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Preparation of RuO_2 – silica gel composite microspheres from silicon ethoxide complex dispersion

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A suspension polymerization method was modified for producing composite microspheres of silica gel or silica glass coated by a layer of fine RuO_2 particles. Pre-hydrolysed silicon tetraethoxide (TEOS) was dispersed into a mixed medium comprising cyclohexane and cyclohexanol or cyclohexane and cyclohexanone with pre-dispersed RuO_2 powders. The rate of gelation of TEOS sensitively increased with increasing content of alcohol or ketone in the dispersing medium. Faster gelation brought about smaller composite particles. Better dispersion of RuO_2 in cyclohexanone containing medium resulted in the better coating of RuO_2.

1. Introduction

State of ordering of the second phase in the composite materials has a strong influence on their properties. Uniformity of the dispersion is not always an ideal goal of the materials' design. Instead, advantage is often gained when the second phase orders itself with respect to the first one [1, 2]. One of the present authors has applied a method of suspension polymerization for the purpose of preparing microspheres of organic polymers coated by finely divided inorganic oxides [2, 3]. Since it is a general tendency for the fine particles put into an emulsion to accumulate at the interface between two immiscible liquids [4], the method could be extended to various systems.

In the field of electronic materials, a large amount of conductive pastes are used, for which glass frits, RuO_2 and organic binders are admixed together. Since the state of ordering of the conductive phase, RuO_2, is decisive, it is interesting to know whether the formation of RuO_2-glass complex unit plays any role on the electronic properties of the paste.

The purpose of the present study is to develop the method of preparation of such composite particles by extending the concept presented in the previous study into the polymerization of inorganic silicate materials.

2. Experimental procedure

To a 27 g of silicon tetraethoxide (TEOS), 60 g ethanol, 47 g water and 0.08 g ammonium hydroxide were admixed to obtain a reaction mixture (RM). Pre-hydrolysis of RM was carried out at 25 °C for 24 h. For the synthesis of coated microspheres, RuO_2 (Johnson–Matthey, 800/5B, 0.1 micron) was pre-treated with a titanium coupling agent, isopropyl tri(dioctylpyrophosphato)titanate (KR38S, Ajinomoto). Surface treatment was carried out either by refluxing and drying or by ball-milling in a 0.1 wt % cyclohexane solution of KR38S. RuO_2, pre-treated by the latter method, was stored in cyclohexane to prevent agglomeration due to drying. Gelation time, t_G, was determined by a simple bare-eye observation on the mixture of RM and the medium in a test tube. Contact angle of RuO_2 and dispersing media was measured from the rate of liquid permeability into a powder compact. Surface tension of the medium was measured by a drop volume method.

A 1 g of RuO_2 was dispersed into a 0.45 dm^3 of the mixed medium comprising cyclohexane and cyclohexanol or cyclohexanone under ultrasonication for 5 min to obtain a suspension of RuO_2 (MMR). The pre-hydrolysed RM was then dispersed into MMR. After a rigorous mixing with a homogenizer (Biomixer BM-4, Nippon Seiki) at 23000 rpm for 10 min, a well dispersed microemulsion was obtained, which turned into microspheres of silica gel during vigorous mixing. Complex microspheres thus obtained were dried under reduced pressure (< 10 torr) at 90 °C for 12 h in a rotary evaporator. Abbreviations of the preparation condition are summarized in Table I.

3. Results and discussion

3.1. Geometry of the composite particles

Representative particle size distribution of the composite microspheres, determined by a laser diffraction method (Seishin, SK7000S), is shown in Fig. 1. The shape of the distribution curve did not change significantly with varying composition of the medium. Median particle size, d_{50}, decreased significantly with the fraction of the polar constituents, X_L or X_N, where X_L is the fraction of cyclohexanol in a mixed medium and X_N of cyclohexanone, in a medium, as shown in Fig. 2a and b. It is also to be noted that the elimination

TABLE I Abbreviation of the preparation condition

Character		Meaning
1. alphabet	L	medium containing cyclohexanol
	N	medium containing cyclohexanone
2. alphabet	H	surface modification by refluxing
	B	surface modification by ball-milling
numerals		volume per cent of the cyclohexanol or cyclohexanone

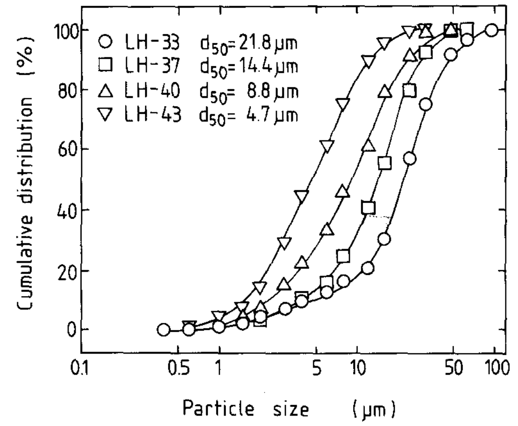

Figure 1 Cumulative particle size distribution of the composites. Effects of cyclohexanol concentration are shown.

of the agglomerates of RuO_2 by a ball-mill method reduced appreciably the particle size, as shown in Fig. 3.

3.2. Amount of adhesion

The amount of RuO_2 adhered to the surface of the composite was analysed by a wet analysis after a complete dissolution of the whole composite and summarized in Table II. The percentage by weight scattered between 26 and 47%. A possible error due to an incomplete separation of the composites from the non-adhered RuO_2 could not perfectly be eliminated. The assumption of the complete gelation of TEOS is not exactly correct, due to the partial dissolution of TEOS into the medium. For the samples LH-33 and NH-60 where the elimination of the non-adhered RuO_2 was successful by using a microsieve with 15 micron holes, the error must be minimal. The exceptionally high value for NH-67 may be attributed to the overestimation due to the incomplete elimination of non-adhered RuO_2.

3.3. Surface morphology of the composite particles

Representative results of the microscopic observation of the composites are shown in Fig. 4. The RuO_2 particles are severely agglomerated when the surface modification was carried out by a reflux method (Fig. 4a to c), so that they are not capable of covering the small globules because of their geometry. Much better coating on the smaller composite particles was achieved when RuO_2 was modified in a ball-mill without any drying process, as shown in Fig. 4d. RuO_2 particles were located exclusively on the surface of the silica gel particles and not internally, detected by the EPMA of the cross sectional view, as shown in Fig. 5.

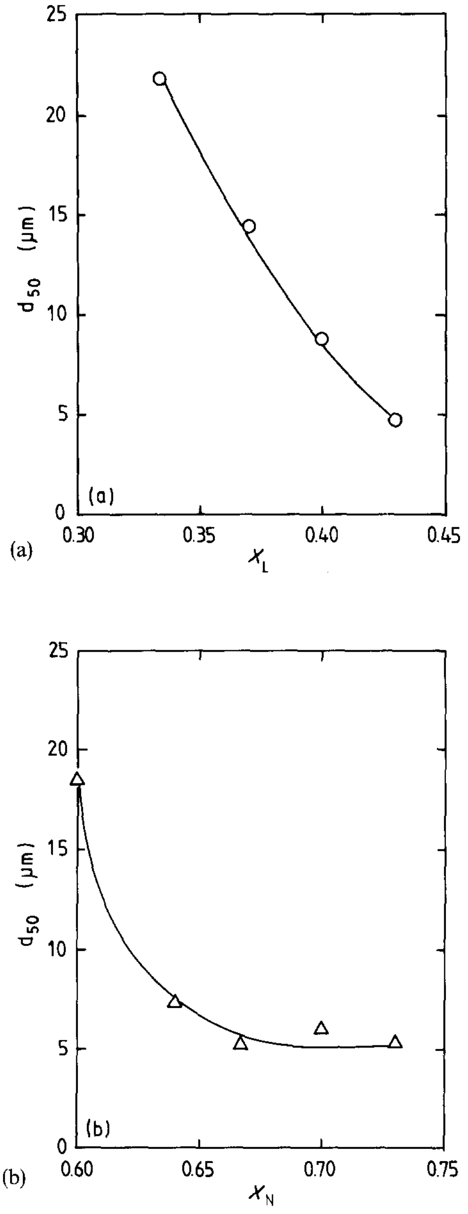

Figure 2 Variation of median particle size with the fraction of (a) cyclohexanol, X_L and (b) cyclohexanone, X_N.

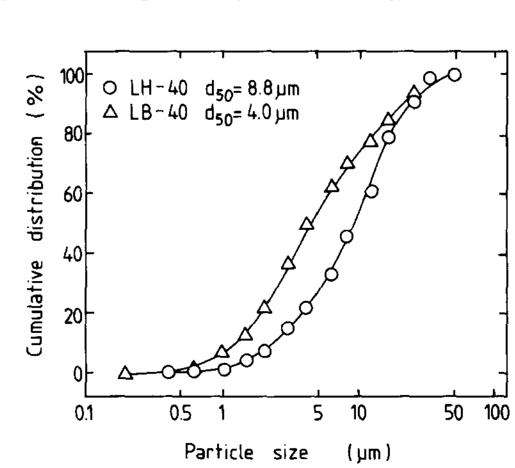

Figure 3 Cumulative particle size distribution of the composites. Methods of surface treatment are ○ by refluxing and △ by ball milling.

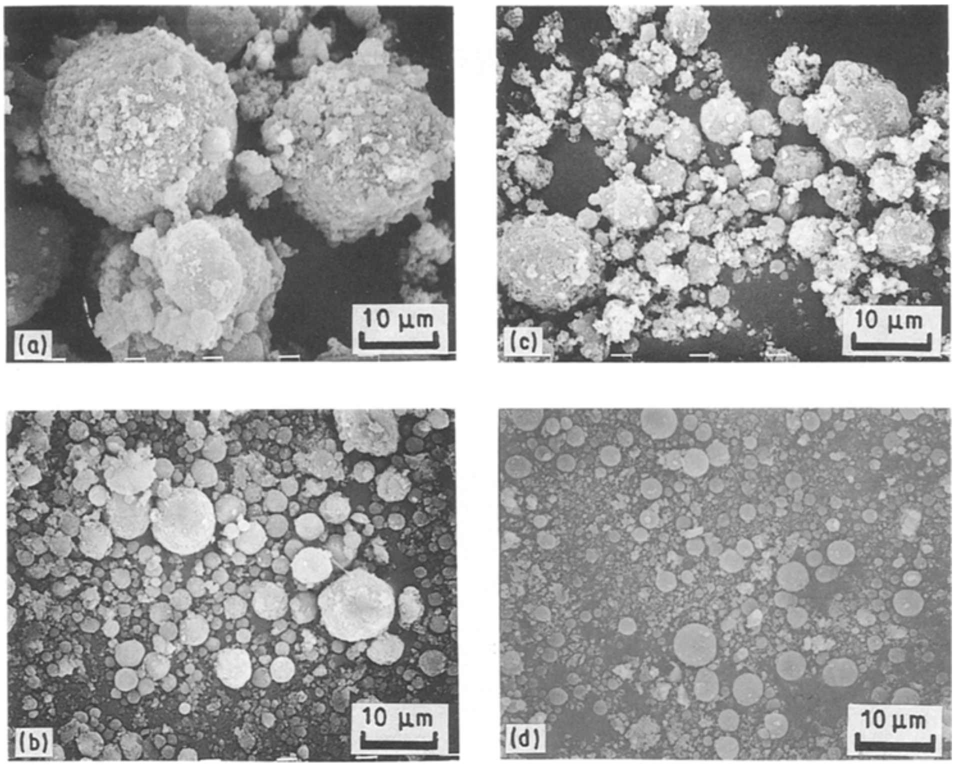

Figure 4 Scanning electron micrographs of the composites (a) NH-60, (b) NH-67, (c) LH-40, (d) LB-40.

TABLE II Percentage adhesion of RuO_2

RuO_2%	Sample
26.3	LH-40
47.0	NH-67
31.8	LH-33
34.7	NH-60
33.8	NB-67

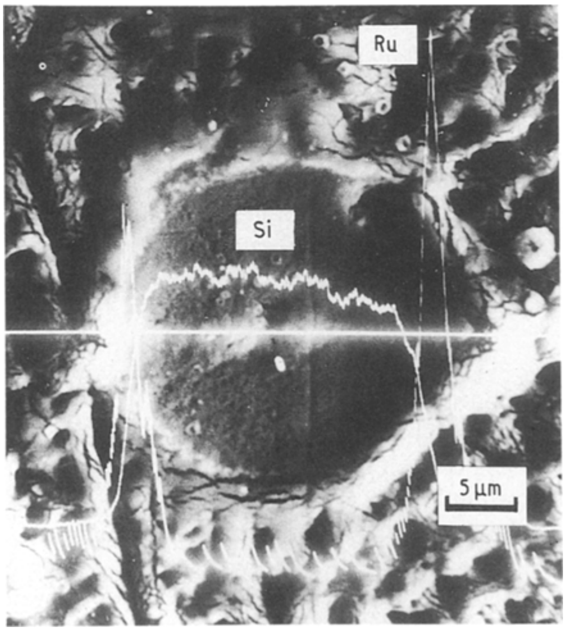

Figure 5 EPMA line scanning analysis of Ru and Si on the cross-section of a composite particle.

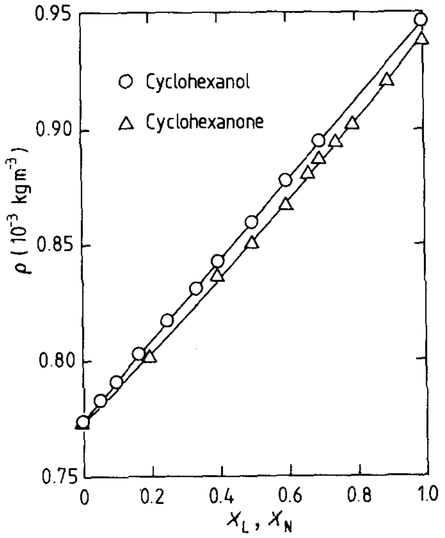

Figure 6 Variation of density, ρ, of the medium with X_L or X_N.

3.4. Dispersion of RuO_2 in the medium

Whereas the density of the two mixed media were similar and varied with composition almost linearly as shown in Fig. 6, the change in the viscosity was quite non-linear, and that with cyclohexanol was much more viscous than with cyclohexanone, as shown in Fig. 7a and b. Surface tension of both media were almost identical, as shown in Fig. 8a and b.

Contact angle of the medium on the untreated RuO_2 was higher than that on the surface-treated RuO_2, as shown in Fig. 9a and b. They decreased only slightly with increasing amount of polar constituents. The arrows A and B in Fig. 9 are the contact angles of

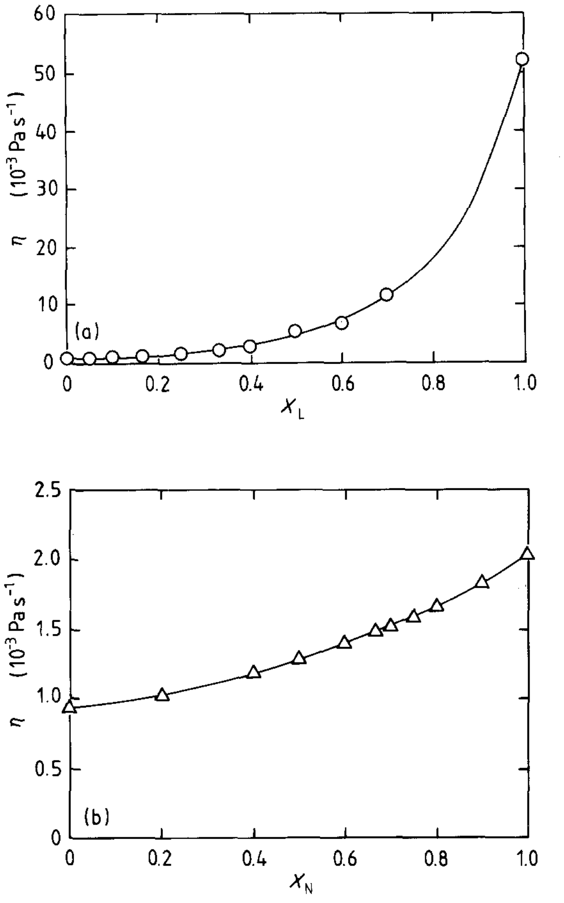

Figure 7 Variation of viscosity, η, of the medium with (a) X_L and (b) X_N.

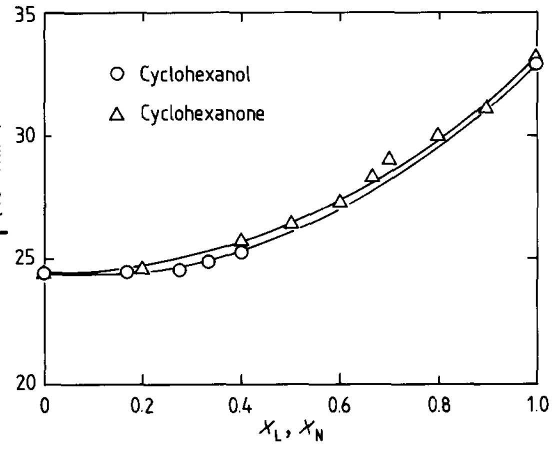

Figure 8 Variation of surface tension, γ, of the medium with X_L or X_N.

the mixed alkoxide against untreated A and treated B RuO_2, respectively.

Surface modification of RuO_2 using a titanium coupling agent only slightly increased the contact angle against the media, but substantially decreased the contact angle against the mixed alkoxide. This is quite natural, since the mixed alkoxide is much more polar than the media comprising a perfectly non-polar cyclohexane mixed with its derivatives, the latter being slightly polar.

Apparent particle size distribution of RuO_2 in the various media was measured to estimate the degree of its dispersion. The median particle size, d_{50}, decreased with increasing amount of polar constituents in the medium, as shown in Table III. The surface modification with the titanium coupling agent, KR38S, increased d_{50}, i.e., the surface modification of RuO_2 made its dispersion worse in the mixed media. The median particle size of the composite decreased significantly by carrying out the surface modification of RuO_2 in a ball-mill. This means that the apparent deterioration of the dispersion is not solely attributed to the unfavourable surface chemical condition between RuO_2 and cyclohexane. Rather, agglomeration of RuO_2 must have taken place during drying as well.

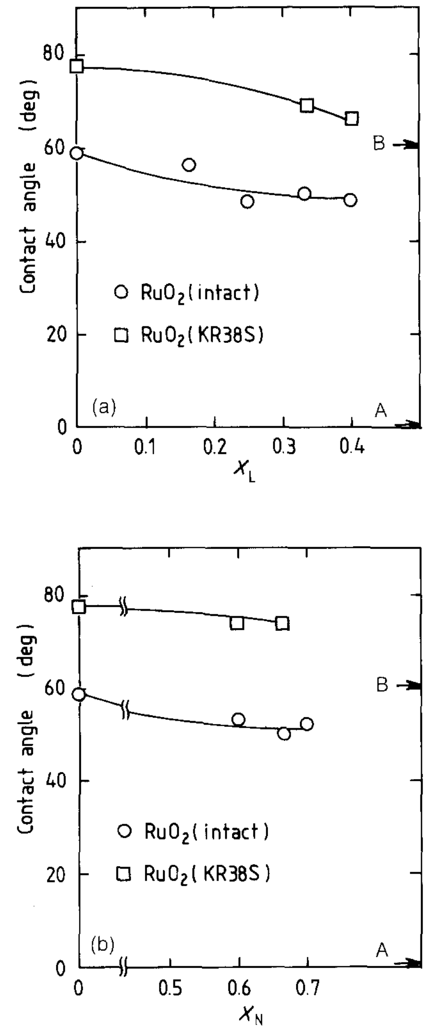

Figure 9 Variation of apparent contact angle with (a) X_L or (b) X_N. The arrows A and B denote the contact angles of the mixed alkoxide against untreated and treated RuO_2, respectively.

3.5. Change in the gelation time

The gelation time, t_G, decreased significantly with increasing content of cyclohexanol or cyclohexanone, as shown in Fig. 10. The relationship between t_G and the solubility of the water is not very significant, as shown in Table IV. Therefore, t_G is not simply explained by the change in the solubility of water. During gelation, however, it is obvious that the exchange of water between the solidifying globule and the surrounding media plays an important role on the

TABLE III Median diameter (μm) of RuO_2

Surface modification	Ageing time (h)	Cyclohexane	Medium			
			$X_L = 0.33$	$X_L = 0.40$	$X_N = 0.60$	$X_N = 0.67$
None	0	3.65	–	2.67	–	2.60
None	24	3.10	–	2.12	–	2.11
KR38S reflux	0	3.78	2.98	2.81	2.61	2.61
KR38S reflux	24	3.31	2.53	2.38	2.30	2.23
KR38S bm[a]	0	1.13	–	1.07	–	0.98
KR38S bm	24	1.08	–	1.10	–	0.90

[a] ball-milling.

TABLE IV Gelation time and water solubility

Fraction of polar constituents in a medium	t_G (min)	Solubilities ($mgH_2O\ cm^{-3}$)
$X_L = 0.33$	170	13.3
$X_L = 0.40$	15	18.5
$X_L = 1.00$		240
$X_N = 0.60$	150	11.2
$X_N = 0.67$	12	14.6
$X_N = 1.00$		120

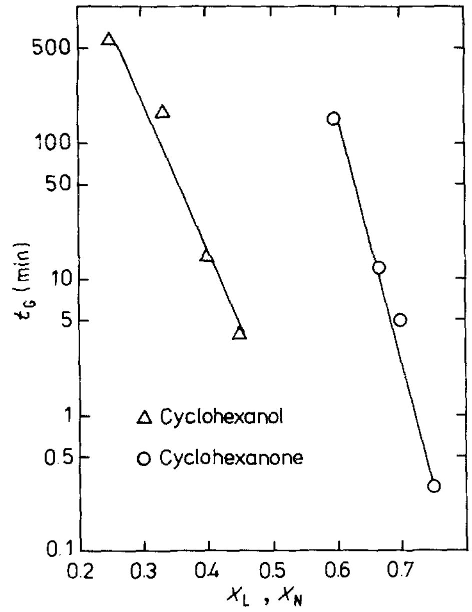

Figure 10 Variation of gelation time, t_G, with X_L or X_N.

properties of the resulting composites. Hence, it seems reasonable to assume that the difference in the gelation time is more significantly attributed to the rate of dissolution of the water into the media than to the solubility, the latter being independent of the time needed to dissolve. The higher rate of water absorption of the mixed solvent containing cyclohexanone seems to be supported by the difference in the polarity. The dipole moment of cyclohexanone is 3.01, which is 1.6 times higher than that of cyclohexanol.

3.6. Relationship between t_G and the particle size of composites

The decrease in the particle size with increasing amount of alcohol or ketone in the medium parallels the decrease in the gelation time. A shorter gelation time, or the higher rate of gelation, brings about the solidified spherical particles immediately from the dispersed soluble globules present at the beginning of the synthesis, without any chance of coalescence.

The rate of coalescence was examined by stopping the homogenization of the complex dispersion after 1 min and observing the complex microemulsion under an optical microscope. As shown in Fig. 11, coalescence in the emulsion with X_N equal to 0.67 ($t_G = 12$ min) was almost negligible (Fig. 11a and b), whereas very significant coalescence was observed for those with X_N equal to 0.60 ($t_G = 150$ min).

When the gelation time is too short, on the other hand, gelation could occur before the globules are reduced too much by mechanical agitation. Therefore, a levelling off of the decreasing tendency of d_{50} was observed, particularly in the case of the media containing cyclohexanone.

Apart from the reaction kinetic factors like the gelation time, surface chemical conditions might give significant influence on the properties of the composite. It is known that the stability of the complex dispersions like those involved in the present synthesis can depend sensitively on the free energy change due to the movement of the solid particle from an oil phase to an aqueous phase [5]. As shown in Fig. 2a and b, the median particle size, d_{50}, of the composite decreased significantly with X_L or X_N. However, d_{50} varied with X_L or X_N within a similar range, as far as the present experiment was concerned. Therefore, it is unlikely that d_{50} is dominated significantly by either the surface chemical conditions or by the bulk properties of the medium, i.e., density or viscosity, since none of them varied proportionally with d_{50}. In other words, the properties of the composites in the present study is not predominated by the properties related with thermodynamic equilibrium, presumably because the synthesis is too rapid for the reaction system to get into the equilibrium state.

4. Conclusion

Composite microspheres of silica gel coated by fine powdered RuO_2 with their diameter in the region of a single micron were obtained from a complex emulsion of TEOS in a mixed medium comprising cyclohexane

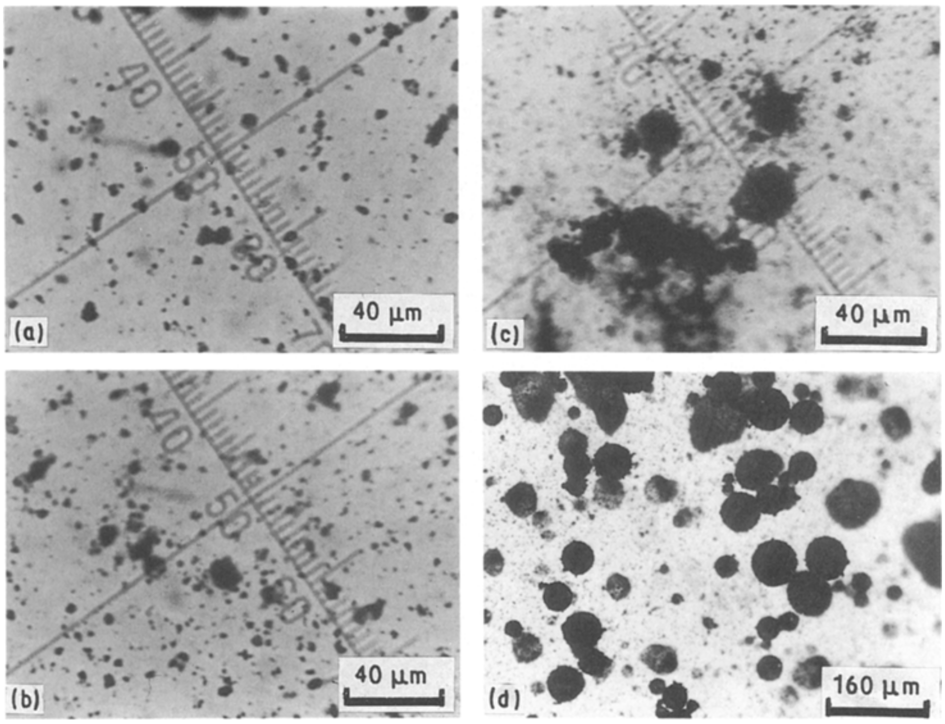

Figure 11 Optical micrographs of the mixed dispersion observed by stopping the homogenization after 1 min. (a) $X_N = 0.67$ after 1 min; (b) $X_N = 0.67$ after 30 min; (c) $X_N = 0.60$ after 1 min, (d) $X_N = 0.60$ after 30 min.

and cyclohexanol or cyclohexanone with pre-dispersed RuO_2. Surface chemical properties do not seem to predominate the particle size of the composite, however, the control of the gelation time plays a decisive role on the properties of the composites.

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