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Electron microscopical examinations of grafted nitrocellulose

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A series of nitrocellulose specimens grafted with methyl methacrylate in homogeneous and heterogeneous media have been examined using electron microscopy. The observations from scanning and transmission electron microscopy demonstrated that the homogeneous grafting changed not only the morphological structure of the surface layer of the supermolecular structure of nitrocellulose but also its internal character, as well as promoting greatly the uniform distribution of grafted polymer over the whole mass of nitrocellulose substrate, and hence decreasing order. X-ray diffraction studies provided further evidence for this view. Conversely, the electron micrographs disclosed that the heterogeneous grafting only altered the surface morphology of nitrocellulose flake.

In addition, the difference of morphological structure between the surface layer and the interior of the supermolecular structure of a homogeneous graft has also been revealed and is discussed briefly in this study.

INTRODUCTION

Graft copolymerization is, no doubt, one of the promising ways of modifying cellulose or polysaccharides and adding new uses against the rapidly growing competition from synthetic polymers. The subject has advanced considerably in conjunction with the general advances in carbohydrate and polymer chemistry (Kennedy, 1974, 1988; Kroschwitz, 1989, 1990). As a result, a number of investigations, particularly on the graft copolymerization of cellulose, have been reported by numerous scientists (Battaerd & Tregear, 1967; Heberish & Guthrie, 1981; Arthur, 1985; Samal *et al*., 1986). Earlier studies have demonstrated that the morphological structure of graft copolymers is an important parameter which dictates their properties and end uses.

Surprisingly, there have been no reports in the literature on the morphological structure of the grafted nitrocellulose despite an ever-increasing use of nitrocellulose as a coating material and its graft copolymers have been prepared by various methods (Badran *et al*., 1981; Srinivasan *et al*., 1982; Takahashi & Sugahara, 1988). It is therefore of interest to use electron microscopy combined with X-ray diffraction techniques to examine the morphological structure of grafted nitrocellulose and the distribution of the grafted polymer branches.

EXPERIMENTAL METHODS

Preparation of grafted nitrocellulose

The homogeneous grafting was carried out by dissolving nitrocellulose (RS1/2 grade with 11·4–11·8% nitrogen

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content) in methyl isobutyl ketone, adding inhibitor-free methyl methacrylate (MMA) as monomer and benzoyl peroxide as initiator in nitrogen atmosphere. The polymerization product, called the gross graft in the present study, was isolated with an excess of petroleum ether to precipitate the graft copolymer, and then subjected to selective extraction of the free poly(methyl methacrylate) (PMMA) with benzene. The residue after the first extraction, called the grafted nitrocellulose or grafted specimen, was then subjected to the second extraction of the ungrafted nitrocellulose with methanol. The remainder is called the true graft in the present study.

The heterogeneous grafting was performed by similar procedures with the exception of ceric ammonium nitrate being used as initiator and water used as the heterogeneous medium.

The grafting parameters were defined as follows:

grafting level, % = $(A - B)/B \times 100$
gross grafting, % = $(C - B)/B \times 100$

where A corresponds to the weight of product after copolymerization and extraction with benzene, B the weight of nitrocellulose, and C the weight of the product after copolymerization.

X-ray diffraction analysis

All the X-ray diffraction diagrams were obtained by using a TUR-M62 X-ray diffractometer with Ka radiation.

RESULTS AND DISCUSSION

Surface characterizations

The changes in the morphological structure of fibres or cellulose via grafting have been reported in the literature (Harris *et al.*, 1978; Reinhardt & Arthur, 1978; Abdel-Hay *et al.*, 1980). It is widely accepted that the grafting took place first on the surface of the cellulose substrate and thus changed its morphological structure. Likewise, changes in the surface morphology of the grafted nitrocellulose may also be expected.

Homogeneously grafted nitrocellulose

The Scanning electron micrograph (SEM) of ungrafted nitrocellulose showed a smooth surface with a few undulations and indentations and wrinkles which resulted from the nitration of cellulose (Fig. 1). This fine structure exhibited little significant change when the grafting level was less than 10%. However, when the percentage grafting reached 17% the difference of the surface morphology between the grafted and ungrafted specimens became evident. The surface of the grafted cellulose was covered with a very fine striated texture (Fig. 2(a)). This striated texture of graft, moreover, grew up and protruded as the grafting level increased up to 56% (Fig. 2(b)). Finally, a compact anastomosed texture, coated entirely on the surface of nitrocellulose, appeared as the graft content further increased (Fig. 2(c)).

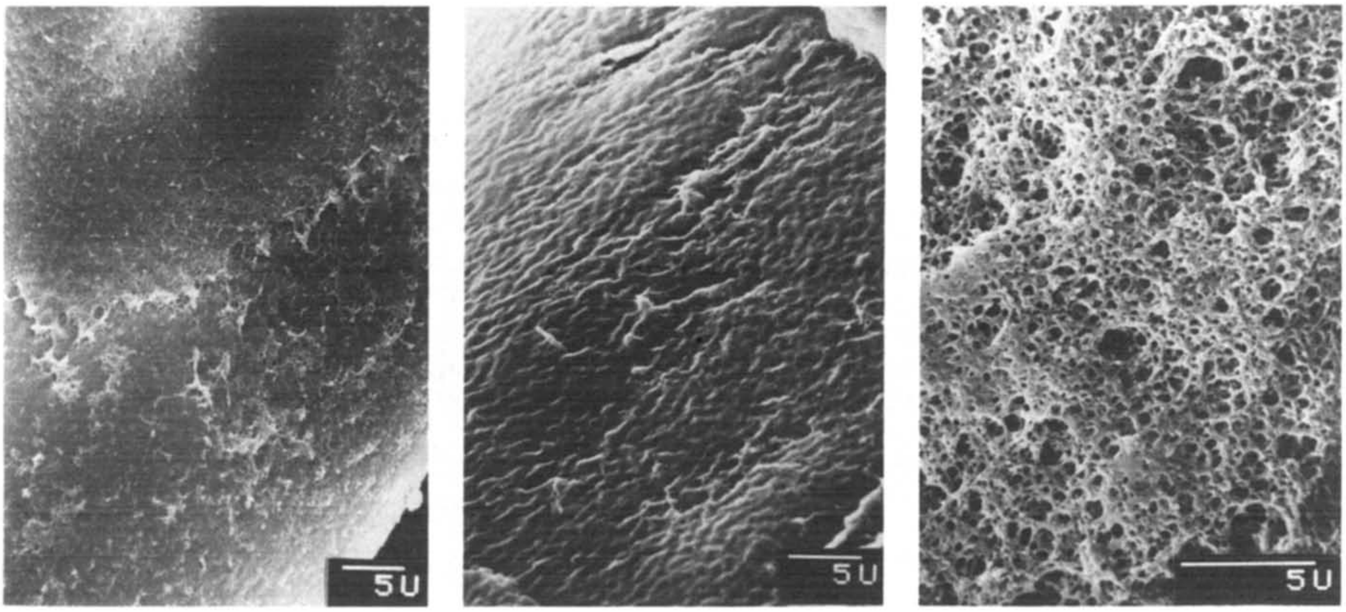
Fig. 1. Scanning electron micrograph of nitrocellulose.

From the scanning electron micrographs, it is obvious that the grafted polymer (PMMA) was aligned in a uniform and regular way on the surface of nitrocellulose specimens. This is quite different from previous similar work, in which the grafted polymer of cellulose substrate distributed in neither a continuous nor a regular way, but into the form of chunks (Williams *et al.*, 1975).

It must be pointed out that the above specimens for the microscopical examinations were achieved by adopting extractive techniques to remove PMMA homopolymer contaminated in grafted nitrocellulose. However, the micrograph of a gross graft, which still contained the free PMMA homopolymer, exhibited a multilayered 'stereoregular' appearance (Fig. 3). It is interesting to note that the 'stereoregular' stereostructure on the surface of the specimen disappeared only when the extractive procedure for homopolymer had been carried out. As a result, a considerable plain anastomosed texture then appeared (see also Fig. 2(b)). This phenomenon implies that most of the homopolymer in homogeneous grafting was located on the top of the surface of the graft microstructure and was therefore easy to remove by conventional extraction techniques.

Heterogeneously grafted nitrocellulose

Contrary to the homogeneous grafting in which the grafted polymer was distributed uniformly over the



(a) (b) (c)

Fig. 2. Scanning electron micrographs of nitrocellulose grafted with poly(methyl methacrylate): (a) 17%, (b) 56%, (c) 77%.

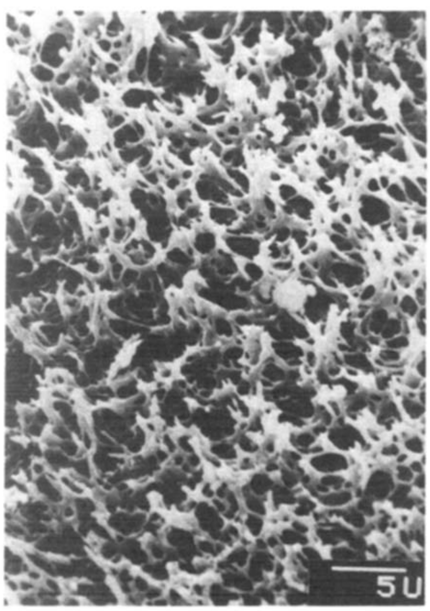


Fig. 3. Scanning electron micrograph of nitrocellulose gross graft with 100% poly(methyl methacrylate).

surface of the microstructure, with the heterogeneous grafting, the electron micrograph disclosed that the grafted polymer was predominantly deposited in the form of large aggregates on and in the vicinity of the surface of nitrocellulose flake (Fig. 4). The only noticeable change in morphology upon heterogeneous grafting was that the smooth surface obtained a coarse appearance.

Features of internal morphology

The SEM observations described above have manifested that nitrocellulose grafting involved a polymer reaction by which PMMA molecules were chemically connected to the surface of cellulosics. It is more important, nevertheless, to clarify whether the grafting is essentially localized on the surface of the cellulose substrate or penetrates more or less into the interior of

Fig. 4. Scanning electron micrograph of nitrocellulose grafted with 71% poly(methyl methacrylate) in heterogeneous medium.

its microstructure. Transmission electron microscopy (TEM) can be used to predict this kind of information and was thus employed in the present study.

Homogeneously grafted nitrocellulose
Initially, it was considered that there might be no difference in the morphological structure of the grafted specimens observed with SEM and TEM since the homogeneously grafted products in these experiments were obtained by means of precipitation from the reactive solution (Fig. 5).

Surprisingly, the TEM examinations showed that not only was a distinctive morphology, which differed markedly from that of SEM observation, found; also the change of the morphology as a function of grafting was found to be very interesting.

Unlike the surface changes observed with SEM, even at a lower grafting level, the change in the internal morphological structure of grafted nitrocellulose was remarkable (Fig. 6). Obviously, this block-texture is greatly different from the ungrafted specimen, in which an internal morphology with the oriented structure and some irregular spaces was identified by TEM (Fig. 5). The electron micrograph of grafted nitrocellulose revealed that the grafted polymer appeared in separated microblocks of about 0·2–1·2 μm in size and the spaces existing in the ungrafted specimen seem to be filled with PMMA. This clearly suggested that the graft copolymerization occurred in the interior of the supermolecular structure of nitrocellulose as well as in its internal spaces.

As the grafting increased, furthermore, the extent to which the grafting reaction took place towards the interior of the supermolecular structure and caused the greater change in the morphological structure of nitrocellulose could be ascertained by the ultramicroscopical technique. For instance, TEM examinations in the present study showed that the ultrathin section of a gross graft with 100% PMMA was coated completely in frozen molten MMA polymer (Fig. 7). As can be seen from the figure, the morphology of the specimen in the micrograph is somewhat hazy due to the presence of a lot of homopolymer. A morphological structure with protruding blocks, therefore, was discerned only after removal of the homopolymer trapped in the microstructure (Fig. 6(b)). It is also of interest to recognize that, at this grafting level, the grafted polymer still appeared in separated blocks which followed in a definite pattern. This was not always the case. At the

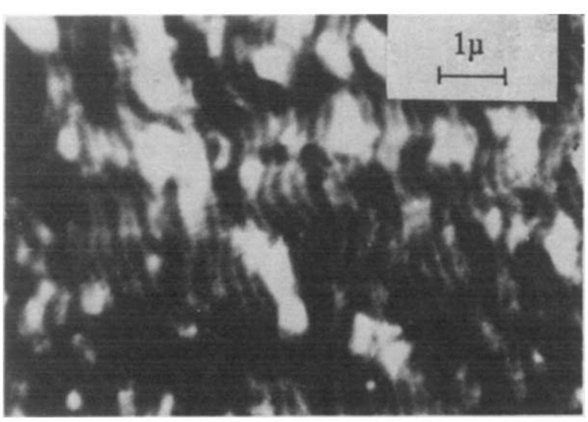


Fig. 5. Transmission electron micrograph of nitrocellulose.

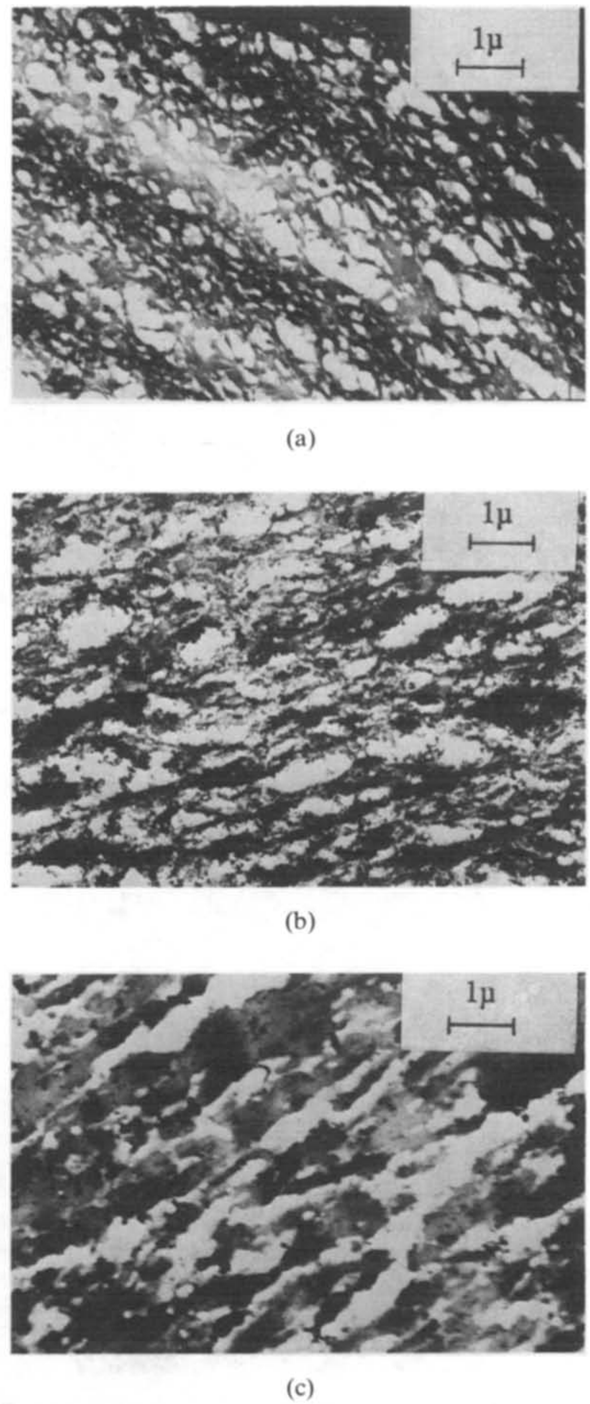


Fig. 6. Transmission electron micrographs of nitrocellulose grafted with poly(methyl methacrylate): (a) 17%, (b) 56%, (c) 77%.

higher grafting level the separated blocks sometimes developed into continuous molten ridges embedded partly in the microstructure of the cellulose substrate (Fig. 6(c)). Besides, the micrograph also showed the occurrence of polymer bridges between individual ridges. These variations in morphological behaviour may be considered as the result of the advanced development of grafting reaction in the interior of the supermolecular structure of nitrocellulose.

As revealed by SEM and TEM observations, the homogeneous grafting changed not only the morphological structure of the surface layer of the supermolecular structure of nitrocellulose, but also its internal character, that is, for nitrocellulose, the homogeneous grafting took place in both the surface layer and the interior of the supermolecular structure of cellulose. This is very different to the earlier result obtained by Muratov, who reported that the grafting only occurred on the surface layer of the supermolecular structure of the fibre (Muratov *et al*., 1977).

Based on the present observations, it seems that the increased degree of grafting resulted in the grafted polymer being distributed uniformly over the whole mass of the cellulose substrate, in which some of the ordered structure was involved. The available evidence in favour of this judgement comes from the disappearance of the certain ordered structure of the grafted specimens reflected by the electron micrographs and X-ray diffraction analyses. In X-ray photographs, some halos of the grafted specimen (Fig. 8) were diffused, shifted or had disappeared compared with those of the ungrafted product (Fig. 9). The diffusivity of some halos suggested an increase in the degree of disorder in nitrocellulose molecules due mainly to the invasion of the grafted branches. In other words, the homogeneous grafting for nitrocellulose has occurred in both the amorphous and the ordered domains of the precipitated nitrocellulose substrate.

In spite of the uniformity of grafted polymer distributed over the grafted specimens, the differences in morphological behaviour between the surface and the interior of the supermolecular structure have been revealed in the present study, i.e. the striations or anastomosed texture (Fig. 2(a), (b)) and the blocks or molten ridges (Fig. 6(a)–(c)) respectively. This could be ascribed to the fact that under homogeneous grafting the nitrocellulose substrate is completely dissolved in such solvent systems capable of breaking the hydrogen bonds. All parts of nitrocellulose molecules, including the surface and the interior of the microstructure, are equally accessible to monomer and initiator being grafted on (Immergut, 1965). It is likely that under homogeneous conditions the grafting reaction starts simultaneously at both the surface and the interior of the supermolecular structure of nitrocellulose. For example, the introduction and subsequent polymerization of MMA extended into the microstructure of cellulose gave rise to the formation and growth of grafted chains, that is, the formation of the new microblocks in the interior of the supermolecular structure.

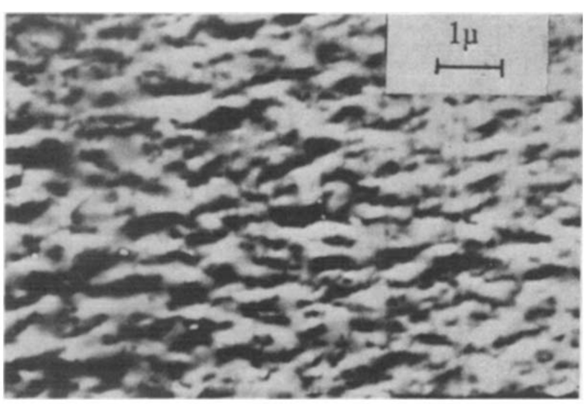


Fig. 7. Transmission electron micrograph of nitrocellulose gross graft with 100% poly(methyl methacrylate).

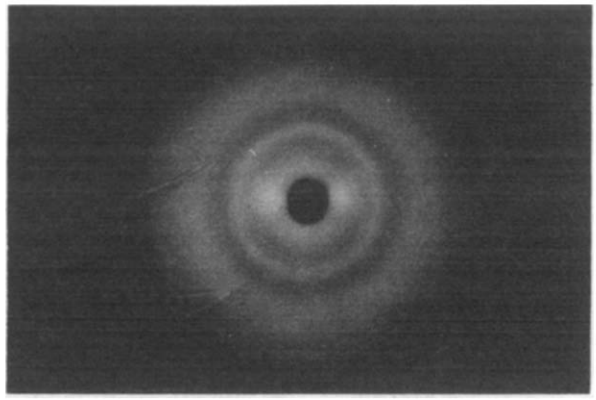


Fig. 8. X-ray diffractogram of nitrocellulose.

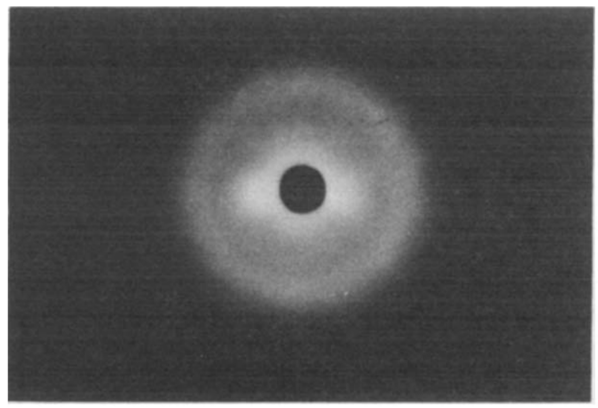


Fig. 9. X-ray diffractogram of nitrocellulose grafted with 62% poly(methyl methacrylate).

The grafted polymer, eventually found in the form of ridges due to the development in size and number of the microblocks, is remarkably different from the striated texture presented in the surface layer of the supermolecular structure of nitrocellulose. Naturally, it is also envisaged that certain PMMA homopolymer molecules entrapped in the interior of the supermolecular structure do not find it easy to diffuse out because of their large molecular size.

Although the fact that homogeneous grafting has the above-mentioned advantages, these experiments also indicate that a part of the nitrocellulose carried no grafted branches. Hence a true (pure) cellulosic graft can be achieved by the solvent-extraction techniques to remove the ungrafted nitrocellulose and homopolymer existing in the grafted specimen. Accordingly, TEM can also be employed as a means of identifying the various features of morphology among the nitrocellulose-PMMA true graft (Fig. 10), PMMA homopolymer (Fig. 11), and ungrafted nitrocellulose (Fig. 5). In other words, TEM techniques may assist further in proving the coexistence of the graft, homopolymer and the ungrafted substrate in a grafted substance.

Heterogeneously grafted nitrocellulose

It is well known that grafting of any vinyl monomer to cellulose material in a heterogeneous medium is essentially affected by the contact areas between cellulose and monomer and is markedly dependent on the diffusion factors (Wilkov *et al.*, 1973). The use of a Ce^{4+}-based redox system in the present study to initiate nitrocellulose grafting is a heterogeneous process and the diffusion of monomer into the inner structure is very difficult. No changes in the morphological structure in such medium have been observed with TEM examinations (Fig. 12). It implies that no reaction has occurred in the interior of the supermolecular structure of nitrocellulose. This can also be explained by the fact that the diffusion for monomer into the internal microstructure of nitrocellulose was hindered by a grafted 'shell' which covered the surface of nitrocellulose flake which increased in graft content.

CONCLUSIONS

From what is proven and discussed above, homogeneous grafting is the optimum manner of distribution of PMMA grafts to get the best results for nitrocellulose.

The observations from SEM and TEM disclosed that the homogeneous grafting changes the surface layer as well as the internal morphological character of the supermolecular structure of nitrocellulose. This is very different to results of earlier research which concluded that the grafting only occurred on the surface layer of the supermolecular structure of the fibre. The present study has shown that the extent of the morphological changes varies with increasing content of grafted polymer. It has been noticed that the increase in the graft content produced a uniform distribution of grafted polymer over the whole mass of cellulose substrate, in which a certain ordered structure is involved. X-ray diffraction analysis has strongly supported this judgement.

Notwithstanding this, differences in the morphological structure between the surface layer and the interior of the supermolecular structure of homo-

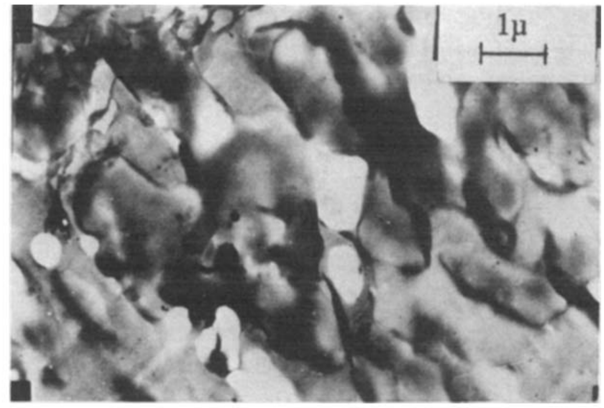


Fig. 10. Transmission electron micrograph of nitrocellulose true graft without ungrafted nitrocellulose and homopolymers.

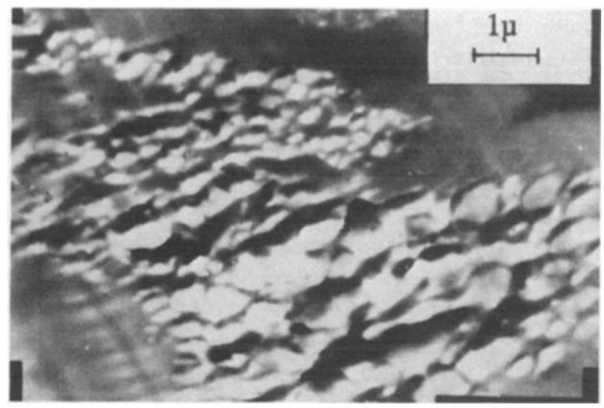


Fig. 11. Transmission electron micrograph of poly(methyl methacrylate) homopolymer.

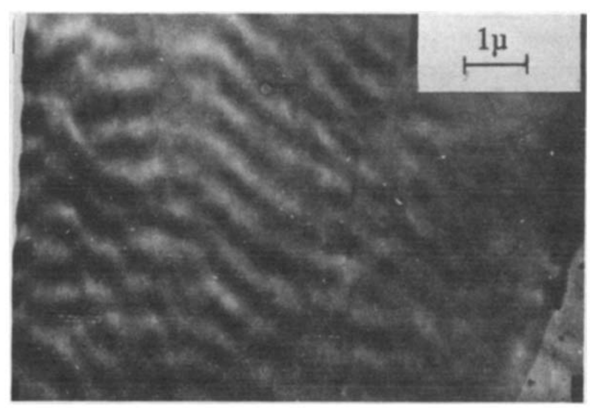


Fig. 12. Transmission electron micrograph of nitrocellulose grafted with 71% poly(methyl methacrylate) in heterogeneous medium.

geneously grafted nitrocellulose have been found in the present study, i.e. the striations and ridges texture respectively. On the other hand, TEM observations also indicated very little change in the internal morphology of the heterogeneously grafted nitrocellulose. The heterogeneous grafting only occurred on and in the vicinity of surface of nitrocellulose flake in the present study.

The results presented here suggest that the application of electron microscopy in conjunction with X-ray diffraction to the grafted specimens may give rise to a greater overall understanding of the homogeneous grafting of nitrocellulose and the changes of the morphological behaviour in the grafted products. Clearly, the unique morphological structure, i.e. the striations on the surface of the microstructure while the ridges texture is in its interior, is certainly associated with the performances and end-use of coatings based on the grafted nitrocellulose.

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