JOURNAL OF MATERIALS SCIENCE 25 (1990) 5109-5117

Grinding of muscovite: influence of the grinding medium

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Muscovite was ground in water, alkaline chloride solutions, methanol and toluene. The influence of the grinding medium was investigated using several methods, in particular by electron microscopy. It was found that the addition of lithium ions in aqueous media or NH_3 to methanol facilitates the breakdown of the muscovite structure. The results are explained supposing that water or methanol form lubricating films on the mineral surface, the lubricating properties of both liquids being lost when a hydrogen-bond disrupting agent (Li^+, NH_3) is present in the grinding medium.

1. Introduction

Minerals such as silica and calcium carbonate, but also clays like kaolin, sepiolite, talc and mica have found increasing use as fillers for thermosetting resins and, more and more, for important technical thermoplastics like polypropylene. Polypropylene is largely employed in the automotive industry for the manufacturing of instrument panels, seats, bumpers, etc., allowing a significant weight reduction accompanied by a valuable reduction of the fuel consumption of cars.

The incorporation of mica, particularly muscovite, into polymer matrices leads to the production of materials which, owing to the plate-like morphology of the mica particles, exhibit a very pleasant surface finish. Among the main advantages of the use of mica worth stressing is the enhancement of thermal properties of mica-filled polypropylene matrices. The modulus is significantly increased as are the dielectric properties, as expected, but mica plates also give a protective screen against ultraviolet radiation, i.e. a protection against premature ageing of the polymer composite.

Mica tends to replace in part or totally, the glass fibre in its major applications. However, the main drawback of composites containing mica particles is their poor impact strength. Adequate surface treatments of the mica particles largely overcome this difficulty [1-3].

In order to achieve optimum performance, mica particles must meet a number of conditions. Firstly, particles should have small dimensions in order to enlarge the particle/polymer interface. Secondly, their shape factor, i.e. the ratio between diameter and thickness, is important, to make the best advantage of the plate-like structure of the mica. Thirdly, the distribution of the particle dimensions should be uniform in order to avoid zones of inhomogeneity and hence weakness, in the polymer matrix. Finally, the surface properties should be adequate for optimum particle dispersion and interaction with the matrix.

Mica particles with more or less these characteristics must be prepared by grinding, either in the dry state or in the presence of water.

The object of this study was to demonstrate the pronounced influence of the grinding medium on the shape and structure of the ground mineral. The surface properties of the ground mica have been described elsewhere [4].

2. Experimental procedure

2.1. Mica

Mica from Bihar (India) had the elemental composition shown in Table I. X-ray diffraction indicated that the structure of the sample was muscovite of rather high purity.

2.2. Grinding apparatus

Muscovite was cut into small pieces using rotating knives. These pieces were sieved to obtain particles in the 1 to 2 mm diameter range. Grinding was performed in an attritor consisting of a thermostatted stainless steel cylinder, 6 cm diameter and 20 cm high, which was equipped with a stirrer consisting of five cylindrical blades, 1.2 cm diameter and spaced 1.5 cm from the end of the stirrer. About 1600 stainless steel balls of 2 mm diameter, were introduced into the cylinder with 10 g mica dispersed in 250 ml liquid. This medium was rotated at 285 runs/min, at 15° C. After grinding, the mica was recovered by filtration, washed with distilled water and dried at 100° C before analysis. Grinding experiments were conducted in distilled

0022-2461/90 $03.00 + .12

TABLE I Elemental analysis of muscovite ground in aqueous solutions

	Grinding conditions			
	Initial, 0 h	H_2O, 24 h	H_2O (+ KCl), 24 h	H_2O (+ LiCl), 24 h
SiO_2	46.65	44.16	38.70	30.03
Al_2O_3	34.68	27.95	24.84	19.64
K_2O	9.74	8.93	11.43	4.01
$\left.\begin{matrix}SiO_2\\Al_2O_3\end{matrix}\right\}$	1.34	1.33	1.31	1.52
$\left.\begin{matrix}Al_2O_3\\K_2O\end{matrix}\right\}$	3.56	3.71	2.57	4.89
Fe_2O_3	2.32	3.10	5.53	13.91
Na_2O	0.73	0.72	0.40	0.41
MgO	0.33	0.60	0.26	0.25
TiO_2	0.28	0.28	0.15	0.15
P_2O_5	0.02	0.03	0.08	0.21
ΔW(%) (1050° C)	5.26	8.61	12.57	25.81
Total	100.05	99.97	98.64	94.49

water to which KCl or LiCl were eventually added, in methanol and in toluene.

2.3. Specific surface areas

The specific surface areas were measured by nitrogen adsorption, at liquid nitrogen temperature, using a volumetric apparatus (Micromeritics 2100 D, from Coultronics). The results were reproducible within 10% of error.

2.4. Infrared spectroscopy

Infrared spectra were recorded using a Perkin Elmer 580 B spectrometer, in the transmission mode through KBr discs containing 0.5% by weight of mica.

2.5. Electron microscopy

Ground muscovite samples were dispersed, using ultrasound, in toluene. A drop of the diluted suspension was deposited on a grid covered with a collodion-carbon membrane. Then the solvent was evaporated and the grid examined by transmission electron microscopy and selected-area electron diffraction (SAD) with a JEM 100 B microscope. High-resolution pictures were obtained using the phase-contrast mode. Scanning electron microscopy was also used with the JEM 100 B scanning attachment.

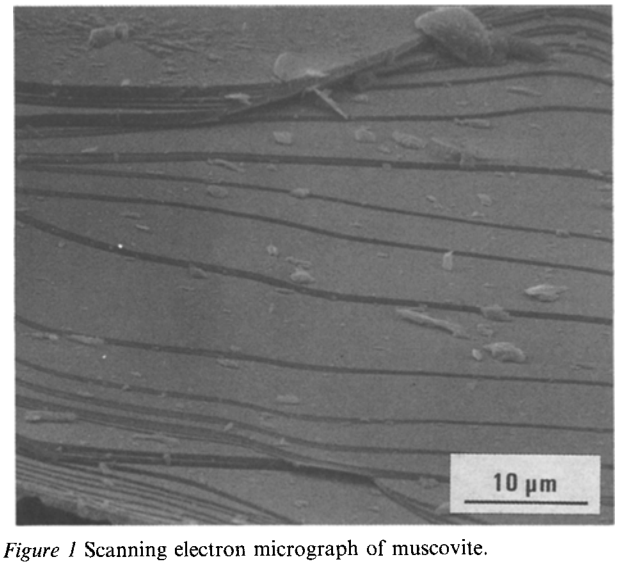

Figure 1 Scanning electron micrograph of muscovite.

2.6. Chemical attack

The ground samples were submitted to an acid (HCl 1/1) leaching, at 25° C, over 24 h. The weight loss was measured gravimetrically.

2.7. Cation exchange capacity

The cation exchange (NH_4^+) capacity of the muscovite was determined according to classical procedures [5] for clay materials: 1 g mica was treated, for 1 h with a 0.1 N NH_4Cl solution. After centrifugation, this treatment was repeated three times. Finally, the cation exchanged sample was purified by repeated water washing, and dried at 100° C. The NH_4^+ uptake was measured using the Kjeldahl method after mineralization (H_2SO_4 + H_3BO_3) of the mica.

2.8. X-ray diffraction

X-ray diffraction patterns were recorded, using Cu$K\alpha$ radiation (Philips Spectrometer), on muscovite powders.

3. Results

3.1. Grinding in aqueous media

3.1.1. Elemental composition of ground muscovite

Fig. 1 illustrates the plate-like morphology of muscovite. Muscovite belongs to the group of phyllosilicates having an interlaminar distance of 1.0 nm. The elemental layer is formed by the superposition of tetrahedral

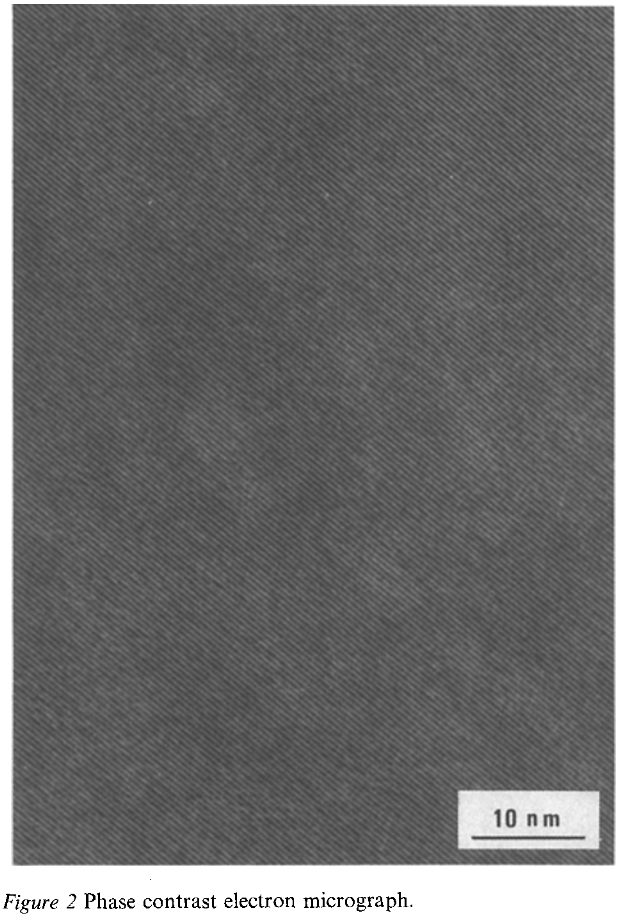

Figure 2 Phase contrast electron micrograph.

SiO_4 sheets and octahedral sheets containing hexacoordinated Al^{3+} ions. In the tetrahedral sheet, one Si^{4+} out of four is replaced by Al^{3+} giving rise to a total negative layer charge. This negative charge is compensated by a K^+ cation located between two layers. Fig. 2 is a high-resolution electron micrograph illustrating the very regular array of the layers separated by 1.0 nm. When such a structure is cleaved, K^+ ions are freed and, in the presence of water, are replaced by protons; i.e. the water medium becomes basic. To examine the eventual influence of K^+ ions during the grinding process, experiments were performed using a dilute solution of KCl as the grinding medium. For comparison, other experiments were carried out with LiCl solution, because Li^+, in the dry state, is the smallest cation.

Table I shows the results of the elemental analysis of mica samples before and after 24 h grinding in various aqueous media. It is seen that 24 h grinding in water does not fundamentally change the composition of muscovite. The addition of KCl seems to affect somewhat the course of grinding, whereas a dramatic modification occurred when mica was ground in the presence of Li^+ ions. This change is most apparent when comparing the ratios of the main components of muscovite, i.e. Al_2O_3 and K_2O. It is also seen that the ferrous impurities are increased after comminution, the iron obviously coming from the stainless steel balls. Table I also indicates the weight loss, ΔW, of the samples heated to 1050° C. The slight increase observed between the initial muscovite and the sample ground in pure water can be easily explained because grinding increases the specific surface area, and thus the lateral surface area of the mica plates where the hydroxyl groups (Si–OH, Al–OH) are located. Heating will cause the condensation of these groups and a loss of H_2O. The very high value of ΔW of the sample ground in LiCl solution is possibly not accounted for by the same dehydroxylation mechanism.

3.1.2. Structure of ground muscovite samples

X-ray diffraction allows the eventual modification of the muscovite structure to be followed at least qualitatively. Indeed it is seen that the intensity of some peaks is diminished as expected from the thinning of the mica plates, but the very striking indication is that the sample ground in the presence of Li^+ has become practically amorphous!

TABLE II Ions present in the grinding solutions after grinding in various aqueous media

	Grinding time (h)	Al^{3+} (p.p.m.)	K^+ (p.p.m.)	Si^{4+} (p.p.m.)
H_2O	1	–	–	–
	2	–	–	–
	3	–	1.5	–
H_2O + KCl	1	–	–	–
(10^{-3}M)	2	–	–	–
	3	–	–	–
H_2O + LiCl	1	0.7	1.5	–
(10^{-3}M)	2	1.5	1.5	–
	3	3.0	1.5	3

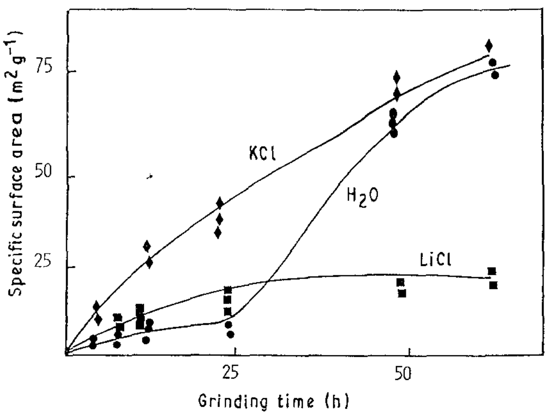

Figure 3 Variation of the specific surface area of muscovite upon grinding in aqueous media.

Analysis of the grinding solution by classical flame ionization spectrometry indicated that the presence of Li^+ causes the breakdown of the muscovite structure, because Al^{3+} ions become detectable after only 1 h grinding (Table II), whereas the presence of such ions could not be demonstrated in other cases, even after prolonged (3 h) treatment.

3.1.3. Specific surface area of ground muscovite samples

Fig. 3 shows the results of the specific surface area determinations of muscovite ground in the various conditions. In pure water, i.e. after a given time in alkaline solution, because K^+ ions are liberated and exchanged by H^+ during the cleavage and fracture of the mica platelets, the kinetic curve is rather complex, pointing to several grinding mechanisms. There is a sudden acceleration after about 25 h treatment. Finally, the curve joins that corresponding to grinding in the medium to which KCl was initially added. Apparently then, the presence of K^+ ions facilitates grinding. Possibly K^+ acts like a wedge which enters the border of the mica plate in a way proposed to explain the weathering of muscovite [6]. Indeed qualitative electron microscopic observations are in favour of such an hypothesis: platelets are thinner when mica is ground in the presence of KCl than in water. Obviously, this was observed only at the beginning of the treatment because later the grinding course was too complex to be analysed by electron microscopy.

On this graph, it can also be noted that the addition of Li^+ ions modifies dramatically the course of the grinding experiment. It is seen that the specific surface areas of the ground samples remain at a relatively low value even for extended grinding times. In fact, one would expect, because the hydrated Li^+ ion is much larger than the K^+ ion, that Li^+ would be a passive ion. But this is far from being the case.

3.1.4. Ion exchange capacities

Table III shows the values of the ion exchange capacities of muscovite samples comminuted under various experimental conditions. Ion exchange capacity increases as expected because the lateral surface area, where exchangeable ions are located, is significantly increased. However, this is not the case for the residue of the grinding experiment performed in the presence of Li^+. Further, when analysing the loss of K^+ in the

TABLE III Ion exchange capacities of muscovite after grinding in various aqueous media

	t (h)	meq/100 g	S(m^2/g)	meq/m^2 (× 100)	Loss of K^+ (%)
H_2O	12	13.5	5	2.7	2.5
	36	7.0	48	1.0	3.9
	72	56.0	90	0.6	4.9
H_2O + KCl	12	50.0	27	1.9	4.2
	36	55.0	48	1.1	5.0
	72	63.0	88	0.7	5.2
H_2O + LiCl	12	5.0	11	0.5	2.2
	36	6.1	17	0.5	6.1
	72	10.0	21	0.5	10.0

ground samples, it is clear that the samples ground in LiCl solution are the most perturbed.

It is also interesting to note that the samples ground for 36 h in water or in water + KCl have comparable surface areas, but very different ion exchange capacities, confirming the fact that grinding is also very sensitive to the presence of K^+ ions. From this result, it may be concluded that the lateral surface area of mica ground in the presence of KCl is significantly higher than that of mica treated in water. If so, because polar groups, essentially hydroxyl groups, are located on the peripheral surface, it is expected that the weight loss due to elimination of physically adsorbed water and of water coming from the thermal condensation of hydroxyl groups, should be significantly different when comparing samples either ground in water or in the presence of KCl. The results are shown in Fig. 4, the weight loss being monitored by thermogravimetry. Samples having quite different total surface areas, 27 and 48 $m^2 g^{-1}$, respectively, nevertheless lose the same weight upon heating: this is exactly what the preceding experiments suggested.

3.1.5. Infrared spectroscopy

Still further evidence of the important role played by Li^+ ions during the course of grinding is provided by infrared spectroscopy. Particularly interesting are the spectral regions corresponding to the infrared absorption of structural hydroxyl groups (3635 cm^{-1}) and to complex deformation vibrations of the silicate skeleton from 1100 to 200 cm^{-1}.

When comparing the infrared spectra (Fig. 5) of the initial sample and of muscovite ground for 12 h in LiCl solution, major differences are observed. The peak corresponding to the hydroxyl (fine structure) of the silicate has practically vanished, whereas a broad peak due to strongly bonded water also appears in the 1600 cm^{-1} region. Muscovite samples ground either in water or in KCl solution behave differently (Fig. 6) because even after 60 d grinding, the fine structure of silicate is still present even though the amount of strongly adsorbed water becomes more significant.

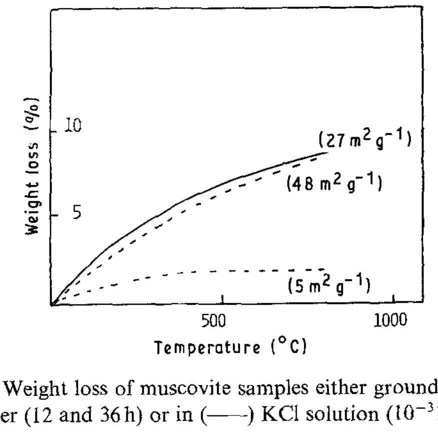

Figure 4 Weight loss of muscovite samples either ground in (– – –) pure water (12 and 36 h) or in (——) KCl solution (10^{-3}M) (12 h).

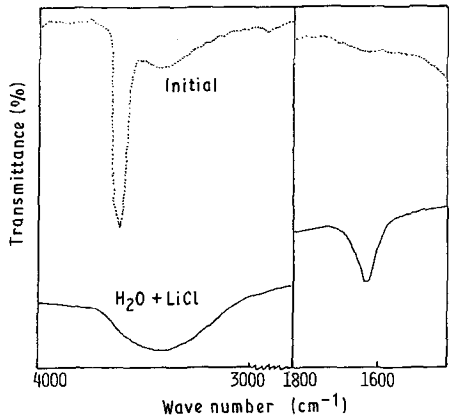

Figure 5 Infrared spectroscopy of initial muscovite and of a sample ground in LiCl solution.

3.1.6. Electron microscopy

Although a given sample produces various images and SAD patterns, thorough observations allow demonstration that the grinding process is most dependent on the nature of the liquid environment. For instance, Fig. 7 illustrates the preserved flake-like aspect of the muscovite ground 24 h in water. The SAD pattern confirms that the crystalline structure has been retained, whereas some phase-contrast micrographs indicate that larger distortions are probably occurring.

Electron microscopy on mica submitted to attrition in the presence of LiCl solution show larger alterations to the morphology and the crystalline structure.

Before attempting to understand the specific action of lithium ions on the comminution process of muscovite, experiments were made in the presence of other ions such as Cs^+, Ca^{2+}, etc., but none of these caused such a dramatic change in the grinding course as did Li^+, which definitely must have some peculiar property. Further, a series of grinding experiments was performed in organic media: toluene and methanol.

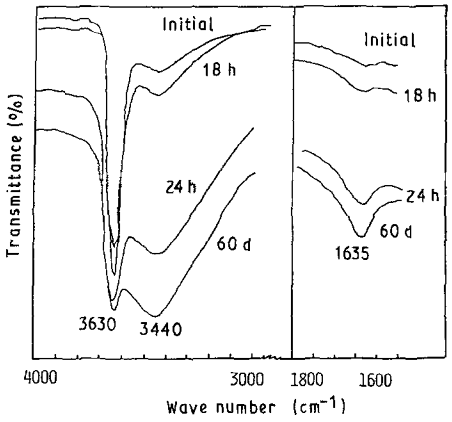

Figure 6 Infrared spectroscopy of initial muscovite and of muscovite samples ground, for increasing times, in KCl solution.

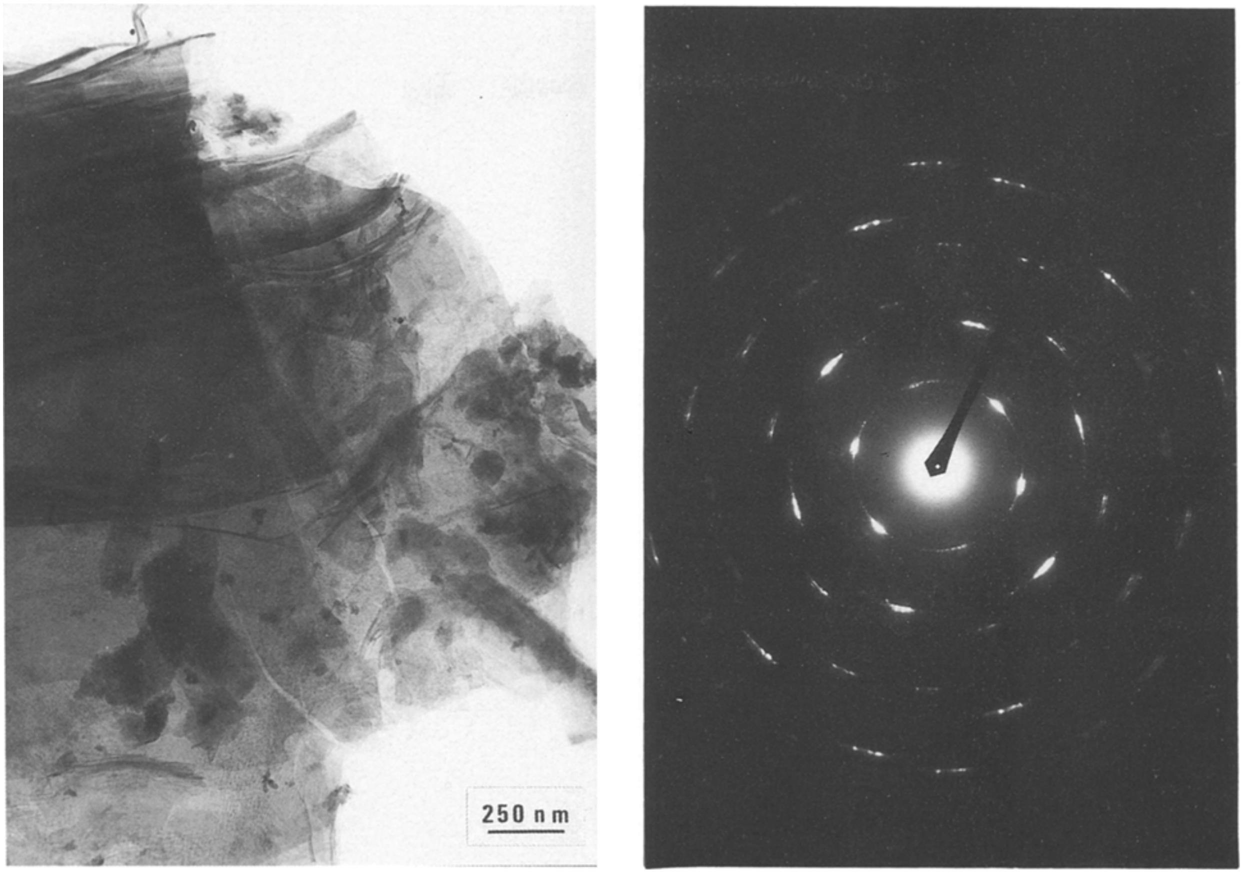

Figure 7 Transmission electron micrographs of muscovite ground for 24 h in water.

3.2. Grinding in organic media

Muscovite was treated in methanol or in toluene following exactly the procedure worked out previously. The ground samples were submitted to similar analysis as before, but only the major results will be presented in this instance.

3.2.1 Specific surface area

Fig. 8 compares the specific surface areas of samples ground in toluene or in methanol. Again, a very striking observation may be made as before [7] when looking at the comminution of asbestos: in methanol, the muscovite samples attain very high values of surface area, whereas in toluene, after a significant initial increase during the first hours of grinding, the specific surface area drops very rapidly. Such a behaviour is often observed during a grinding process and is attributed to the reagglomeration of the fine particles. However, this raises the question: why is it so for toluene and not for methanol?

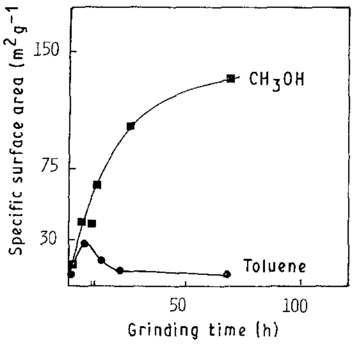

Figure 8 Variation of the specific surface area of muscovite upon grinding in organic media.

3.2.2. Infrared spectroscopy

The infrared spectrograms of muscovite samples either ground in methanol or in toluene are presented in Fig. 9. As mentioned earlier, the spectral region between 200 and 1100 cm^{-1} contains much information. The adsorption band at 1025 cm^{-1} corresponds to deformation of the silica tetrahedra, the band at 930 cm^{-1} is relative to Al–OH groups, whereas that at 798 cm^{-1} is attributed to the infrared absorption of Al–O groups. The muscovite sample ground in CH$_3$OH shows these infrared absorption characteristics, whereas that treated in toluene hardly shows absorption bands at all. Possibly, its structure is destroyed: a conclusion which is verified by X-ray

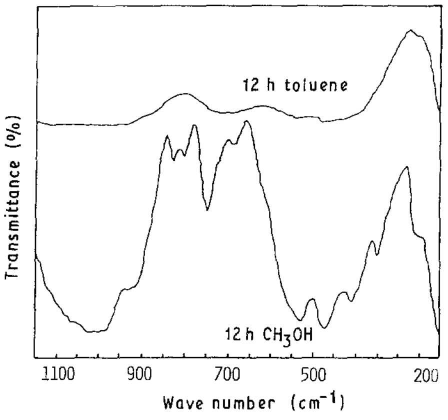

Figure 9 Infrared spectroscopy of muscovite ground for 12 h in toluene or in methanol.

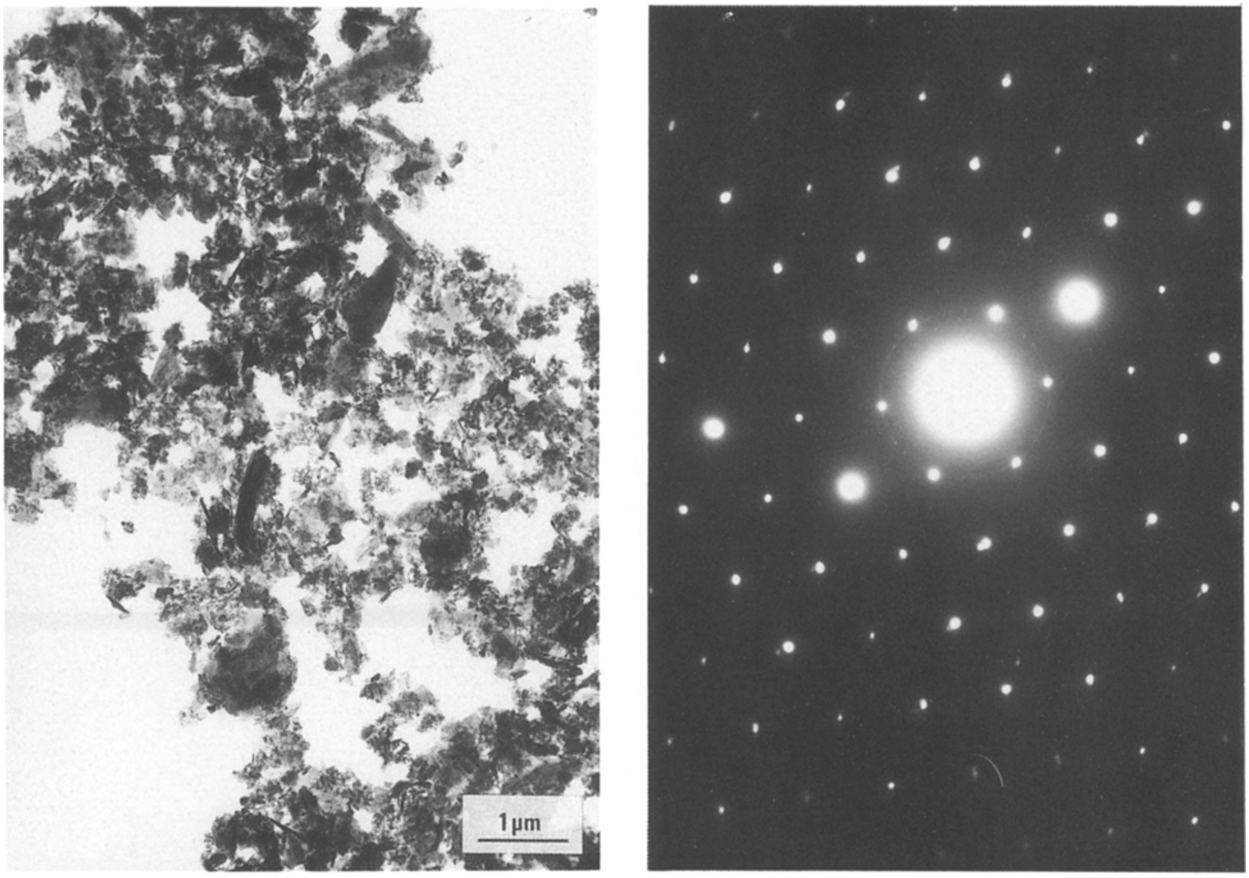

Figure 10 Transmission electron micrographs of muscovite ground for 24 h in methanol.

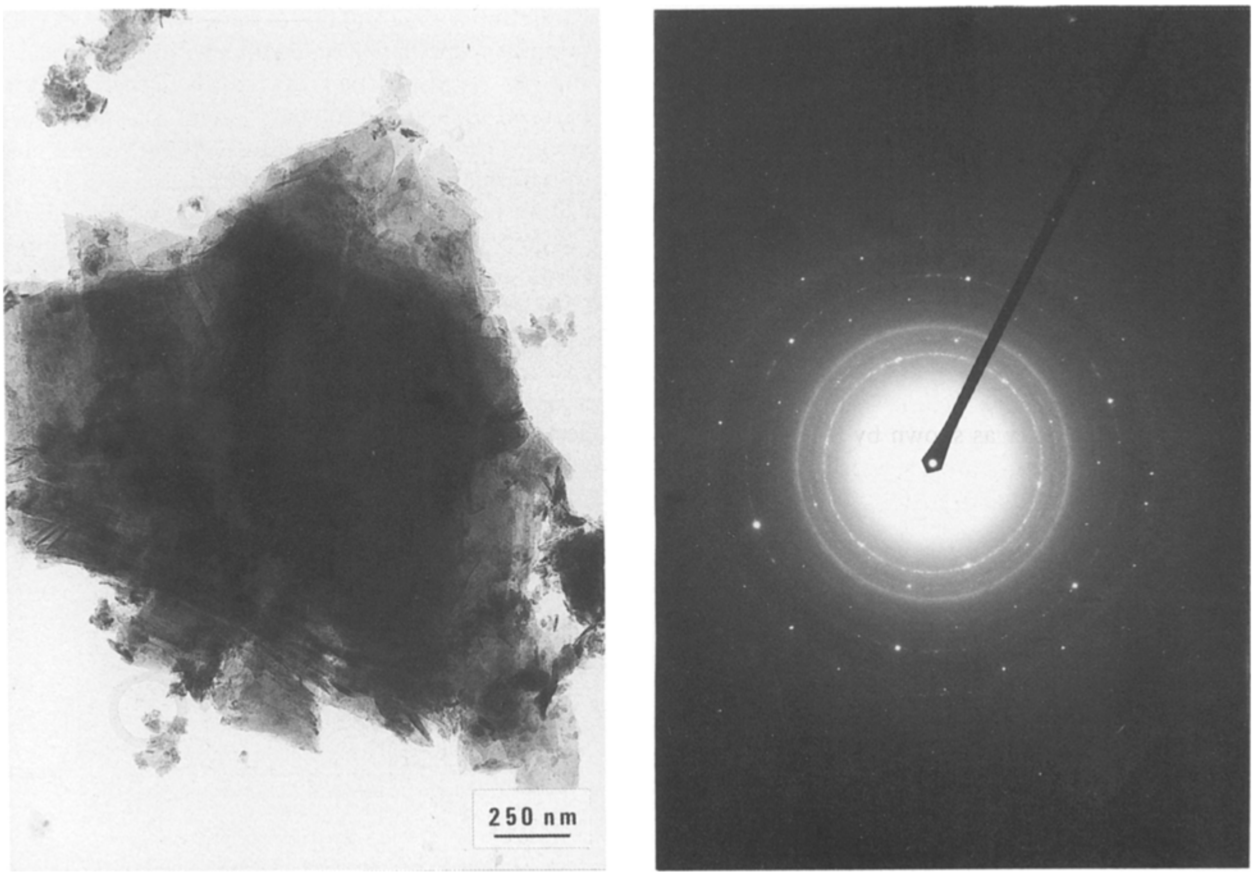

Figure 11 Transmission electron micrographs of muscovite ground for 72 h in methanol.

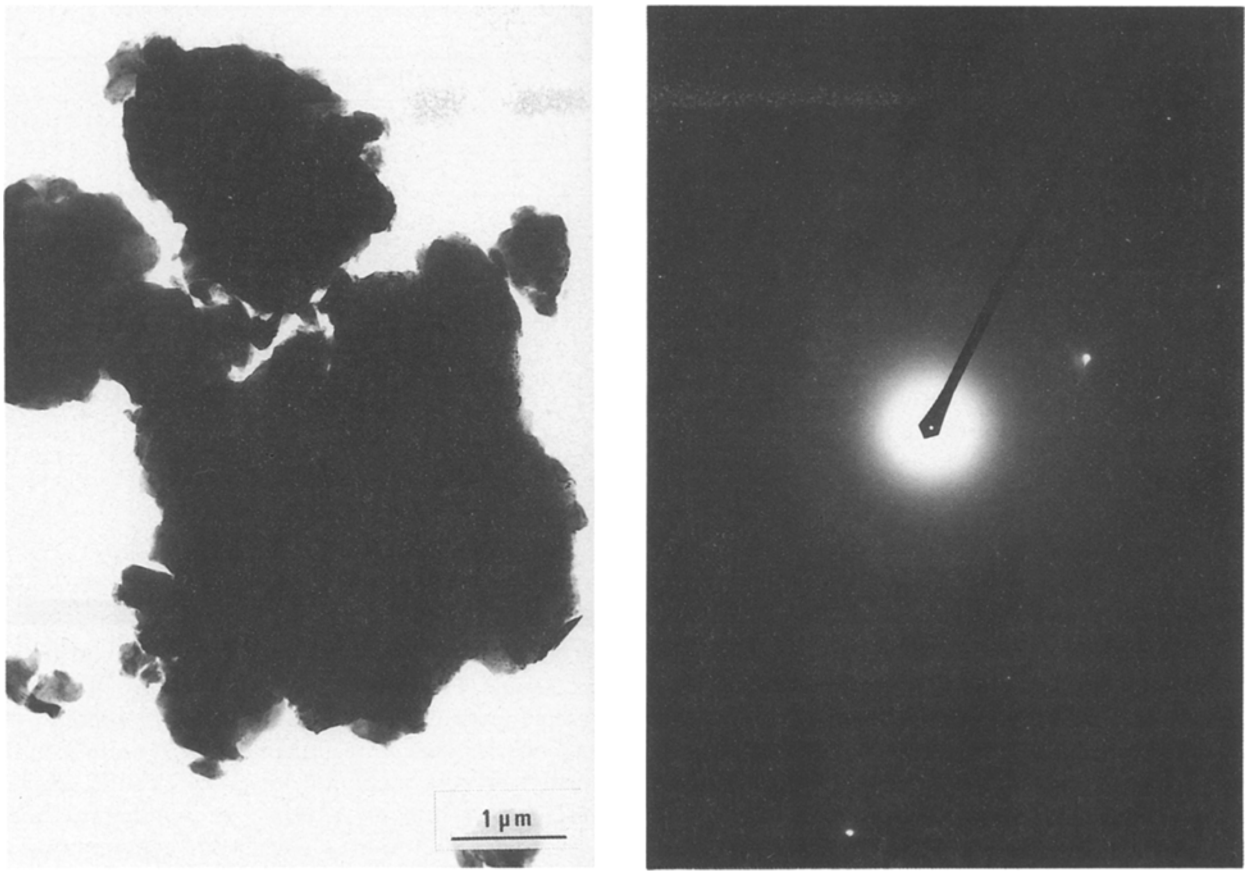

Figure 12 Transmission electron micrographs of the residue after grinding muscovite for 72 h in toluene.

diffractometry, and also as will be seen, by electron microscopy.

3.2.3. Electron microscopy

Fig. 10 illustrates the morphology of muscovite, ground for 24 h in methanol. The plate-like structure, even of the very tiny particles, can be easily recognized. Selected-area electron diffraction confirms the unaltered muscovite structure of the ground material. High-resolution electron microscopy shows that the crystalline structure is entirely preserved.

Fig. 11 shows the mica sample, but after 72 h grinding, it is seen that the major characteristics of the mineral are maintained after such a severe treatment.

When operating under the same experimental conditions, but in a toluene suspension, the grinding residue resembles a mass of agglomerated particles having lost their crystallinity as shown by SAD (Fig. 12).

In addition to X-ray and electron diffractometries, the amorphization of muscovite may be demonstrated by a chemical method.

3.2.4. Chemical attack

The treatment of muscovite with a hot concentrated solution of HCl (1/1) causes an attack on the mineral. The rate of attack is proportional to the specific surface area, but is dependent also on the degree of crystalline perfection of muscovite.

Fig. 13 shows the results obtained with initial muscovite, and samples treated in methanol and in toluene. Obviously, and as expected, the sample ground in toluene is also the most sensitive to the chemical alteration again demonstrating the major influence of the grinding medium on the grinding process.

4. Discussion

This study has highlighted the importance of the grinding medium which largely determines the size, structure and, as shown elsewhere [3], the surface properties of muscovite samples. Further, quite unexpected behaviour was observed both in aqueous and in organic media. Questions arise such as: why do Li^+ ions promote comminution and amorphization? Why do water and methanol avoid amorphization? Why does toluene lead to agglomeration and amorphization? These questions may now be answered.

Agglomeration in organic media is often explained by the absence of particle stabilizing processes in organic media compared to the mechanisms of, say, electrical stabilization in aqueous media which prevents the formation of larger blocks. This possibly explains why muscovite undergoes amorphization in toluene.

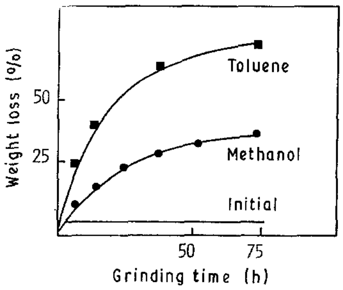

Figure 13 Weight loss during HCl-attack of muscovite samples ground in various conditions.

Even in methanol, there is no particular reason why mica particles should be better dispersed and why the muscovite should be protected against amorphization, as was the case with grinding in water. Yet muscovite behaves similarly in water and methanol!

The same question may be postulated but in other terms. What are the parent properties of water and methanol because both media preserve the crystalline structure of mica? An obvious answer is the fact that both liquids enter into strong hydrogen bonding, i.e. both liquids are highly associated.

It is known [8] that water molecules on the surface of mineral oxides, and particularly on the surface of clays, adopt special conformations. In other terms, the properties of water molecules, which are influenced by very high electrical fields near the solid surface, are different from those of bulk water. Consequently, the water film also possesses special mechanical properties, the idea being that this water film on the muscovite surface may act as a lubricant, i.e. by changing the stress transmission and stress distribution on the mica surface submitted to principally shearing forces in the attritor. A non-uniform film or a disruption of the film continuity would cause the loss of the lubricating properties.

Li^+ ions have hydrogen-bond rupturing properties. Thus, it may be postulated that the addition of Li^+ ions to the water medium disrupts the homogeneity of the water film on the mica surface, erasing its lubricating properties and finally causing the breakdown of the structure.

In this respect methanol shows much similarity with water and hence we should observe during grinding of muscovite similar effects after the addition of Li^+ ions.

TABLE IV Elemental analysis of muscovite ground in methanol

	Grinding conditions		
	Initial, 0 h	CH_3OH, 24 h	CH_3OH (+ LiCl), 12 h
SiO_2	46.65	37.24	32.18
Al_2O_3	34.68	27.95	24.84
K_2O	9.74	8.08	4.48
SiO_2 Al_2O_3	1.34	1.52	1.29
Al_2O_3 K_2O	3.56	4.89	5.54
Fe_2O_3	2.32	10.64	3.18
Na_2O	0.73	0.60	0.34
MgO	0.33	0.35	0.28
TiO_2	0.28	0.25	0.19
P_2O_5	0.02	0.14	0.04
ΔW(%)	5.26	10.13	29.33
Total	100.05	95.49	94.49

This is indeed shown by the results of elemental analysis (Table IV). The chemical composition of the sample ground for only 12 h, but in the presence of Li^+ ions, is much more altered than that of the sample treated in pure methanol for 24 h. Yet the specific surface areas are only 12 $m^2 g^{-1}$ after adding Li^+ ions to CH_3OH, and 68 $m^2 g^{-1}$ when the comminution is carried out again over 12 h, but in pure methanol. This difference in surface areas possibly indicates an agglomeration process, promoted by Li^+ ions. Indeed, Fig. 14 points to such a process and shows particle agglomerates which, as demonstrated by electron diffraction, have almost lost their structure.

Hence the role of Li^+ ions now seems more

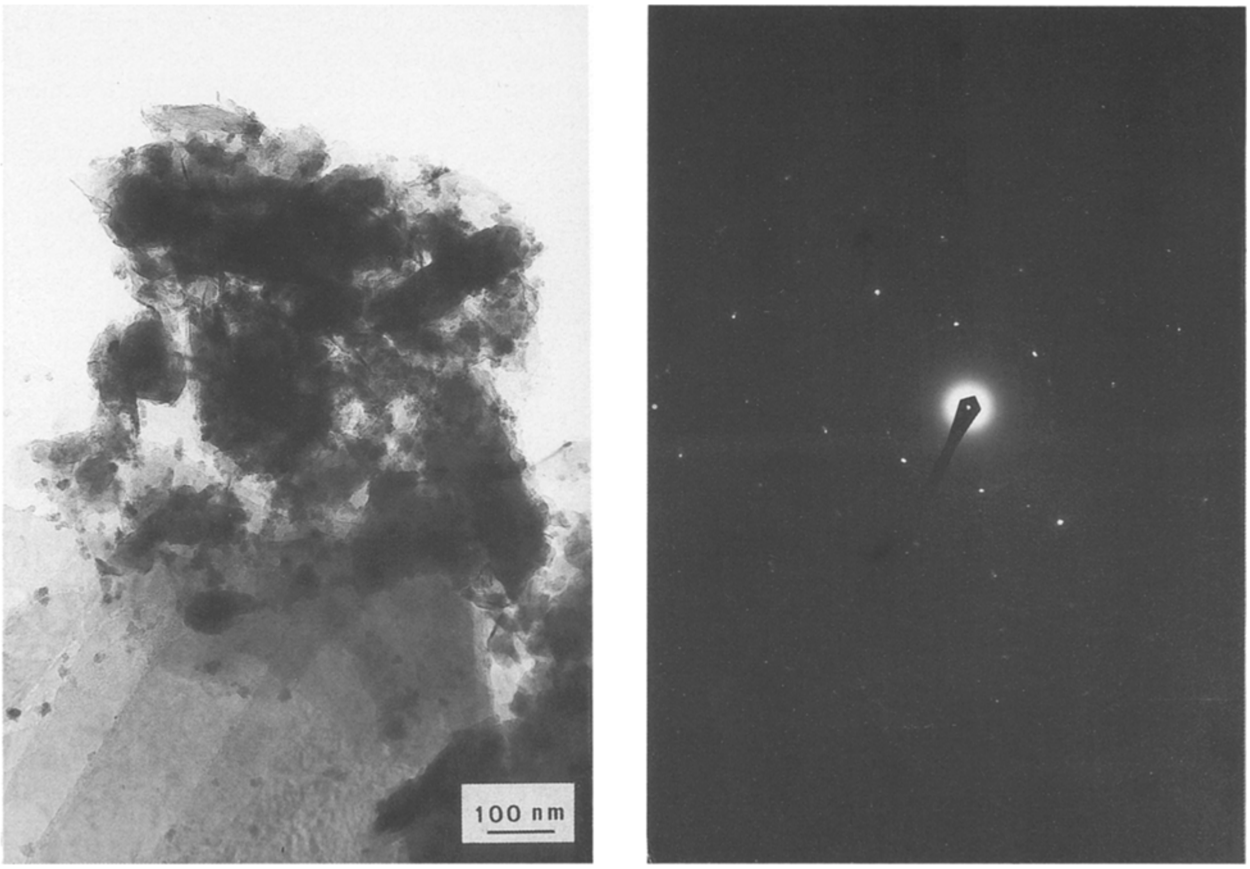

Figure 14 Transmission electron micrograph of muscovite ground for 12 h in methanol in the presence of Li^+ ions.

apparent: Li^+ ions, on approaching the muscovite surface, change the properties of the adsorbed water or methanol film. Possibly, the film is disrupted and its lubricating action is thus lost.

Still further evidence of the intervention of hydrogen-bond breaking agents is obtained using a different hydrogen-bond breaking agent, i.e. when studying the influence of dry ammonia added to methanol. Indeed, NH_3 is known to be a very effective hydrogen-bond rupture agent. The dramatic influence of NH_3 is shown using the same methods as employed previously for grinding with LiCl methanol solution. For instance, the specific surface area of the muscovite ground for 12 h is $13\,m^2\,g^{-1}$, a value much lower than that recorded when grinding in pure methanol ($68\,m^2\,g^{-1}$).

5. Conclusion

This study has confirmed that grinding is far from being an easy research subject. The nature of the mineral to be ground, the grinding machine (ball milling [9] instead of attrition), the grinding medium, etc., are variables which should be considered when studying the grinding phenomena. It is our opinion that progress will only be made when scientists from various horizons pool their knowledge. Indeed, it is not possible to assemble under one discipline all the required competences in physicochemistry of solid surfaces, mechanics, clay science, etc.

Further, grinding is an important industrial operation which consumes much energy, because only about 10% of the energy input is used for comminution. Energy saving and the preparation of even more adequate divided solids would certainly result from a more scientific approach to the grinding phenomenon.

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Received 12 June
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