

A STATISTICAL ANALYSIS OF INTERACTION BETWEEN CRYSTALLINITY AND ELONGATION IN PLASTICIZED BIOPOLYMER

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Introduction

Biopolymer such as amylose starch, when mixed with plasticizers has excellent potential in forming thin film for various food and packaging applications. In this study, the influences of moisture content, plasticizer type and content have been investigated on the tensile elongation and crystallinity of starch biopolymeric material. Biopolymeric samples prepared with starch (LA) and two types of plasticiser with different molecular weights, namely Glycerol (GLA, Mwt - 92) and Xylitol (XLA, Mwt - 152), were employed, which also have different number of hydroxyl (OH) groups (3 for glycerol and 5 for xylitol). A statistical analysis based on a design of experiment (DoE) was performed on the sample responses (i.e. elongation and crystallinity) by varying the moisture content, plasticizer type as well as plasticizer content.

Experimental

Materials and Testing Procedures

The raw starch and plasticizers were added on a dry basis. For example, GLA10 contained 90 grams of LA starch and 10 grams of glycerol in dry solid form. These mixtures were first dry mixed using Hobart planetary mixer (Model No: N50-619, Hobart, Australia) and subsequently extruded in a counter-rotating twin-screw extruder ZSK-16 (D=16 mm, L:D=16, Brabender®, Duisburg, Germany) at 140 rpm in the temperature profile of 90/137/110°C. Extruded samples were allowed to cool to room temperature, ground to fine powder using bench-top food grinder, and sealed in polyethylene bags before subjected to control Humidity conditions.

Design of Experiments

Table 1 Factors and levels in DoE work

| Factor | Description | Level 1 | Level 2 |
|--------|---------------------------|---------|---------|
| A | Moisture content (%) | 13 | 96 |
| B | Plasticizer type | GLA | XLA |
| C | Plasticizer content (wt%) | 5 | 20 |

Taguchi DoE [1,2] is widely used to plan and optimize the processing parameters in the modern manufacturing. This work focused on a 2 level

fractional factorial DoE analysis with the three main effects such as moisture content (Factor A), plasticizer type (Factor B), plasticizer content (Factor C) and four additional interactions (Factors AB, AC, BC, ABC) as shown in Table 1. Totally 8 runs of experiments (L_8) have been performed to replace the conventional 128 full factorial ones. In order to maximise the tensile elongation as one of DoE major responses, the “larger-the-better” characteristic is utilized with the signal-to-noise (S/N) ratio expressed as

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (1)$$

A “smaller-the better” characteristic also applies for the minimisation of crystallinity as another response with S/N ratio given by

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right) \quad (2)$$

where n is the number of samples in each trial and y is measured response values, namely the elongation and the crystallinity. Mathematically the greater S/N ratios reflect the more robust quality in DoE work irrespective of the categories of characteristics.

Analysis of Variance (ANOVA)

Instead of using the conventional ANOVA table and F-tests, a special Pareto ANOVA technique [2] is employed to analyze the significant factorial effects on the performance characteristics of the parameter design. The contribution percentage (CP) can be calculated as

$$CP(\%) = \frac{S_i}{S_T} \times 100\% \quad (3)$$

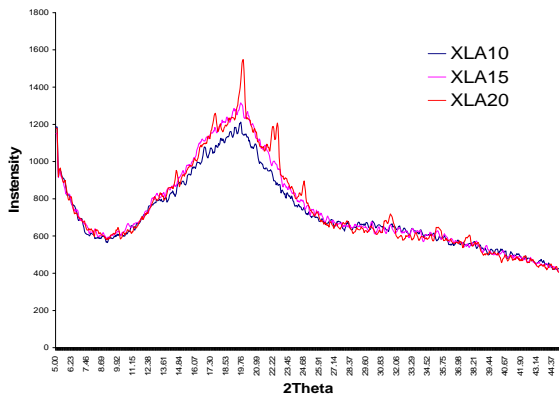
where S_i is the sum of squared difference from the variability of S/N ratios for the i th factor ($i=1, 2, \dots, n$) and S_T is the total sum of squared difference for all factors. The significant factors are gauged on the basis of cumulative CP of about 90% along with the technical and economic considerations for non-significant factors.

Results and Discussion

Statistically, plasticizer content has greater significance than plasticizer type for both elongation and crystallinity. B pattern (peak at $2\theta \sim 20^\circ$) has been found in all XRD results with XLA contents of

10, 15 and 20 wt%, Figure 1. In terms of increasing the tensile elongation, both Factors C and A show significant influence with CP values of 43.0 and 38.7%, respectively, Fig.2(b), followed by interaction AC (CP: 8.7%) as the third significant factor. As expected, the generally better ability to increase the elongation from XLA becomes manifested with the higher *S/N* ratio for B₂ (Factor B and Level 2), Figure 2(a), and this ability is more visible at lower water activity. An optimal combination of factors of A₂B₂C₂ can be then attained with the maximum elongation of 68.58%.

Fig.1 XRD pattern of LA samples plasticized by xylitol.



To minimise the crystallinity, Factor A is found to be the most prevalent factor (CP- 68.9%), Figure 3. Factor C and its interaction with moisture content (AC) become similarly less significant (CP values of 11.6 and 11.2%, respectively).

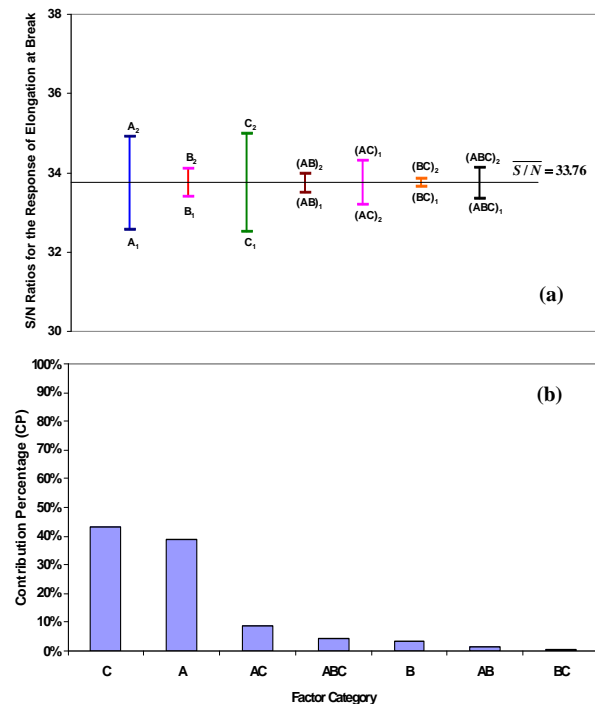


Fig.2 DoE work for the response of tensile elongation: (a) estimated factorial effects; (b) contribution percentage in ANOVA.

The overall crystallinity values show that xylitol is able to suppress crystallinity as compared to glycerol. An optimal combination of factor of A₂B₁C₂ is also determined with the minimum degree of crystallinity of 4.50%. Due to its smallest size, water is found to be the most significant factor, as expected, since its size allows greater interaction with the starch.

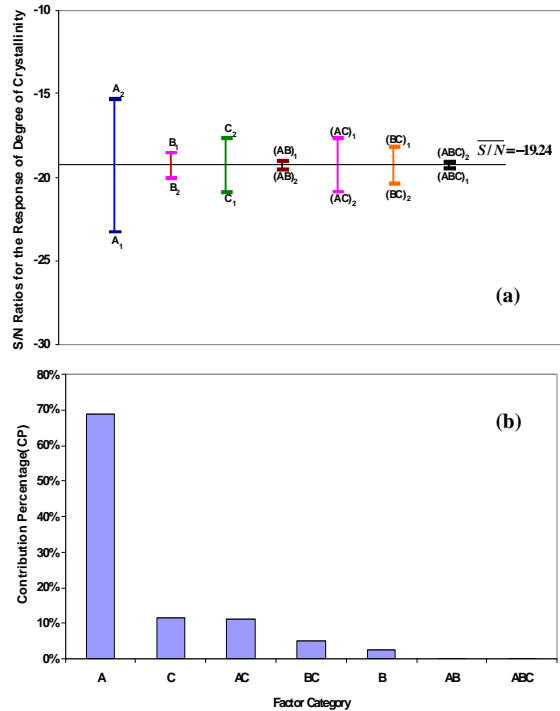


Fig.3 DoE work for the response of degree of crystallinity: (a) estimated factorial effects; (b) contribution percentage in ANOVA.

Conclusion

In terms of elongation and crystallinity, the statistical DoE analysis has provided a quantitative ranking of moisture and plasticizers and overall, the moisture content plays the predominant role in these two responses, followed by the plasticizer content, as expected. In addition, the plasticizer content also dominates the elongation response compared to the degree of crystallinity. Interestingly, plasticizer type is shown to have a minor effect in its manifestation on these responses, but multicomponent interaction between water, plasticizers and amylose chains, has shown significance in crystallinity, which is likely as they are strongly hydrophilic.

References

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