The Density of Cellulose Nitrate

Cellulose nitrate (N/C) is a partially crystalline polymer. A knowledge of the extent of the crystallinity would be of help in determining the degree of colloidization the polymer undergoes in the presence of plasticizers or solvents. Calculation of the degree of crystallinity could be carried out from the density, provided values were available for the density of completely crystalline and completely amorphous material.

The density of N/C may be expected to vary with the nitrogen content, i.e., the extent of nitration, and with the degree of crystallinity. Urbanski[1] collected available data which showed that the density of N/C nitrated in the fibrous form from cotton was 1.65–1.67 g/cm^3 in the range of 11.6%–13.1% nitrogen content at 15°–20°C. (Throughout the text, it is to be understood that density values are in g/cm^3 or g/ml, which are the same to five significant figures.) The increase with increasing nitrogen content was very small. The commonly accepted value for N/C cast from solutions is 1.58. Although fibrous N/C is partly crystalline as shown by x-ray diffraction patterns, the lowering of the density to 1.58 does not necessarily indicate a more amorphous condition for cast films.

Miles[2] showed that nitrocellulose forms compounds with various solvents, including acetone, presumably by hydrogen bonding. The degree of formation of these compounds depended on the nature of the solvent, the rate at which films were dried, and the concentration of the casting solution. There was evidence that films cast from poor solvents, i.e., butyl acetate, retained less solvent than films cast from good solvents, i.e., acetone. Films of N/C cast from solution and dried at moderate temperatures never have densities greater than 1.60 at 25°C even though analysis shows the absence of solvent. Preparation of solvent-free films is sometimes difficult. Films cast from acetone may retain solvent for months and will have a low density on this account. Soaking these films in methylene chloride for 2 hr followed by drying 2 hr at 80°–85°C was found to allow the films to consolidate and possibly partly crystallize, and the density rose to 1.65.

The density of a completely crystalline polymer may be calculated from x-ray diffraction data. The necessary information for such a calculation has been given for N/C by Peiser, Rooksby, and Wilson.[3] However, published values in the literature[4,5] for the x-ray unit cell density of N/C based on this information are not correct.

The calculation of unit cell densities consists in dividing the sum of the atomic weight units in a unit cell by Avagadro's number and by the volume of the unit cell. If the crystal axes are at right angles to each other, as they are with N/C, the volume of the unit cell is the product of the three cell dimensions as determined from x-ray diffraction data. Peiser et al.[3] calculated the cell dimensions as 25.4 AU by 12.25 AU by 9.0 AU for cellulose trinitrate, giving a volume of 2800.4 AU^3, and 25.4 AU by 12.25 AU by 8.0 AU for cellulose dinitrate, giving a volume of 2489.2 AU^3. The substituted glucose unit weight is 297.14 for the trinitrate and 252.13 for the dinitrate. Peiser et al.,[3] Mathieu,[6] and Meyer[7] agree that the cellulose nitate unit cell contains two polymer chains each five glucose units long making a total of ten glucose units per unit cell. The densities are, therefore,

$$\text{density N/C trinitrate, } 25°\text{C} = \frac{297.14 \times 10}{2800.4 \times 10^{-24} \times 6.0225 \times 10^{23}}$$

$$= 1.762 \text{ g/ml}$$

$$\text{density N/C dinitrate, } 25°\text{C} = \frac{252.13 \times 10}{2489.2 \times 0.60225}$$

$$= 1.682 \text{ g/ml}$$

Cellulose dinitrate contains 11.11% N, and the trinitrate, 14.14% N. For products of intermediate nitrogen content, say, 12.75% N, corresponding to 2.5 nitrate substitutions per glucose unit, one may assume that the unit-cell thickness is halfway between 8.0 and 9.0 AU, as seems actually to be the case,[6] or, better, one may treat the system as a mixture of equal weights of di- and trinitrate.[8] The latter procedure gives a density of 1.721 g/ml for 100% crystalline N/C of 12.75% N content. Figure 1 shows the unit cell density of N/C as a function of nitrogen content. At 12.6% N, the density is 1.717 g/ml. Over the range of ballistic interest from 12.0% to 13.1% N, the density increase is only 1.8%.

Values of the density of a material measure two things; first, the sum of the atomic weights of the

Journal of Applied Polymer Science, Vol. 22, 309–313 (1978)

0021–8995/78/0022–0309$01.00

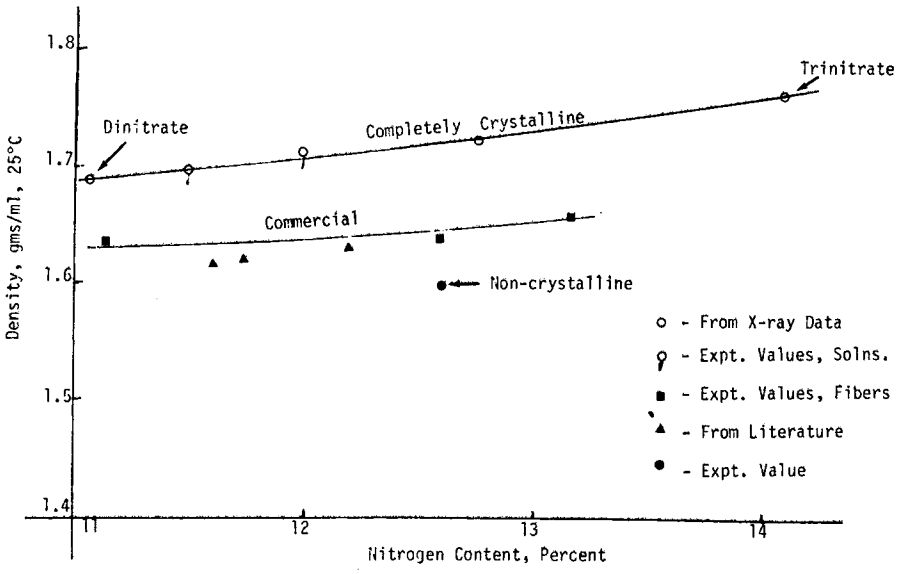

Fig. 1. Density of cellulose nitrate.

atoms in a given volume, and second, the packing of atoms or, if you wish, the lack of voids in the volume. We assume that the most stable crystalline form in a particular environment gives the closest packing of the atoms or the least voids possible, while a random configuration results in voids between and perhaps within molecules and hence a lower density. However, if polymer molecules are randomly arranged in a low molecular weight good solvent, the number of voids will be at a minimum, just as in a crystalline phase of the polymer and polymer densities calculated from the density of a fluid solution will be the same as that found for the polymer crystal. This will be particularly true in the case of N/C, which forms molecular association compounds with its solvents. The corresponding conclusion will not hold true for solutions of low molecular weight compounds in solvents or for solvents alone since the molecules of these materials are free to move under the influence of thermal energy. Densities corresponding to a random configuration of a polymer will be found in solid or viscous media such as polymers above the melting point or in plasticized systems where the plasticizer lowers the melting point to below the temperature where the density is measured.

Using volumetric flasks, it was found possible to measure the densities of 18% solutions in methyl ethyl ketone of two samples of half-sec N/C, Hercules Lot 1352 of 11.60% N content and Lot 3569 of 11.95% N. Five-sec N/C proved to be too viscous for the purpose. Calculated N/C densities at 25°C were 1.697 at 11.60% N and 1.715 at 11.95% N, in agreement with the above values for unit-cell densities.

The density of samples of fibrous N/C was measured by what will be described as the "sink or swim" method. The sample is placed in 5–10 ml of an inert solvent mixture of known density. The composition of the solvent mixture is adjusted until a specimen of the sample neither sinks nor floats. The density of the solvent mixture is then that of the sample. Carbon tetrachloride is a solvent which is almost completely inert toward nitrocellulose. It has a density of 1.584 at 25°C. Mixtures of CCl_4 with bromoform ($d_{25°} = 2.878$ g/cm^3) and with n-hexane ($d_{25°} = 0.6548$ g/cm^3) were employed using the sink-or-swim technique (Fig. 2). In using this method, a number of standard solvent mixtures were made up at various concentrations. By then mixing different solutions, and density desired could be obtained. Measurements could be made on film samples to the third decimal place and on powder samples to the second decimal place. Time of immersion of the film sample to equilibration in the small volume of solvent was only about 2 sec.

Typical reproducibility of densities is shown by values obtained at 25°C on a film of Hercules Lot 2234 N/C, 12.64% N, 10–15 sec viscosity, which were 1.585, 1.575, 1.590, 1.568, and 1.543. Neglecting the last figure, the average value was 1.579, with an average deviation from the mean of 0.007. Using this technique, determinations were made on dry fibrous N/C. Hercules Lot 9183, 11.15% N, had a density of 1.64 at 25°C. Lot 2247L, 12.6% N, had a density of 1.64, and Lot 9038, 13.15% N, had a density of 1.66. These values together with some from the literature values[9] are plotted in Figure 1 and show a slight rise with increasing nitrogen content.

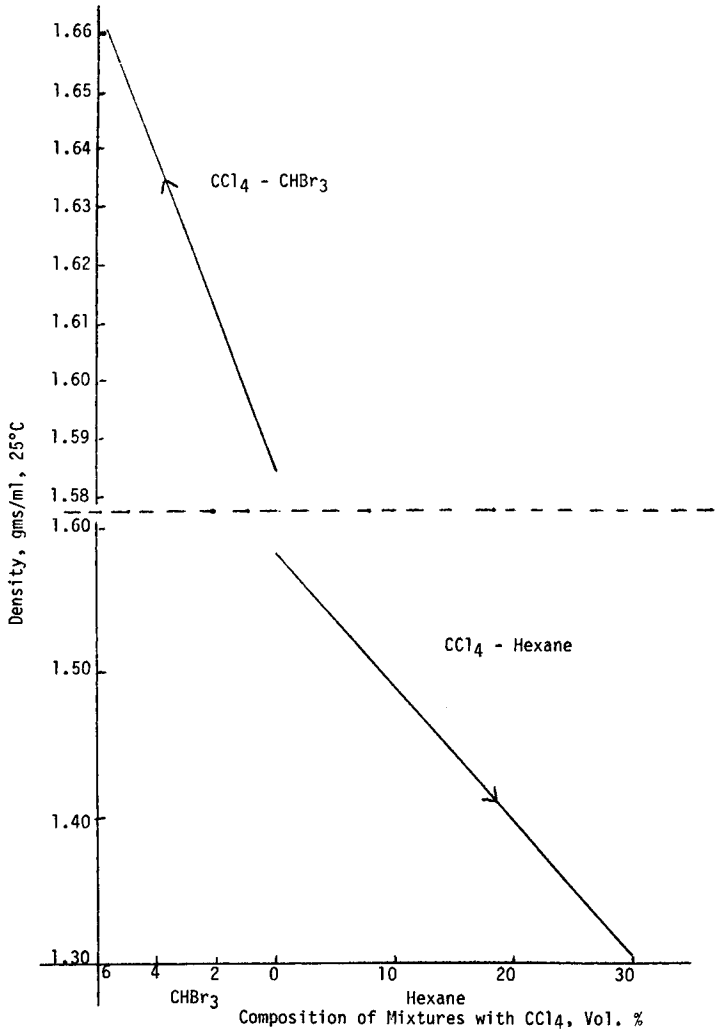

Fig. 2. Solvent mixtures for sink-and-swim method.

Having determined the densities of completely crystalline N/C and of dried as-received fibrous N/C, values for the amorphous material would be desirable. Attempts were made to use plasticized films for this purpose. Films of Lot 2247L N/C, 12.6% N, containing glyceryl triacetate (triacetin) were prepared from butyl acetate solution. Butyl acetate was more readily removed from these films than acetone or tetrahydrofuran. The films were dried at ambient temperature for 1 hr, then with gradually increasing vacuum for 6 hr, and finally with full vacuum for 6 hr. Infrared absorption measurements on one sample showed the absence of butyl acetate. The films contained 13.4%, 22.7%, and 40.0% triacetin as determined by loss in weight on extraction. Densities were 1.52, 1.48, and 1.390, respectively. From the known composition and density of triacetin (1.156 g/cm^3 at 25°C), the density of the nitrocellulose in the plasticized films at 25°C was calculated to be 1.60, 1.61, and 1.607, respectively.

Forziati et al.[10] found that 20-mesh cotton fiber could be converted almost completely from the crystalline state to amorphous cellulose by milling for about 1 hr with steel balls in a vibratory mill at 1800 vibrations per minute. A mill of the type described was not available. However, some N/C was milled in a "Wig-L-Bug," a vibratory mixer used by dentists (Crescent Dental Mfg. Co., 7750 W. 47 St., Lyons, Ill., 40534). The Wig-L-Bug performs 3200 vibrations per minute, and its steel ball is said to strike the steel capsule containing the sample four times during each vibration. Lot 2247L N/C, 12.6% N, 0.2 g with 1.3 ml of FC-75, a liquid perfluorocyclic ether, was agitated for 30

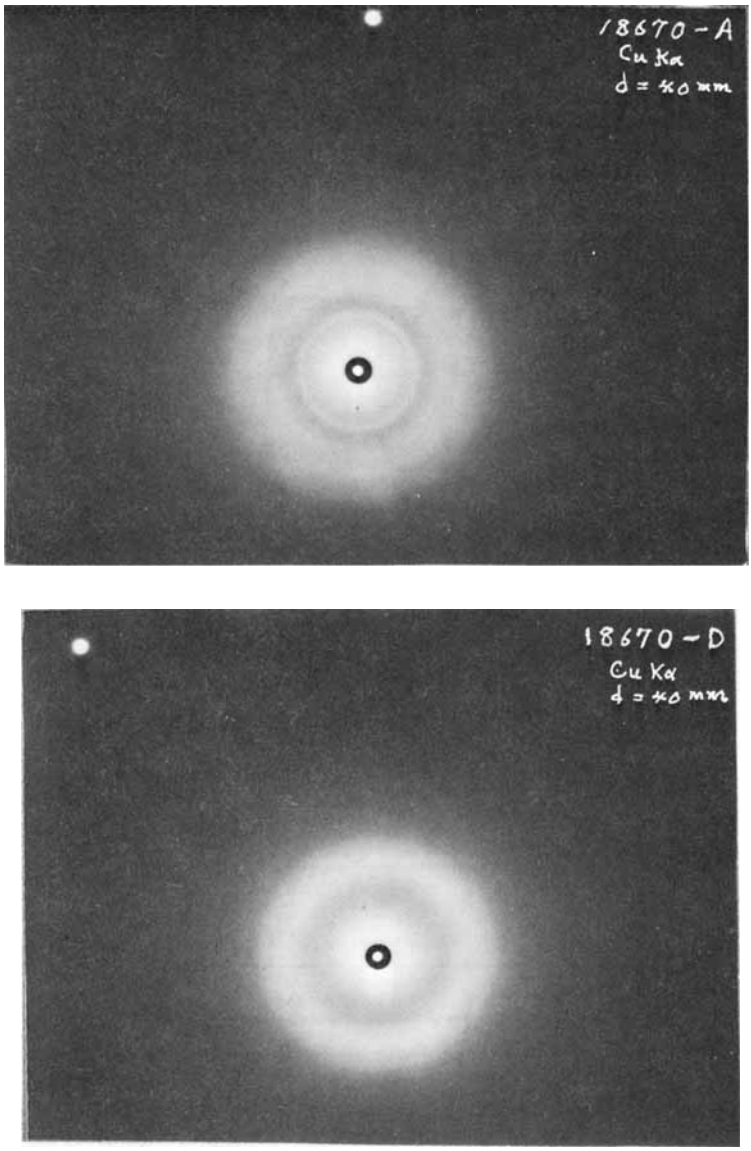

Fig. 3. X-Ray diffraction patterns of N/C fibers and plasticized film.

min in a steel capsule containing a steel ball. Compressed air was blown over the capsule during operation. The experiment was carried out remotely, and no trouble was experienced.

The milled N/C powder was not uniform with respect to density. The particles varied in density from 1.60 to 1.65. Some particles were below 1.61 and some above 1.64, with the bulk in between. The value 1.60 was the lower limit, in agreement with measurements on plasticized samples. The various values for possibly amorphous N/C averaged 1.602.

The film of Lot 2247L N/C, 12.6% N, containing 40.0% triacetin was checked for the presence of crystallinity by x-ray diffraction. The x-ray radiation employed was the $K\alpha_2$ line of copper (wavelength = 1.5416 AU). The specimen was exposed to a narrow x-ray beam emanating from a pinhole slit. The diffracted beam exposed photographic film 40 mm from the specimen. Photographs of the diffraction patterns of dried as-received fibers (18670-A) and of film containing 40.0% triacetin (18670-D) are shown in Figure 3. Sharp bands are apparent in the photograph from the fibers, while the plasticized sample shows quite diffuse rings. The densitometer tracings of the negatives, Figure

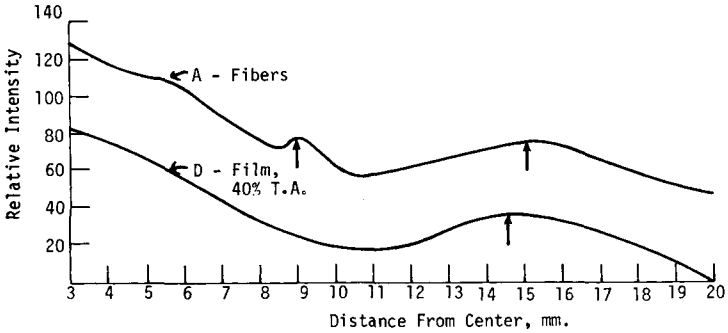

Fig. 4. X-Ray diffraction densitometer traces, 12.6% N nitrocellulose.

4, show disappearance of crystallinity on plasticization. An outer ring at 14.5 mm remains which is characteristic of an amorphous polymer. The value of 1.60 g/ml for the density of amorphous N/C at 25°C is probably nearly correct.

Other photographs and densitometer traces showed that the outer ring became more diffuse and less intense as the nitrogen content decreased from 13.2% to 12.0%, indicating that the nitrocellulose was becoming progressively more amorphous. This qualitative result and calculated atomic spacings agree with Mathieu's findings.[11] However, determination of a quantitative degree of crystallinity in relation to nitrogen content by x-ray methods was prevented by unavailability of nitrocellulose film samples that were completely crystalline.

Using 1.60 as the density of amorphous N/C leads to a value of 40.2% by weight of crystalline phase in as-received N/C of 12.6% N content having a density of 1.645 at 25°C.

This work was carried out under Naval Sea Systems Command Task SEA-331-003-067-1/UF31-332-303, Messrs. John Murrin and Robert Cassel, monitors. The author wishes to thank Dr. F. Wang, Irene Mosher, S. Feldman, and Dr. C. E. Bell for discussions and some experimental work. The opinions or assertions made here are those of the author and are not to be construed as official or reflecting the views of the Department of the Navy or the Naval Service at large.

References

1. T. Urbanski, *Chemistry and Technology of Explosives,* Vol. II, Pergamon Press, New York, 1965, pp. 240–243, 373.

2. F. D. Miles, *Cellulose Nitrate,* Interscience, New York, 1955, pp. 96–97, 124–127, 131–133.

3. H. S. Peiser, H. P. Rooksby, and A. J. C. Wilson, *X-Ray Diffraction by Polycrystalline Materials,* Reinhold, New York, 1960, pp. 538–9.

4. R. L. Miller, and L. E. Nielsen, *J. Polym. Sci.,* **44,** 391 (1960); *ibid.,* **45,** 643 (1961), quoted in P. H. Geil, *Polymer Single Crystals,* Interscience-Wiley, New York, 1963, p. 529.

5. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook,* Interscience, New York, 1966, p. III–30.

6. M. Mathieu, *Compt. Rend.,* **199,** 55 (1934).

7. K. H. Meyer, *Natural and Synthetic High Polymers,* Interscience, New York, 1942, p. 309.

8. F. Happey, *J. Text. Inst. Manchester,* **41,** T381 (1950); F. Happey, J. M. MacGregor, and I. F. Trotter, *Br. J. Appl. Phys.,* **1,** 162 (1950).

9. *Jahresber. Chem. Techn. Reichsanstalt,* **5,** 100 (1926), quoted in T. Urbanski, *Chemistry and Technology of Explosives,* Vol. II, Pergamon Press, New York, 1965, p. 243.

10. F. H. Forziati, W. K. Stone, J. W. Rowen, and W. D. Appel, *J. Res. Natl. Bur. Stand.,* **45,** 109 (1950).

11. M. Mathieu, *Trans. Faraday Soc.,* **29,** 122 (1933).

DAVID M. FRENCH

Propellants Chemistry Branch
Propellants Division
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Received December 8, 1976
Revised February 4, 1977