the whole set of samples: projection of the observations in the plane formed by the two first factorial axes. (●) Talc 00B, (○) talc 0083, (△) chlorite 00C.

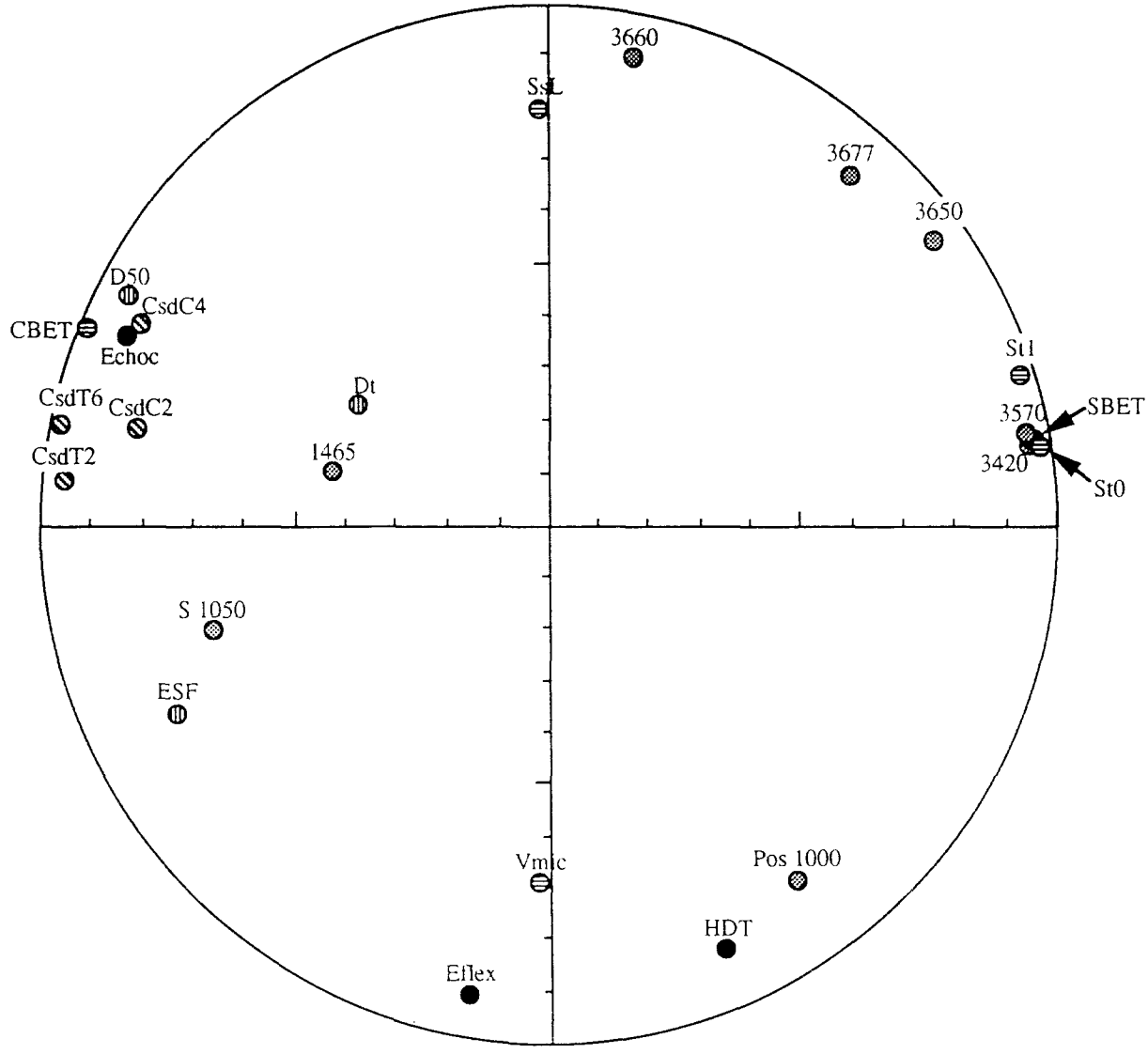


Figure 4 Normalized principal component analysis on talc 00B: projection of the variables in the plane formed by the two first factorial axes. (◍) Size distribution parameters, (⊘) X-ray parameters, (⊛) infrared parameters, (⊜) parameters obtained by gas adsorption, (●) mechanical parameters of talc-filled polypropylenes.

CsdC2 and *CsdC4*) and the size of the grains as seen by *D50*. The best models obtained by multiple regression are as follows:

$$Eflex = -43.29\,SsL + 486.3\,ESF - 35.98\,1475 - 23.04\,Vmic + 4387$$

$R = 1.00$ with $R(Eflex, SsL) = -0.96$

$$Echoc = 0.33\,D50 + 3.67\,ESF - 0.073\,CsdT2 + 0.056\,CsdT6 - 0.029\,St1 + 18.29$$

$R = 1.00$ with $R(Echoc, D50) = -0.91$

$$HDT = -0.20\,SsL + 0.054\,Pos1000 - 9.123660 - 8.45\,ESF - 0.039\,St1 + 89.79$$

$R = 1.00$ with $R(HDT, SsL) = -0.71$

The models obtained are now usable. They exhibit the tendencies noted in the principal component analysis: the flexural modulus and heat distortion temperature are strongly affected by the shape of the talc particles, whereas the impact strength is mainly influenced by the size of the particles.

3.2.2. Sample 0083

The projection resulting from normalized principal component analysis is presented in Fig. 5. 84% of the statistical information is contained in the two first factorial axes. It shows the same type of patterns as sample 00B. The best models obtained by multiple regression are as follows:

$$Eflex = 23.883420 - 932.9\,Dt + 4.72\,CsdC2 + 70.72\,Vmic + 239.6\,ESF + 472.6$$

$R = 1.00$ with $R(Eflex, 3420) = 0.96$ and $R(Eflex, Dt) = -0.81$

$$Echoc = -0.168\,St0 + 0.012\,CsdC2 + 0.13\,Pos1000 + 1.52\,ESF - 112.9$$

$R = 1.00$ with $R(Echoc, St0) = -0.99$

$$HDT = 4.773677 - 0.12\,CsdC4 + 0.06\,CsdC2 - 0.024\,CsdT2 + 69.1$$

$R = 1.00$ with $R(HDT, 3677) = 0.80$

In this case as well, the models obtained are simple and seem to describe correctly the mechanical characteristics of filled polypropylenes.

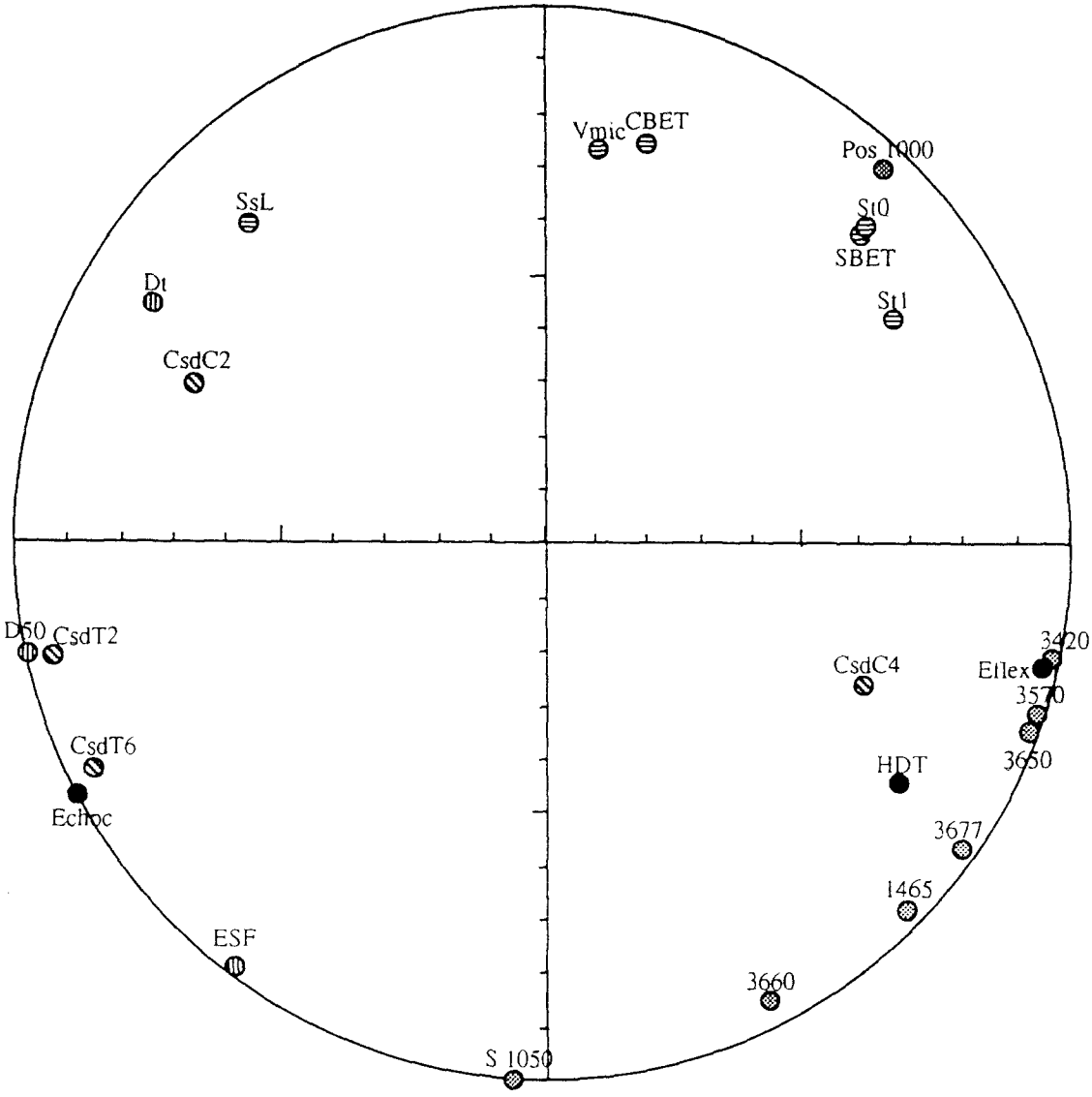


Figure 5 Normalized principal component analysis on talc 0083: projection of the variables in the plane formed by the two first factorial axes. (◍) Size distribution parameters, (⊘) X-ray parameters, (⊛) infrared parameters, (⊜) parameters obtained by gas adsorption, (●) mechanical parameters of talc-filled polypropylenes.

3.2.3. Sample 00C

The projection resulting from normalized principal component analysis is presented in Fig. 6. 75% of the statistical information is contained in the two first factorial axes. It shows the tendencies already observed, i.e. the flexural modulus and the heat distortion temperature are normally correlated with parameters describing the shape of the particles and anti-correlated with the impact strength. This latter characteristic is normally correlated with parameters describing the size of the particles. The best models obtained by multiple regression are as follows:

$$Eflex = 30.28\,1465 - 27.523420 - 10.61\,CsdT2 + 9.58\,CsdC2 - 91.46\,ESF + 6551.7$$

$R = 1.00$ with $R(Eflex, 1465) = 0.87$

$$Echoc = -2.78\,Pos1000 - 0.403570 - 32.32\,Dt - 0.016\,CBET - 7.733660 + 2886.3$$

$R = 1.00$ with $R(Echoc, Pos1000) = -0.80$

$$HDT = -0.693420 - 1.086\,Vmic + 0.046\,SBET + 0.703570 - 0.045\,CsdC2 + 133.5$$

$R = 1.00$ with $R(HDT, 3420) = -0.72$

In the case of chlorite 00C, the quality of the models obtained is still very good. The infrared parameters seem to be more important than in the case of more talqueous ores.

This global modelling study shows that one can obtain good predictive models of the mechanical parameters of talc-filled polypropylenes, provided that a single mineralogical type of sample is used. However, the number of parameters introduced in the models is still too big and prevents their practical use.

3.3. Partial modelling

In all the models a certain number of parameters appear more often than others. They are *3660*, *3570*, *3420*, *1465*, *Pos1000*, *CsdT2*, *CsdC2*, *Vmic*, *St1*, *SsL*, *Dt* and *ESF*. It would be interesting to check the possibility of obtaining models by using only these particular parameters.

For reasons of clarity, the results of this analysis are presented in Table I. The quality of these partial models suggests that it is possible to describe the mechanical behaviour of filled polypropylenes from a knowledge of a few parameters from the fillers. In this

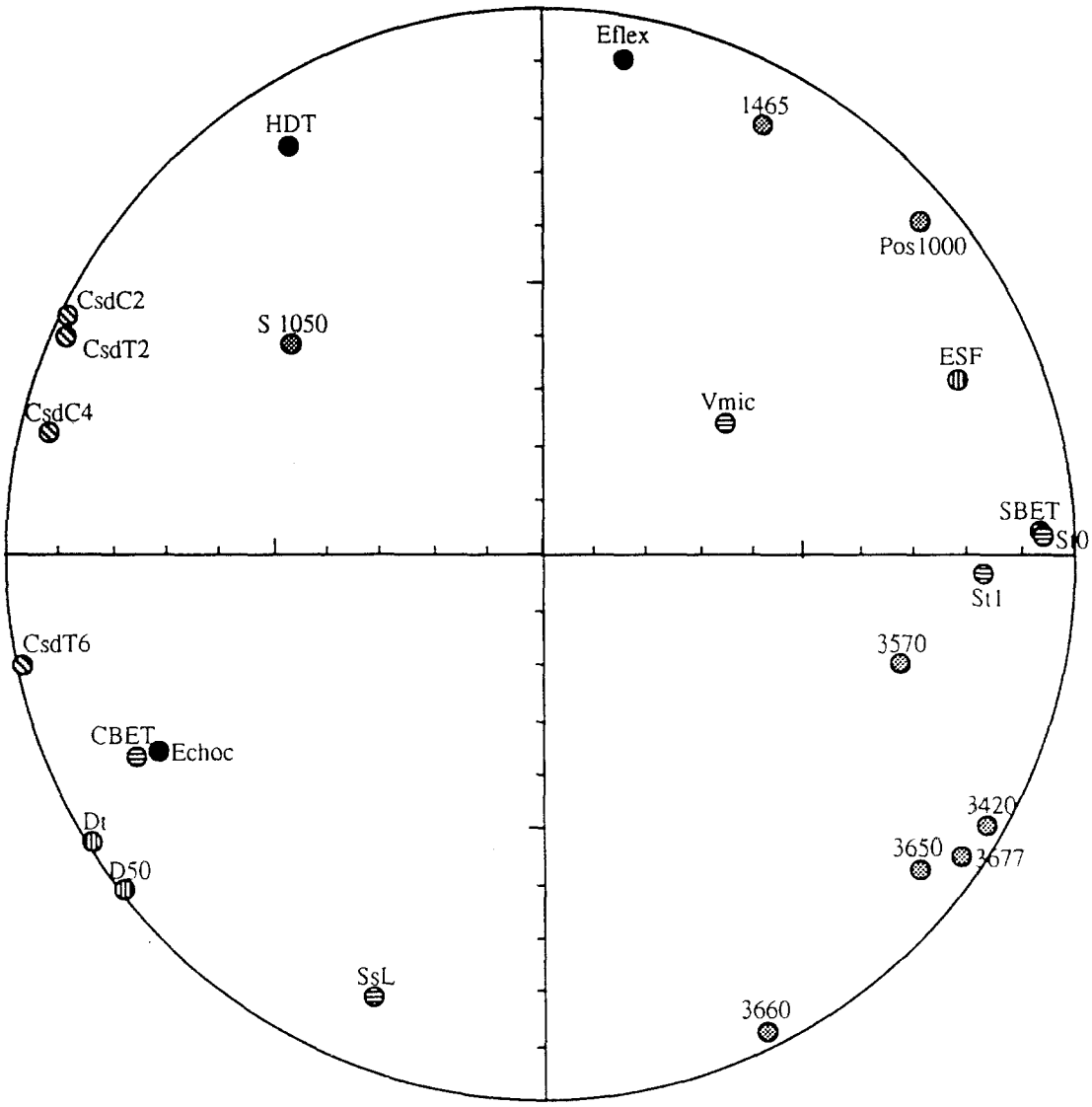


Figure 6 Normalized principal component analysis on chlorite 00C: projection of the variables in the plane formed by the two first factorial axes. (◍) Size distribution parameters, (⊘) X-ray parameters, (⊛) infrared parameters, (⊜) parameters obtained by gas adsorption, (●) mechanical parameters of talc-filled polypropylenes.

TABLE I Parameters of multiple partial linear regressions obtained for partial modelling of the mechanical characteristics of talc-filled polypropylene; for each regression bold characters correspond to the most prominent parameter of the regression

	3660	*3570*	*3420*	*1465*	*Pos1000*	*CsdT2*	*CsdC2*	*Vmic*	*St1*	*SsL*	*Dt*	*ESF*	Constant	*R*
00B														
Eflex				− 35.89				− 23.04		**− 43.29**		+ 438.3	+ 4387	1.00
Echoc			**− 0.069**	+ 0.449				+ 0.507		+ 0.216			+ 9.91	1.00
HDT				− 0.566	**+ 0.230**		− 0.025			− 0.44	+ 22.47		− 126	1.00
0083														
Eflex			**+ 23.88**				+ 4.72	+ 70.72			− 932.9	+ 239.6	+ 472.6	1.00
Echoc					**− 0.182**	+ 0.037		− 0.50		+ 0.071			+ 187.8	1.00
HDT			**+ 4.77**	− 1.17	− 0.85	− 0.050			+ 0.069				+ 935.2	1.00
00C														
Eflex			− 27.52	**+ 30.28**		− 10.61	+ 9.58					− 91.46	+ 6552	1.00
Echoc		− 1.39		+ 0.67	**− 1.76**	− 0.101			− 0.084				+ 1867	1.00
HDT	+ 17.87		**− 0.82**	+ 0.33			− 0.104	+ 1.09					+ 129.4	1.00

TABLE II Parameters of multiple partial linear regressions obtained for "industrial" modelling of the mechanical characteristics of talc-filled polypropylene; for each regression bold characters correspond to the most prominent parameter of the regression

	Pos1000	*CsdT2*	*CsdT6*	*CsdC2*	*CsdC4*	*SBET*	*D50*	*Dt*	*ESF*	Constant	*R*
00B											
Eflex	+ 16.25					− 17.9		**− 4174**	− 687	− 6669	1.00
Echoc		− 0.054	+ 0.041				**− 0.41**		+ 3.07	+ 5.74	0.99
HDT	**+ 0.33**	− 0.39		+ 0.13		− 0.342	− 0.177			− 107.1	1.00
0083											
Eflex	− 33.61		− 5.31	+ 2.61	+ 6.52			**− 103.5**		+ 36398	1.00
Echoc				+ 0.014		**− 0.155**				+ 19.98	1.00
HDT	− 0.98	**− 0.138**			+ 0.102			+ 16.24	− 7.25	+ 1082	1.00
00C											
Eflex	− 40.31					− 9.67	**− 216.3**			+ 45333	0.93
Echoc	**− 0.465**		+ 0.055			+ 0.044				+ 465.9	0.85
HDT	− 1.99			**+ 0.307**	− 0.24		− 3.30			+ 2091	0.93

first partial modelling, we chose to use the most frequently encountered parameters on the basis of the global models. However, it would be much more useful to use parameters easily measurable by an industrial laboratory. We then decided to try to model the different mechanical characteristics of polypropylene from the parameters accessible to the control laboratory of Talcs de Luzenac SA. They are: *Pos1000*, *CsdT2*, *CsdT6*, *CsdC2*, *CsdC4*, *SBET*, *D50*, *Dt* and *ESF*. This would lead to an "industrial" modelling.

In the case of polypropylenes filled with 00B the extension of the lateral faces *SsL* was always an important parameter. It was then necessary to check if that parameter could be modelled by others. The linear regression is the following:

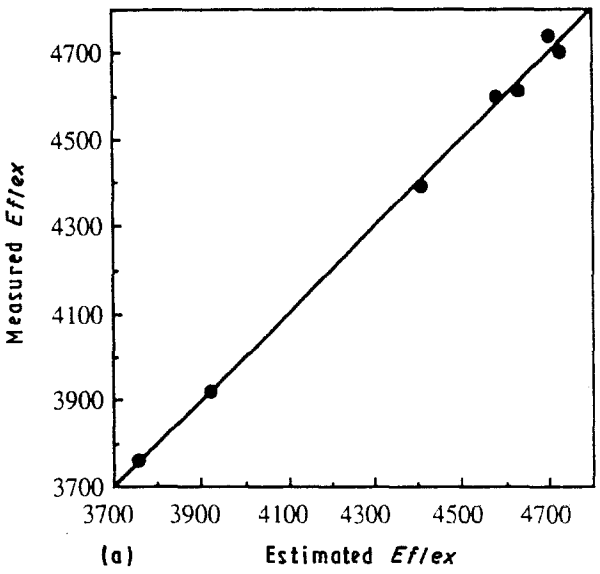
$$SsL = 115.9Dt + 0.45SBET + 27.196ESF - 140.84$$
$$R = 1.00$$

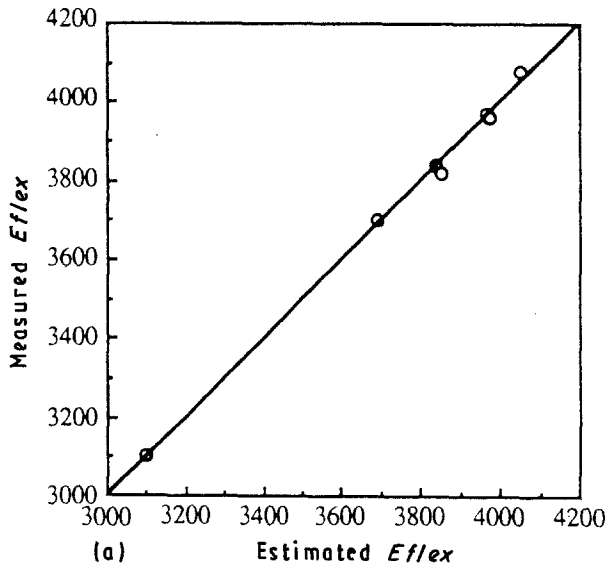
It should then be possible to obtain good estimations of the mechanical parameters of 00B-filled polypropylenes, even without taking into account the extension of lateral faces. For the other samples, talc 0083 and chlorite 00C, this preliminary step is not needed. The best models obtained are presented in Table II.

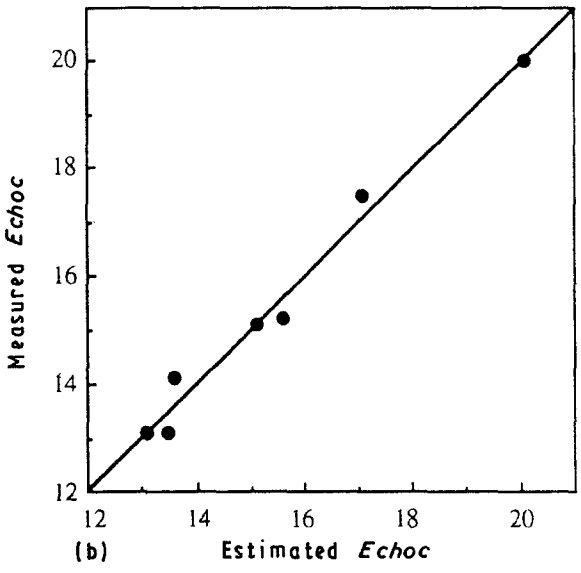
In order to check the quality of these estimations, we have plotted estimated values versus the measured ones. These graphs are presented in Figs 7, 8 and 9 for samples 00B, 0083 and 00C, respectively.

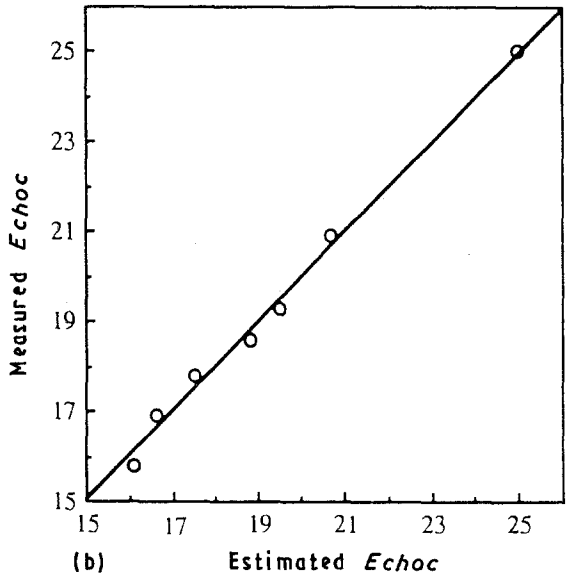
The graphs corresponding to sample 00B (Fig. 7) exhibit an excellent correspondence between the values estimated by the model and the measured values. This is also the case when polypropylenes are filled with talc 0083. Fig. 8 shows an excellent correspondence between the measured values and the estimated ones. This is particularly noteworthy in the case of the heat distortion temperature where the two values, estimated and measured, are strictly the same.

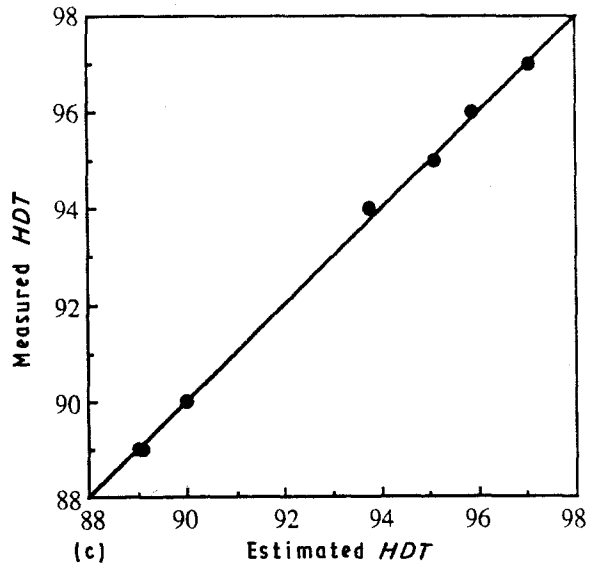
The situation is different when polypropylenes are filled with chlorite 00C. As evidenced by the values of the correlation coefficients (Table II, last column), the models in this case do not appear to be really satisfactory. This is confirmed by Fig. 9. The estimated values are scattered and do not succeed in describing the measured values. This could be due to the presence of outliers in the system. More likely, this can be due to the fact that for the description of a chlorite ore, the use of the infrared parameters appears to be crucial. In the "industrial" model, these parameters have been omitted. It might be possible, though, to find one or











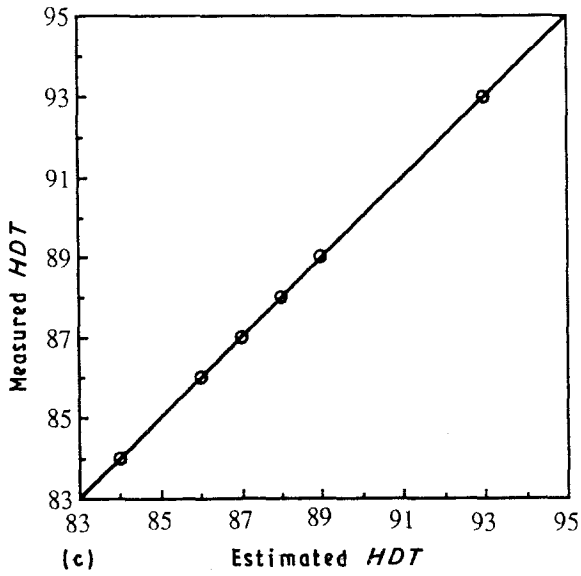
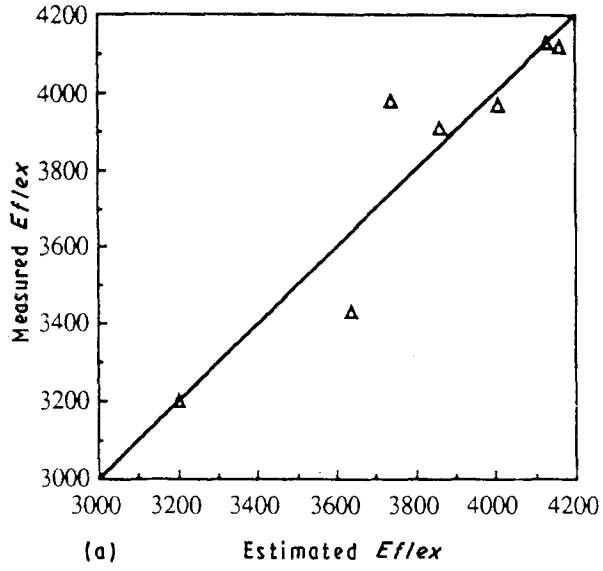
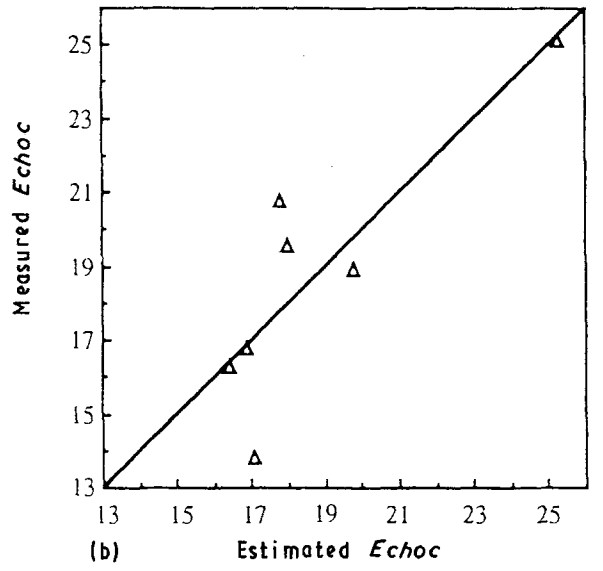


Figure 7 Plot of measured values versus values estimated by the "industrial" model for talc 00B: (a) flexural modulus, (b) shock strength, (c) heat distortion temperature.

Figure 8 Plot of measured values versus values estimated by the "industrial" model for talc 0083: (a) flexural modulus, (b) shock strength, (c) heat distortion temperature.





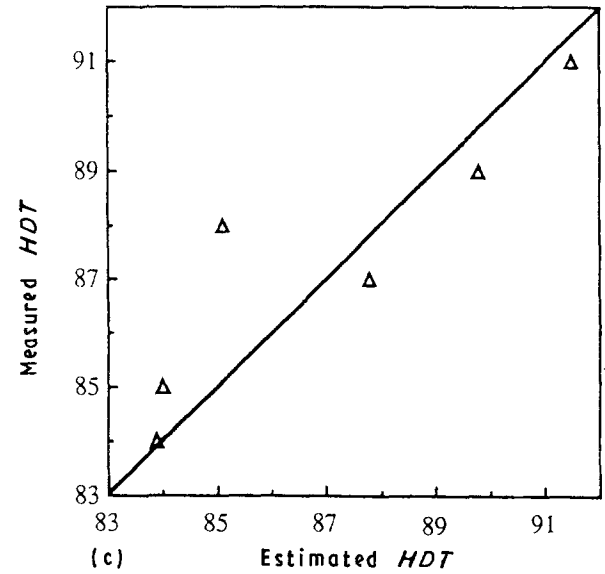


Figure 9 Plot of measured values versus values estimated by the "industrial" model for chlorite 00C: (a) flexural modulus, (b) shock strength, (c) heat distortion temperature.

several substitution parameters which could be more easily measurable while carrying the same information as the infrared parameters. Measurement of the cation exchange capacity or the quantity of mobile magnesium in the sample could maybe fulfill that role. Indeed, these two parameters could indicate, like the infrared parameters, the advance of the dissolution of the brucite-like layer of chlorite, due to grinding [18]. This attack of the brucite layer is very likely to have a significant influence on the mechanical properties of chlorite-filled polypropylenes.

4. Conclusion

We have demonstrated in this paper that, in the case of talqueous ores, it is possible to predict the mechanical properties of talc-filled polypropylenes from the measurement of only a few easily measurable physico-chemical parameters of the filler. In the case of more chloritic ores, the problem is slightly more difficult as infrared parameters, which are difficult to obtain in an industrial environment, are prominent in the models. This difficulty could certainly be ironed out by measuring more easily obtained parameters such as the cation exchange capacity or the amount of leachable magnesium in the sample. The modelling approach should be tested on more filler samples in order to prove more definitely its viability at an industrial level.

The statistical method developed in this paper yields some classical correlations between fillers and composites such as the importance of the aspect ratio or the particle size. It also shows some correlations between the mechanical properties of talc-filled polypropylenes (keeping the mineralogical composition constant) and other physico-chemical parameters, such as the crystallinity of the samples. Even if caution should be used when trying to interpret the physical meaning of correlations obtained by a statistical analysis, these results suggest, however, complex mechanisms that should be studied more thoroughly.

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