Critical Molecular Parameters for Fibrillation of Poly(vinyl alcohol) during Saponification

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Abstract

To identify the effect of critical molecular parameters of poly(vinyl alcohol) (PVA) such as syndiotacticity, degree of saponification, and molecular weight on the change of morphology, we prepared various PVAs. Also, the structures of these PVA were investigated.

Introduction

Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible, and biodegradable polymer, which is widely employed in various applications such as fibers for clothes and industries, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials.

Since the first work by Herrmann and Haehnel, high strength and high modulus PVA fibers have been achieved by zone drawing, crosslinking and wet spinning, crystal mat drawing, and gel drawing, all of which are relatively complex multi-step processes. Recently, Lyoo *et al.* reported that PVAs with well-oriented fibrillar structures are formed by saponification of poly(vinyl pivalate) (PVPi) under low shear conditions (stirring), provided that the microstructure is significantly syndiotactic. These PVAs had a number-average degree of polymerization (P_n) > 4500, and formed fibrils that were similar in appearance to native cellulose fibers. Lyoo *et al.* showed that these structures were formed only by PVAs that were significantly syndiotactic. A range of PVAs were produced by saponification of poly(VPi/vinyl acetate) P(VPi/VAc) in which the syndiotactic diad (*S*-diad) content ranged from 52-63%, and it was found that fibril formation occurred only for *S*-diad contents greater than ~57%. At lower *S*-diad contents (52-55%) only shapeless, globular morphologies were observed [1,2].

Also, rheological and morphological properties as well as crystal characteristics of syndiotacticity-rich ultrahigh molecular weight PVA were studied with consideration of degree of saponification (*DS*). The well-oriented microfibrillar structure was observed in the syndiotacticity-rich PVA with high *DS*, which resulted from the hydrogen bonding generation during saponification [3].

It is reasonable to expect that *in situ* fibrillation during stirred saponification will depend on molecular weight, and in the present paper we have extended the above work to consider the effect of lower molecular weight on the fibrillation process. PVAs with P_n in the range 330-820 and *S*-diad contents 61-63% were prepared by saponification of PVPis that had been synthesized at different temperatures with different amounts of initiator, using tetrahydrofuran (THF) as solvent because of its high chain transfer constant. It will be seen that a fibrous morphology analogous to that for the high molecular weight materials previously studied was obtained only for molecular weights in excess of $P_n \approx 800$. As P_n declines, there is a steady change in morphology to the more globular, shapeless morphology typical of higher molecular weights closer to random microstructure [4].

Experimental

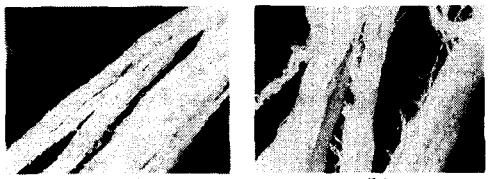
Bulk copolymerization of VPi and VAc, ultraviolet-ray-initiated bulk polymerization of VPi, and solution polymerization of VPi in THF and successive saponification of P(VPi/VAc) and PVPi were conducted. [1-4]

The surface morphology of PVA was examined by Olympus BH-2 optical microscope at magnify-cation x 200. Wide-angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) patterns were recorded on Kodak Direct Exposure X-ray film using Ni-filtered CuKα radiation and pinhole collimation under vacuum.

Results and Discussion

Recently, we prepared novel syndiotactic PVA microfibrils using optimum combination of

stereoregularity, *DS*, and molecular weight of PVA during saponification. Firstly, the structures of these PVAs show a consistent sharp transition between 55 and 56% *S*-diad content. Specimens with lower *S*-diad contents had shapeless morphologies, but at 56% *S*-diad content the polymers were fibrous, with a higher degree of crystallinity and orientation of the crystallites. At *S*-diad content of 55.3% (Fig. 1a), the fully saponified products had a fiberlike appearance. Fibrous morphology is also obtained for higher *S*-diad content (Fig. 1b) with the general trend that the fibrils become longer and narrower as the degree of syndiotacticity increases.



(a) (b)

Fig. 1. Optical micrographs of PVAs with different *S*-diad contents: (P_n, *S*-diad content, *DS*) (a) 7800, 55.3%, 99.9%; (b) 7800, 56.2%, 99.9%.

Secondly, the microfibrillar structure of the PVA with *DS* of 90.3% (Fig. 2b) is more developed than that of the PVA with *DS* of 87.8% (Fig. 2a). The fibrous morphology developed as *DS* increased with trends that the fibrils become longer and narrower. Also, a strong elliptical scattering was observed due to the presence of regular and elongated microvoids. It is interesting that although two PVA specimens in Fig. 2a and 2b had similar fibrillar morphologies, the tensile strength of the PVA with *DS* of 90.3% (over 12 g/d) was much higher than that of 87.8% (easily breaking into pieces and nearly no tensile strength). By drawing the PVA fibril, the tensile strength reached the very high value of over 45 g/d (5.5-6.0 GPa).

(a) (b)

Fig. 2. Optical micrographs of PVAs with different *DS*s: (P_n, *S*-diad content, *DS*) (a) 14000, 64.5%, 87.8%; (b) 14000, 64.5%, 90.3%.

Thirdly, the PVA with P_n of 800 and *S*-diad content of 62.5% (Fig. 3b) revealed a well-defined fibrous morphology. Each fiber was composed of a number of microfibrillar fibers, which is well-revealed in SAXS and WAXD patterns. As the P_n of PVA decreased, some morphological change was observed. The specimen with P_n of 660 and *S*-diad content of 62.4% formed a longitudinally developed precipitate during saponification. Distinct difference of this specimen is that it did not exhibit a fibrous morphology nor include a fiber-like inner structure. Considering that both PVA (Fig. 3a and 3b) have the same syndiotacticity, the morphological difference may arise from the molecular weight of PVA. With syndiotacticity of 62%, the microfibrillar PVA fibers were essentially obtained when the P_n is higher than 800.

(a) (b)

Fig. 3. Optical micrographs of PVAs with different molecular weights: (P_n, *S*-diad content, *DS*) (a) 660, 62.4%, 99.9%; (b) 800, 62.5%, 99.9%

Conclusions

As the *S*-diad content, *DS*, molecular weight of PVA increased, microfibrillar morphology was developed, indicating that stereosequence, *DS*, and molecular weight have a significant role in *in situ* fibrillation of PVA. It is expected that these PVAs can be used as environmentally friendly fibers such as water-soluble fiber for non-woven fabric, embolic fiber for cancer-cell killing, ultra-low denier fiber, and pulp for paper based product owing to its high fineness, excellent alkali resistance, good biocompatibility, and good binding property.

References

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