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Aggregate Morphologies Formed from a Thickener, 4,4'-Bis-(3-decylureido)-diphenylmethane, of Urea Grease

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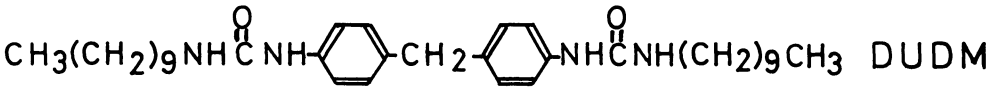
The aggregate morphologies formed from 4,4'-bis(3-decylureido)-diphenylmethane in a mineral oil at 180 °C were investigated by electron microscopy. The formed aggregates consisted of fiber with the tube-like shape which had not been observed in lubricating grease, and helices.

In the study of grease, it is very important to know the aggregation behavior and the aggregate morphology of a thickener in base oil, because the physical properties and the performance of grease are mainly determined by them. It has been well known by electron microscopic study that crystalline aggregates of metal soap in lubricating grease consist of fibers in the form of ribbon, twisted ribbon and helical rope.[1-3] There are, however, few systematic studies on the aggregate morphology of a thickener in urea grease which has long life at a high temperature and is widely used in various industrial applications.

This letter describes the aggregate morphologies formed from 4,4'-bis(3-decylureido)-diphenylmethane(DUDM) which is one of the thickener of dialkyldiurea greases.

DUDM was prepared from 4,4'-diphenylmethanediisocyanate(MDI) and n-decylamine(DA) in paraffinic mineral oil at 110 °C, and then grease was made by heating the dispersion liquid at 180 °C.

Specimens for electron microscopic observation were made by depositing a droplet of a dilute suspension of the DUDM grease in toluene on a grid, and further by allowing it to stand for a day in toluene/hexane(1:1) bath



DUDM

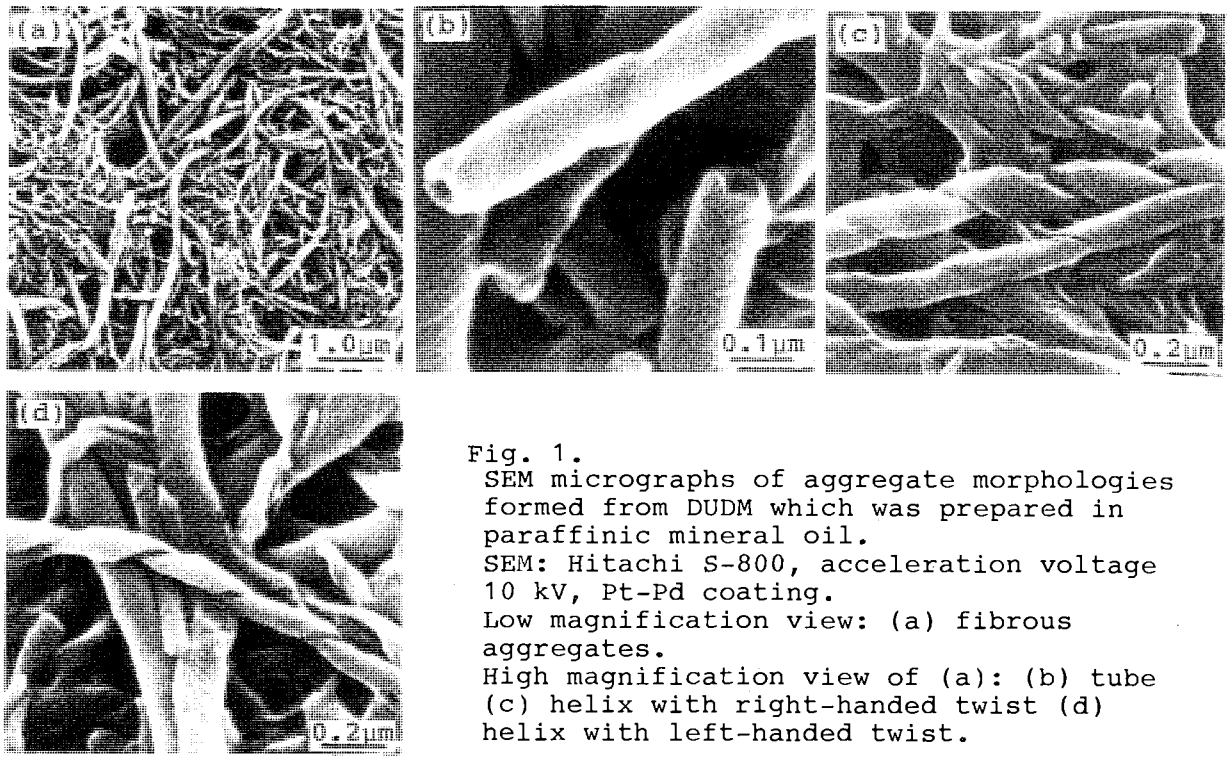


Fig. 1.
SEM micrographs of aggregate morphologies formed from DUDM which was prepared in paraffinic mineral oil.
SEM: Hitachi S-800, acceleration voltage 10 kV, Pt-Pd coating.
Low magnification view: (a) fibrous aggregates.
High magnification view of (a): (b) tube (c) helix with right-handed twist (d) helix with left-handed twist.

in order to remove residual oil.

Figure 1 shows those electron micrographs. The fibrous structures were observed under low magnification(a). As is well known, these structures are similar to those of some crystalline aggregates of metal soap in lubricating grease.[1] At the higher magnifications, these structures were seen to consist of two different elements: tube-like structure(tube) (b), and helical structure possessing right-handed(c) or left-handed twists (d). The latter has been already observed in that of fibrous aggregates of metal soap grease and discussed on the direction of the twist.[2] However, the tube has not been found in other greases.

The residue of excess amine or isocyanate in urea grease is hardly avoidable under the usual manufacturing conditions. We were interested in those influences on aggregate morphologies. Therefore, the DUDM was prepared from MDI and a small excess DA in tetrahydrofuran at 15 °C. Filtration of the precipitate and the subsequent Soxhlet extraction method used acetone was carried out in order to remove excess DA. Grease was prepared by heating this DUDM particle dispersed in paraffinic mineral oil at 180 °C.

The aggregate morphologies in this grease are shown in Fig.2. The formed fibrous aggregates as shown in Fig.2(a) were the same as those of Fig.1(a) and they had a well-regulated form as a whole. The fibrous aggregates had mostly tubes with the outer diameter of 0.1-0.2 μm and with

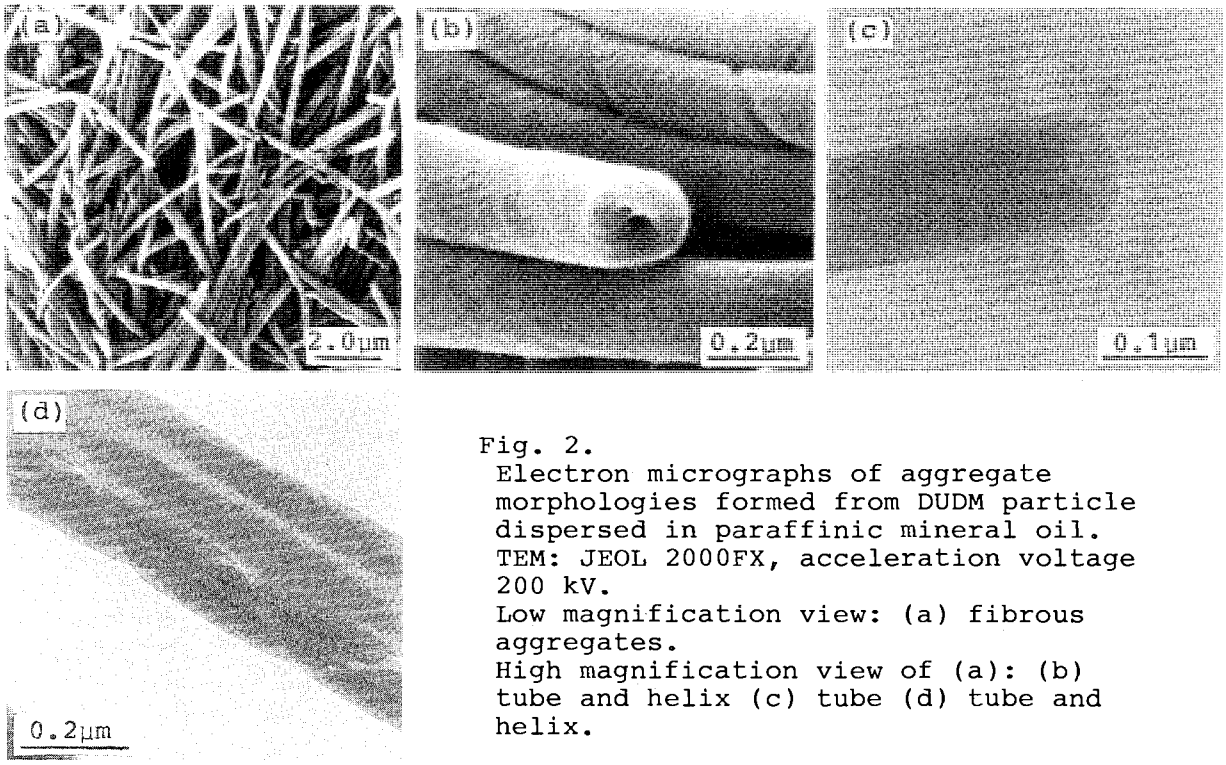


Fig. 2.
Electron micrographs of aggregate morphologies formed from DUDM particle dispersed in paraffinic mineral oil.
TEM: JEOL 2000FX, acceleration voltage 200 kV.
Low magnification view: (a) fibrous aggregates.
High magnification view of (a): (b) tube and helix (c) tube (d) tube and helix.

the hole-diameter of 0.02-0.04 μm(b-d). But some helical structures with the helical pitch of ca. 0.3 μm(b,d) also existed. It is revealed that these morphologies could be formed also from some compounds yielding bilayer.[4-5)]

The aggregate morphologies formed from the DUDM particle dispersed in base oil were well-regulated in comparison with those formed from the DUDM which was prepared in base oil. We considered that the crystallinity of DUDM in mineral oil before heat-treatment affected the shape of aggregates. As was shown in Fig.3, the X-ray diffraction patterns for DUDM samples before heat-treatment revealed that crystallinity of (a) and (b) were distinctly different. Tube and well-regulated helix tended to form from high crystalline DUDM, while helix or ribbon tended to form from low crystalline one. It may be, accordingly, considered that tube is the final structure and helix and ribbon are the intermediate one.

As was shown in DSC curve of Fig.4, the DUDM had two thermal inter-crystalline transitions(I,II). These transitions were closely related to the formation of the fibrous structure. In order to make its formation, the DUDM particle dispersed in paraffinic mineral oil had to be heated above the temperature of transition II. Micrographs of Fig.5 show the temperature dependence of the fiber formation from DUDM particle. The variation in shape could be little observed below the temperature of transition II, while above the temperature the fibrous aggregates were formed.

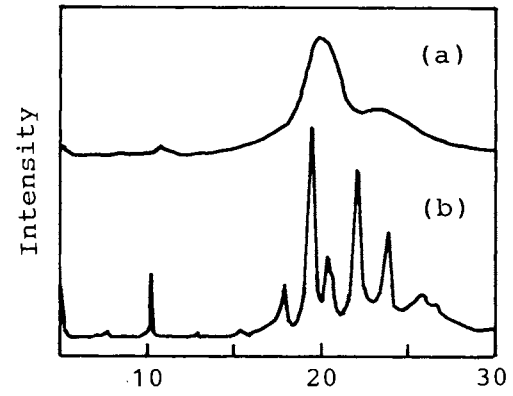


Fig. 3.
X-Ray diffraction patterns of DUDM samples.
(a) Prepared in paraffinic mineral oil. Soxhlet extraction method used hexane was carried out in order to remove oil.
(b) Prepared in tetrahydrofuran.

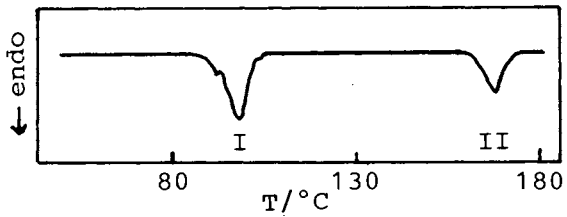


Fig. 4.
DSC curve of DUDM.
Heating rate: 10 °C/min.
Atmosphere: flowing nitrogen.
DUDM: recrystalized in N,N-dimethylformamide at 55 °C.

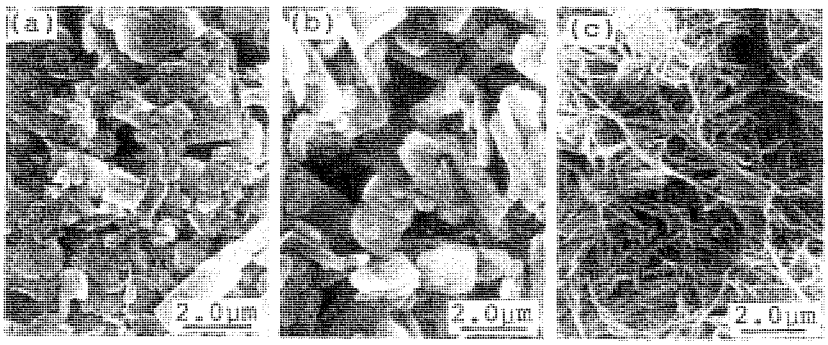


Fig. 5.
SEM micrographs of DUDM samples obtained in paraffinic mineral oil at various temperature.
(a) RT (b) 145 °C
(c) 180 °C.

The existence of oil was also necessary for the formation of the fibrous aggregates because it was not observed without oil.

Because thin sheets with thickness of 0.05-0.1 μm and width of ca. 0.3 μm appeared above the temperature of transition II as observed in Figs.1 and 2, the crystal structure of DUDM may have successive layers and the oil insertion into such inter-layers may take place.

References

1) C. J. Boner, "Manufacture and Application of Lubricating Greases," Reinhold, New York (1954), p.21.
2) T. Tachibana and H. Kambara, Bull. Chem. Soc. Jpn., 42, 3422 (1969).
3) Y. Uzu, Yukagaku, 24, 55 (1975).
4) Y. Ishikawa, T. Nishimi, and T. Kunitake, Chem. Lett., 1990, 25.
5) J-H. Fuhrhop, P. Schnieder, E. Boekema, and W. Helfrich, J. Am. Chem. Soc., 110, 2861 (1988).

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