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Cold Water-Soluble Films from Cyanoethylated Polyvinyl Alcohol

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Synopsis

The cyanoethylation of polyvinyl alcohol and the merits of using NaCN as the catalyst are discussed. The application of cyanoethylated PVA to cold water-soluble films is specifically discussed. The use of NaOH catalysis was found to lead to nitrile hydrolysis which resulted in humidity-susceptible films. By using NaCN catalysis, it was found that the reaction temperature and per cent solids could be increased resulting in a decrease in undesirable by-product formation. It was found that films could be cast from cyanoethylated PVA with a degree of cyanoethylation between 5 and 10 mole-% which were readily soluble in cold water and which had physical properties very similar to several commercial water-soluble films.

INTRODUCTION

It is well known that if polyvinyl acetate is completely hydrolyzed, the resulting polyvinyl alcohol is not soluble in cold water, i.e., at 25°C., because hydrogen bonding prevents complete solvolysis by the water molecules.[1] If between about 5 and 20% of the acetyl groups remained unhydrolyzed, then the resulting partially hydrolyzed polyvinyl alcohol is soluble in cold water. Similarly, if other than ester groups are present to interfere with hydrogen bonding and the resulting crystallization of the polymer, the modified polyvinyl alcohol may be soluble in cold water. Hydroxyethylation, for example, will increase the cold water solubility of polyvinyl alcohol.[2–4] Similarly, cyanoethylation of polyvinyl alcohol will produce a polymer with increased water solubility if the degree of cyanoethylation is controlled.[5–8] There has been some qualitative reference in the literature to the properties of films prepared from cyanoethylated polyvinyl alcohol,[6] but no quantitative results have been reported. The work described in this paper is concerned with the preparation of cyanoethylated polyvinyl alcohol and with some quantitative properties of films cast from aqueous solutions of these polymers.

EXPERIMENTAL

Cyanoethylation of Polyvinyl Alcohol

Polyvinyl alcohol, PVA, (medium molecular weight, 99% hydrolysis) was treated with varying amounts of acrylonitrile in aqueous solution using

either NaOH or NaCN as catalysts. Reaction temperatures of 15–70°C. were studied with PVA concentrations varying from 10 to 50% and acrylonitrile from 10 to 50 mole-% of the PVA. The resulting aqueous solutions of cyanoethylated PVA were analyzed by gas-liquid chromatography for oxydipropionitrile and ethylene cyanohydrin. The extent of cyanoethylation was determined by nitrogen analysis of a sample precipitated in acetone. The experimental procedure for a typical preparation is as follows.

Into a 5-liter, three-necked flask equipped with stirrer, thermometer, and reflux condenser containing 1475 g. of deionized water heated to 90–95°C. was added 525 g. (1.19 moles) of polyvinyl alcohol. After complete solution was obtained (1–2 hr.), the temperature was reduced to 70°C. and 2.0 g. (0.38 mole-% based on PVA) of NaCN in 100 ml. of water was added. This raised the pH of the solution from 6.7 to 9.3. Acrylonitrile (63.1 g., 10 mole-% based on PVA) was added over 5–10 min. with rapid stirring. The acrylonitrile initially stayed on the surface of the viscous solution but slowly dissolved. The temperature was kept at 70°C. for 90 min. The pH, now 10.6, was adjusted to 7.7 with 2*N* HCl, and the reaction mixture was diluted with 1400 ml. of water. The per cent solids was determined to be 15.8% and the viscosity 9900 cpoise (Brookfield viscosity). Gas chromatographic analysis showed the presence of 0.10% oxydipropionitrile and 0.40% ethylene cyanohydrin. A sample precipitated in acetone and dried analyzed 1.97% nitrogen, corresponding to 6.43 mole-% cyanoethylation.

Film Evaluation

Films were cast from the aqueous solutions by drying on a laboratory drum caster. Film sheets, 1.5 mils thick and about 4 ft.^{2} in area were obtained and used for evaluation. Water solubility at 28°C., quantitative physical properties, and qualitative film tackiness and flexibility at 2 and 95% R.H. as well as the low temperature impact strength of fabricated packets were determined. The latter was determined by forming packets approximately 2 × 2 × 1 in. deep containing detergent by moisture sealing, conditioning in a freezer at 0°F. in a polyethylene barrier for 24 hr., and then dropping the free packets onto a hard surface from a 6-ft. height. The second-order glass transition temperature was determined by differential thermal analysis.[9]

RESULTS

Results of Cyanoethylation

When NaOH was used as the catalyst in concentrations of 1–5 mole-% (based on PVA) cold water-soluble films could be cast from resins containing between 2 and 30 mole-% cyanoethyl groups. Films were cold water-insoluble above and below this range of cyanoethylation. It was found that if the reaction was run at elevated temperatures, i.e., 50–60°C., there was nitrile hydrolysis (observed by analysis of the infrared absorption

of thin films), and the resulting carboxylate-containing films were usually brittle at low and very tacky at high relative humidity. In order to prevent hydrolysis, lower temperatures had to be used, which meant that relatively long reaction times (8 mole-% cyanoethylation required 16 hr. at 25°C. with a 11% PVA solution containing 25 mole-% acrylonitrile) and low per cent solids were necessary. The latter was required in order to maintain a workable viscosity at this temperature. As a result of the high water-to-PVA ratio, it was found also that cloudy films resulted from the high percentages of oxydipropionitrile (5%) and ethylenecyanohydrin (10%) that were formed during the reaction. Reprecipitated polymers would yield clear films.

The disadvantages found with NaOH were eliminated by using NaCN as the catalyst. Reaction temperatures at least as high as 70°C. could be used without any nitrile hydrolysis. Higher per cent solids (up to 50%) could then be handled, reaction rates were improved (8 mole-% cyanoethylation in 60 min. at 70°C. with a 24% PVA solution containing 15 mole-% acrylonitrile), and by-product formation was reduced (less than 0.5% oxydipropionitrile and ethylene cyanohydrin). Clear films could be cast from these products without any purification.

Results of Film Analysis

As the extent of cyanoethylation was increased, the tensile strength of the film decreased and the flexibility increased, i.e., the modulus decreased. The tear strength of the film also increased. Table I summarizes the physical properties of some representative films that were evaluated.

Above about 10 mole-% cyanoethylation, films became tacky and weak after conditioning at 95% R.H. for 24 hr. It was concluded that between 5 and 10 mole-% was the preferred range to yield flexible films that were cold water-soluble (a 2 in. × 2 in. × 1.5 mil film was completely soluble after 3 min. in 25°C. water) and not adversely affected by high or low humidity.

TABLE I
Physical Properties of Cyanoethylated Polyvinyl Alcohol Films

Cyanoethylation, mole-%	Tensile strength at break, psi[a]	Elongation at break, %[a]	Initial modulus, psi × 10^{-6}[a]	Elmendorf tear strength, g./mil.[b]
0 (PVA)	8200	3	0.50	30
3.6	6010	233	0.02	158
6.4[c]	6470	365	0.02	>1600[d]
10.3	3400	204	0.003	>1600[d]
15.2	3190	298	0.02	>1600[d]
20.7	3755	321	0.001	>1600[d]

[a] ASTM Standards, Pt. 9, Designation D882-61T, 1961.
[b] ASTM Standards, Pt. 9, Designation D1922-61T, 1961.
[c] NaCN catalyst, others used NaOH.
[d] Too extensible to measure.

Several packets containing detergent were fabricated by vacuum drawing one sheet of film into a cavity and moisture sealing another sheet after adding detergent. After sealing in a polyethylene barrier to retain the ambient relative humidity, the packet was conditioned in a freezer for 24 hr. The packet was then released from the polyethylene from a 6-ft. height, allowing it to fall onto a hard surface. For three different series of 10 packets there were no film failures in this test.

The second-order glass transition temperature of a 7 mole-% cyanoethylated film that was reprecipitated and rigorously dried over P_2O_5 was determined to be 45°C. The T_g of a similarly treated film cast from PVA was found to be 62°C. The latter is in fair agreement with the value (64°C.) reported by Ito and co-workers,[10] but the value determined for the cyanoethylated sample is about 15°C. lower than that extrapolated from the measurements made by Ito for the same degree of cyanoethylation. Most likely this difference is due to the method of measurement, i.e., volume–temperature versus differential thermal analysis, or to remaining traces of water which very effectively lower the T_g.

DISCUSSION

The results of this study indicate that completely hydrolyzed PVA can be made readily cold water-soluble by converting 5–30% of the hydroxyl groups to cyanoethyl ether groups. For unsupported, cold water-soluble films, it is preferable to use NaCN as the catalyst rather than NaOH because the latter necessitates longer reaction times, lower temperatures, and less concentrated solutions if undesirable hydrolysis of the nitrile group is to be prevented. Higher overall conversions of acrylonitrile have been realized with NaCN (75%) than with NaOH (50%) also, and the use of NaOH leads to by-products which are incompatible and cause film cloudiness.

TABLE II
Physical Properties of Water-Soluble Films[a]

Film	Tensile strength at break, psi	Elongation at break, %	Initial modulus, psi × 10^{-6}
Commercially available water-soluble film based on poly-(vinyl alcohol)	6350	330	0.01
Another commercially available water-soluble film based on polyvinyl alcohol	6300	252	0.03
Cyanoethylated PVA[b]	6600	276	0.015
Film prepared from 88% hydrolyzed polyvinyl acetate, medium molecular weight	6480	79	0.55

[a] Physical properties as determined in these laboratories.

[b] 6.4 mole-% cyanoethylation, prepared with NaCN catalyst.

With NaCN catalysis, a degree of cyanoethylation of about 6 mole-% offers a cold water-soluble film which remains flexible at low humidity and does not become tacky at high humidity. A comparison of physical properties shows cyanoethylated PVA to have properties very similar to those found for several commercial, water-soluble films (Table II). The "internal" plasticizing effect of the cyanoethyl group can be seen when the observed per cent elongation and modulus are compared with similar values obtained for PVA containing 12% residual acetyl groups.

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Résumé

On discute de la cyanoéthylation de l'alcool polyvinylique et des avantages de l'emploi du cyanure de sodium comme catalyseur. On a discuté spécialement de l'application du PVA cyanoéthylé comme films solubles à froid dans l'eau. On a trouvé que l'emploi de NaOH comme catalyseur conduisait à l'hydrolyse de la fonction nitrile pour former ainsi des films sensibles à l'humidité. On a trouvé qu'en employant du NaCN comme catalyseur la température de réaction et le pourcentage en solide pouvaient être augmentés, ce qui provoque une diminution de la formation de produits secondaires indésirables. On a trouvé que des films pouvaient être obtenus à partir de PVA cyanoéthylé avec un degré de cyanoéthylation situé entre 5 et 10 moles pour cent; ils sont facilement solubles dans l'eau froide et possèdent des propriétés physiques très semblables à plusieurs films commerciaux solubles dans l'eau.

Zusammenfassung

Die Cyanoäthylierung von Polyvinylalkohol und die Vorteile, für diesen Zweck NaCN als Katalysator zu benützen, werden diskutiert. Die Anwendung von cyanoäthyliertem PVA für kaltwasserlösliche Filme wird im besonderen diskutiert. Die Verwendung von NaOH als Katalysator führte zur Nitrilhydrolyse, wobei feuchtigkeitsempfindliche Filme erhalten wurden. Bei NaCN-Katalyse konnte die Reaktionstemperatur und der Festkörpergehalt erhöht werden, was zur einer Abnahme der Bildung unerwünschter Nebenprodukte führt. Im kalten Wasser leicht lösliche Filme, die den handels üblichen wasserlöslichen Filmen sehr ähnliche physikalische Eigenschaften besassen, konnten aus cyanoäthyliertem PVA mit einem Cyanoäthylierungsgrad zwischen 5 und 10 Mol-% gegossen werden.

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