Effects of Casting Solvents on Structure and Properties of Cellulose Acetate Butyrate Films

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ABSTRACT: A systematic study was carried out to determine the influence of a casting solvent on film properties. Thin films of cellulose acetate butyrate were cast from six different solvents. The results of stress-strain measurements indicate that the films cast from a methylene chloride solution have the best mechanical properties while the films from polar solvents are brittle. To elucidate the solvent effects on the mechanical properties of the films, water vapor permeability, density, and thermal behaviors of the films were investigated. Scanning electron microscopic study was employed to obtain an insight into the film structure.

Introduction

The ever rising demand for polymeric materials to deliver optimum performance in their fields of application is nowhere more pronounced than in the area of coatings. Here, the technology associated with the application and use of coatings is further complicated by rules of environmental conservation, which are narrowing and redefining the range of acceptable solvents. Therefore, attention is focused on the response of polymer film properties to the solvents from which these films are formed. Solvents for coatings have been regarded as a source of unwanted expense and simply as a means to permit application of polymeric materials to a surface. The actual facts show that solvents go far beyond this simple function. Solvents have important effects upon mechanical properties, permeability, and surface properties of films, such as smoothness, gloss, and hardness.

The purpose of this study is to investigate the morphology of the polymer films, cast from various solvents to explain the effect of the nature of solvents on the structure and properties of polymer films. The scope of this research includes studies of physical and mechanical properties, scanning electron microscopic studies, and thermal analysis. Cellulose acetate butyrate (CAB) was chosen for the present study because it is widely used in lacquers and is soluble in various common solvents. CAB also has the advantage of being chemically stable during of the experiments. The solvents employed in the study were methylene chloride, ethyl acetate, dioxane, acetone, nitromethane, and dimethylformamide.

Experimental

Materials. The cellulose acetate butyrate employed in this study was Eastman CAB 381-2 with acetyl content 13.6%, butyryl content 37.0%, and hydroxyl content 1.5%. Viscosity average molecular weight was determined to be $3.6 \times 10^6$ g/mol in acetone. All solvents used in the present study were reagent grade and used without further purification.

Film Preparation. CAB polymer solutions in each solvent were cast on a photographic paper with a doctor blade and allowed to dry for one week. The photographic paper, bearing a polymer film was placed between wet blotting sheets for 30 minutes, then the film was stripped from the photographic paper without subjecting it to any mechanical stresses. The free films were dried
again for at least one week before use. The finished films had a thickness ranging from 25 to 50 μm. In order to find out the effect of the nature of substrates on mechanical properties of films, CAB films were also prepared by casting on a glass plate coated with polyvinyl alcohol (PVA). After the film was allowed to dry for one week, the glass plate was immersed in water for 30 minutes and then the film was freed from the PVA coated glass surface with the aid of a razor blade. The mechanical and physical properties of films prepared in this way were compared with those prepared using the photographic paper method. It was found that the properties of films were not affected by the nature of substrates. Unless otherwise indicated, all data obtained were for the films prepared by the photographic paper method.

**Tensile Tests.** Stress-strain measurements were made with Model 1130 Instron at 25°C and 50% relative humidity. Tensile strips, which were trimmed with a razor blade from the film, were 3.5 cm × 0.5 cm. The initial length between grips was 2 cm and a strain rate was 0.5 cm/min. The experimental results represent arithmetic mean values of at least 15 measurements for each sample.

**Water Vapor Permeability.** Water vapor permeability was measured using an aluminum Payne cup of 10 cm² area and 1.5 cm height. Each cup contained 7 mL distilled water and was sealed by the test film. The tests were conducted in a desiccator using calcium sulfate as a desiccant at 25°C. In all cases, the side of the film originally in contact with the substrate faced water. The cups sealed with the films were weighed everyday and the weight loss was recorded.

**Film Density Measurements.** A small piece of test specimen was placed in a glass vial containing sodium bromide salt solution. The vial was placed in a water bath and maintained at 25°C (±0.01°C). If the film sank, the salt solution of greater concentration was added; if it rose, distilled water was added. The procedure was continued until the specimen remained stationary for at least 2 hours. Then the specific gravity of the salt solution was determined with a pycnometer.

**Residual Solvents and Moisture Contents of Films.** The amount of a residual solvent in the polymer films was determined using a Hewlett-Packard 5710-A Gas Chromatograph equipped with a pyrolysis unit (HP-18580A). A small piece of film was inserted into the pyrolysis chamber, and chamber was heated up to 200°C. The amounts of a solvent in the films were calculated from the peak area by comparing to that for known amount of a pure solvent. The moisture content of CAB films was determined according to the procedure of ASTM D-1364-58 using a Karl-Fisher titrimeter.

**Instrumentation.** Scanning electron micrographs (SEM) were taken of cross-sections of the films by using AMR Model 1000A instrument. The films were fractured in liquid nitrogen to avoid deformation of structures. Calorimetric measurements were made on a Perkin-Elmer DSC-1B. The analyses were carried out in a nitrogen atmosphere with a heating rate 10°C/min.

**Results and Discussion**

Figure 1 illustrates the stress-strain curves for CAB films cast from various solvents. This figure shows some striking effects of a solvent choice on mechanical properties of polymer films. The ultimate elongation of the film cast from a methylene chloride solution is 13 times larger than that from a nitromethane solution, and toughness of the film from methylene chloride is much greater than those from other solvents. This finding indicates that mechanical properties of the polymer films can be modified by just changing a casting solvent. CAB films with the best mechanical properties were obtained from the polymer solution in methyl-
ene chloride out of six casting solvents investigated. Films from ethyl acetate exhibit high elongation to break but low tensile strength, and those from dioxane have high tensile strength but low elongation to break. Brittle films with low tensile strength and elongation to break are obtained from the solutions in polar solvents, such as acetone, nitromethane, and dimethylformamide (DMF). Films from DMF exhibit extremely brittle characteristics and could not be prepared for the tensile test. Since there exist many experimental evidences to show that structures and properties of a cast film may be originated from structures formed in solutions, a thermodynamic quality of the casting solvents and concentrated solution viscosities were investigated. However, it is difficult to find any correlations between the results of the mechanical properties of the films and the solution properties.

To investigate whether differences in the amount of residual solvents or moisture in the cast films affect the stress-strain test results, the residual solvent and moisture contents in the films were determined using the gas chromatography and the water titration method, respectively. As shown in Table I, no correlations are observed between the order of the casting solvents in the results of the tensile test (tensile test order: methylene chloride, ethyl acetate, dioxane, acetone, nitromethane, DMF) and the order of the amount of a residual solvent in the films. Furthermore, the amount of residual solvents in all CAB films seems to be too small to affect the mechanical properties of the films. The moisture content of films was about the same for all films within an experimental error. It is thus evident that the differences in residual solvents or moisture contents in the films are not a source of explanation for the observed differences in mechanical properties of the films cast from different solvents.

In order to obtain an insight into film structure, SEM studies of an edge of the films were carried out. As shown in SEM photomicrographs (Figure 2), the cross-sections of CAB films which were fractured in liquid nitrogen to prevent the deformation of the structure exhibit significant differences along with casting solvents. The films from methylene chloride, ethyl acetate, and dioxane show uniform structures while those from acetone, nitromethane, and DMF contain voids. It may be informative to compare the stress-strain results with the structures revealed by electron microscopic studies. The films from methylene chloride, which have the best mechanical properties, are free of voids. The films from ethyl acetate and dioxane, which also show uniform structures, have high elongation to break and high tensile strengths respectively. On the other hand, the films from acetone, nitromethane, and DMF contain many voids and exhibit poor mechanical properties. These observations indicate that there is a good correlation between the mechanical properties of the films and the film structures revealed by SEM. Especially, ultimate elongations of the films can be correlated very well with the size of voids. As the void size increases, the ultimate elongation of the film decreases. Because a large portion of the films with voids does not contain a polymer to provide a strength, these films have poor mechanical properties. It is thus not surprising that such films turn out to be inferior to the more uniform ones in mechanical terms. Therefore, the reason for the differences in mechanical properties of the films cast from different solvents can be explained by the scanning electron photomicrographs of cross-sections of those films.

The rate of water vapor permeation through CAB films cast from various solvents were studied to understand packing structures of polymer chains. As seen in Figure 3, the water vapor permeability of the films changes with the nature of casting solvents. The rate of permeability were found to be in the following order: the highest for films from methylene chloride, then from ethyl acetate, from nitromethane, and the lowest from acetone. At first glance, these data seem to contradict the results of the SEM studies because the

| Table I. Residual Solvent and Moisture Contents of CAB Films |
|----------------|----------|----------|
| solvent        | residual solvent(%) | moisture(%) |
| methylene chloride | 0.04     | 1.36     |
| ethyl acetate   | 0.01     |          |
| dioxane         | 0.07     | 1.39     |
| acetone         | 0.01     | 1.35     |
| nitromethane    | 0.13     | 1.38     |

films from polar solvents, such as acetone and nitromethane, contain voids but transmit less water than those from methylene chloride which do not contain any voids. However, it may be explained in terms of the differences in submicroscopic features of the polymer matrix. Although films from polar solvents contain voids, the polymer matrix in the film is composed of a dense polymer structure. Since the voids are not interconnected throughout the film, the water molecules must penetrate the film through the polymer matrix. Therefore, the rate of permeation of water molecules through the film is mainly governed by the packed structure of the polymer, that is, the availability of free volume.
in the polymer matrix. Based on such an explanation, it can be deduced from the water vapor permeability results that the films from polar solvents have denser packed structures which are responsible for the low water vapor permeability, while films from methylene chloride have a looser packed structure. This loosely packed structure of polymer chains is responsible for the higher water vapor permeability through the film from methylene chloride, although this film does not contain any voids as shown in the SEM picture.

Table II contains the densities of films from six different casting solvents. Even though differences in the experimental values of film densities are small, such differences were clearly observed in the floatation experiment. It is interesting to see that the lowest density was obtained for the film from methylene chloride and it does not contain any voids, whereas the films from polar solvents have many voids and higher densities. Therefore, in order to have higher densities than the films without any voids, the films from polar solvents must have densely packed structures because such films lose masses by the presence of voids. The result of the film density data correlates very well with the water vapor permeability result. The films from methylene chloride were lower in density and higher in water vapor permeability than the films from polar solvents. As indicated by its lower density, the former can be considered to have more free volume than the latter. Therefore, the more rapid penetration of water molecules through the less dense film is consistent with this viewpoint.

It is worth noting that the order of values of the water vapor permeability and densities for the films is the same for that found in the tensile test and the order of the size of voids in the films. Only the films from nitromethane have somewhat higher values of water vapor permeability and lower densities than those from acetone considering the size of voids. Since films from nitromethane contain much larger voids than those from acetone, it is expected that the voids in the former have a much greater contribution to the results of water vapor permeability and densities than the latter. Therefore, even if the films from nitromethane have a more densely packed structure than those from acetone, the former have higher water vapor permeability and lower densities.

Thermal behaviors of CAB films from various solvents were studied by using DSC (Figure 4). The thermograms of CAB films displayed an endothermic peak whose size and position vary with the casting solvents. The films from methylene chloride show the smallest melting peak area and the lowest melting point, while those from DMF have the largest ones. Since the presence of an endothermic transition indicates that an ordered structure is formed in the films, the film from methylene chloride may have the smallest and least perfect domains of order. The observation of the largest heat of fusion and the highest melting point for the CAB film from DMF suggests that it...
contains the greatest fraction of material in an ordered state and the largest domains of order. These findings are in good agreements with the results of the observations in density, water vapor permeability, and SEM studies. Densely packed structures possess strong intermolecular bondings between polymer molecules and thus reduce the freedom of chain segments and molecular mobility, resulting in the higher transition temperatures. On the other hand, intermolecular forces in loosely packed structures are weak, requiring a low temperature and heat to break these interactions. It is thus clear that the films from methylene chloride, which have the lowest melting point and heat of fusion, have a loosely packed structure; while the films from polar solvents, which have higher melting points and heats of fusion, have denser packed structures. This explanation is consistent with those of water vapor permeability and density. Furthermore, the order of the values of melting point and heat of fusion is exactly the same as that of the void size in the films. As the size of the voids increases, the melting point and heat of fusion of the films increase. These results lead to a conclusion that the larger voids in the CAB films the more tightly packed structure those films have.

Conclusions

The effects of casting solvents on structure and properties have been studied for the CAB films. It appears that the nature of a given solvent for CAB is the prime factor which determines film properties such as mechanical properties, permeability, density, and surface properties. The ultimate elongation and toughness of the films cast from a methylene chloride solution are much greater than those from polar solvents. This finding indicates that mechanical properties of the polymer films can be modified by just changing a casting solvent. In order to elucidate the solvent effects on the mechanical properties of the films, the structure of the films has been investigated using SEM, water vapor permeability, density, thermal behavior studies.

The films from methylene chloride have a uniform structure while the films from polar solvents contain many voids in the films. These SEM studies provide a reason for the differences in mechanical properties of the films from different solvents. Although the films from methylene chloride have a uniform structure, these films have higher water vapor permeability and smaller density compared to the films with voids. Based on these observations, it can be deduced that the films from polar solvents have denser packed structures which are responsible for the lower water vapor permeability and higher densities, while films from methylene chloride have a looser packed structure. This loosely packed structure of polymer chains is responsible for the higher water vapor permeability and lower density, although the films from methylene chloride do not contain any voids. Such an explanation is supported by the results of the DSC studies. The films from methylene chloride exhibit the lowest melting point and heat of fusion indicating a loosely packed structure of polymer chains, while the films from polar solvents show higher melting points and heats of fusion. The results of four different experimental methods, i.e., tensile test, water vapor permeability, density, and thermal analysis are consistent with one another for films from different solvents. Furthermore, the order of values of each test for the films from six different solvents correlates with each other. These data are well correlated to the size of voids in the structure revealed by SEM. Ultimate elongations of the films are also well correlated with the size of voids. As the void size in the films increases, ultimate elongation and permeability of the films decreases while density and melting point increase.

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References


K. Song

(6) R. Katz and B. F. Munk, J. Oil Col. Chem. Assoc., 52, 418
(7) M. Yuseen and H. E. Ashton, J. Coat. Techn., 49 (829),
50 (1977).
(8) Y. Iseno and M. Ngasawa, Macromolecules, 13, 862
(1980).
(9) K. S. Gandhi and M. C. Williams, J. Appl. Polym. Sci., 16,
2721 (1972).
(10) V. E. Dreval, A. Y. Maekin, G. V. Vinogradov, and A.
(11) S. Fakirov, V. Kargin, and N. Bakoev, J. Polymer Sci.
Part C, 16, 891 (1967).
(12) A. L. Volynskii, N. B. Znaienko, and N. F. Bakleyev, Pol-
(13) A. A. Tager, V. E. Dreval, and M. S. Lutski, J. Polymer
(14) P. I. Zubov, L. A. Sakhareva, N. I. Seraya, and V. A.
(15) K. Song, in preparation.