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Pyrolysis Behaviors and Thermostability of Polyglycerols and Polyglycerol Fatty Acid Esters

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The weight loss behavior of commercial polyglycerols (PG) and PG with various degrees of polymerization, and polyglycerol fatty acid ester (PGFE) with various carbon numbers of acyl group and various degrees of esterification was studied by means of dynamic programmed thermogravimetry (TG). The relationship between the ratio of weight loss at various temperatures and component compositions was also studied by PG. The thermostability of PGFE was evaluated from the temperature of weight loss initiation in dynamic programmed TG, and from the decomposition time-required for a 5% weight loss in isothermal TG. The results are summarized as follows:

- 1) The temperature of weight loss initiation shifted to the higher temperature side and thermostability was enhanced with increase in the degree of polymerization in the programmed TG of PG. Commercial PG, after removal of water, showed characteristic weight loss pattern depending on the composition of polymerization.
- 2) The ratios of weight loss of PG at room temperature~150°C, 150~250°C, 250~300°C, and 300~350°C were also correlated with the content of water, monoglycerol, the sum of di- and triglycerols, and the sum of tetra- and pentaglycerols in programmed TG, respectively.
- 3) The temperature of weight loss initiation shifted slightly to the higher temperature side with increase in the carbon number of the acyl group in the programmed TG of PGFE. The TG curves from 300 to 400°C showed characteristic weight loss patterns for PGFE with various degrees of esterification, but there was no correlation between the weight loss pattern and degrees of esterification.
- 4) The heat resisting time of PGFE at various temperature was essentially independent of the carbon number of the acyl group as was observed in isothermal TG. However, heat resisting time was reduced and thermostability decreased with increase in the degree of esterification.

1 Introduction

Polyglycerols (PG) have been used as emulsifiers for food for a long time in western countries. However, the use of PG as food additives are not approved in our country. Thus, the major portion of PG produced are used as the starting materials in the production of polyglycerol fatty acid esters (PGFE). In the fields other than food industry, PG have been used as raw material of cosmetics such as creams or the like because these are the excellent humectant.

PGFE, synthesized from PG, are the raw materials for the production of various products possessing the properties either hydrophilic or lipophilic, produced by changing the degree of polymerization and esterification, and kinds of

acyl groups. PGFE possess property with excellent safety¹⁾, and therefore, 80% or more of them are consumed for food industry. PGFE are useful not only for the emulsifiers but also for the viscosity depressants as well as for the crystallization controllers^{2),3)}. Furthermore, PGFE are expected to be used in the field of cosmetics, drugs, and polymer²⁾ because of their excellent acid-resistance, hydrolysis-resistance, and heat-resistance properties. GLC⁴⁾ and HPLC^{2),5)} are used to determine the composition of PG and PGFE in order to evaluate their quality. However, the PG which can be analyzed accurately at present are only up to pentaglycerol by GLC, while up to decaglycerol by HPLC²⁾. On the other hand, the PGFE which can be analyzed by GLC are limited only to mono- and

diester of triglycerol even if these are converted in to the TMS derivatives²⁾, whereas the PGFE can be analyzed by HPLC only roughly up to the triester. We have, therefore, utilized the dynamic programmed thermogravimetry(TG) for the analysis of PG and PGFE in this study in order to determine the polymer compositions of PG, and to estimate the carbon number of acyl groups and the degree of esterification of PGFE on the basis of the initial temperature of weight loss and the weight loss behaviors on TG curve. Furthermore, we have examined the adaptability of TG for the qualitative evaluation of PG and PGFE in their manufacturing process. In addition, the thermostabilities of PGFE were examined by isothermal TG as described previously⁶⁾ since PGFE are used as antiaging agent or dough modifiers in the production of bread and cakes.

2 Experimental

2.1 Materials

Four commercial PG used possess different degrees of polymerization : PG-A, B, C and D. **Table-1** showed the water content of these samples determined by the Karl-Fischer method⁷⁾ and polymer compositions determined by HPLC equipped with an aqueous GPC column (Shodex, S-801). These PG samples with different degree of polymerization were prepared from the commercial PG-A, B and D by fractionating their major peak in the HPLC mentioned above. The three samples thus prepared were the mixtures composed of di- and triglycerols, tetra- and pentaglycerols, and octa-, nona-, and decaglycerols, respectively. The purity of component polyglycerols in each mixture were above 90% as determined by HPLC. The monoglycerol examined simultaneously was that of the biochemical reagent grade (Nakarai Chemical Co., Kyoto).

Three PGFE having lauric acid(PG-C12), palmitic acid(PG-C16), and stearic acid(PG-18) as acyl groups in the monoacyl ester portion were used as the samples. The saponification value of each sample determined by JOCS Standard Method⁸⁾ was almost identical with the calculation value of the corresponding monoester. For the PGFE with different degree of esterification, five PGFE having stearic acid as acyl groups were used as the samples. The PGFE having

saponification value of 76, 97, 131, 154, and 167 were referred to as monoester (PG-Mo), diester (PG-Di), triester (PG-Tr), pentaester (PG-Pe), and heptaester (PG-He), respectively. After saponification of PGFE with the conventional method, a portion of PG was analyzed by HPLC, whereas a portion of fatty acids was analyzed by GLC as the methyl ester derivatives. The PG was found to have the major component of hexaglycerol (above 85%) in each PGFE. Regarding the constituent fatty acids, lauric acid in PG-C12 was above 99%, palmitic acid in PG-C16 was above 96%, and stearic acid in PG-C18, PG-Mo, PG-Di, PG-Tr, PG-Pe and PG-He were above 97%. These PGFE were courteously donated as the gifts by Sakamoto Chemical Industries Co. (Osaka).

2.2 Analytical method

The instrument and their operating conditions of the dynamic programmed TG and the isothermal TG used in this study were the same to those previously reported⁶⁾. The heat resisting time in isothermal TG was expressed in the decomposition time from initial to that with 5% of weight loss after reaching the temperature of determination, and hence, the thermostability could be evaluated by the heat resisting time, as described previously⁶⁾. The determination temperature was lowered by every 10 or 5°C from 265°C.

3 Results and Discussion

3.1 Pyrolysis behavior of PG in dynamic programmed TG

3.1.1 Difference due to degrees of polymerization

Fig.-1 showed TG curves of the monoglycerol, and the mixture of di-and triglycerols, tetra- and pentaglycerols, and octa-, nona-, and decaglycerols provided by HPLC fractionation. The weight loss of the monoglycerol initiated at 53°C which was unexpected since the boiling point of monoglycerol is 290°C⁹⁾. The water content of monoglycerol determined by Karl-Fischer method⁷⁾ was about 2.7%. The ratio of weight loss at the temperature range of room temperature ~ 100°C, *i.e.*, the boiling point of water, calculated from TG curve was about 1.5% and this was lower than that determined by Karl-Fischer method. This might be due to the fact that the evaporation of water was attained not completely

Table-1 The water content and polymer composition of commercial polyglycerols.

	Water content (%)	Polymer composition (%)				
		mono	di+tri	tetra+penta	hexa+hepta	≥octa
PG-A	1.2	7.2	70.5	22.3	0.0	0.0
PG-B	4.8	9.0	24.2	32.6	23.6	10.6
PG-C	9.8	1.4	10.3	27.2	34.1	27.0
PG-D	10.7	4.1	15.0	17.4	21.2	42.3

Fig.-1 TG curves of glycerols with various degrees of polymerization.

since the determination time of TG from room temperature to 100°C was short for about 14 min. However, this weight loss might be caused by the evaporation of water, similar to the case of household margarines reported previously¹⁰⁾. After the evaporation of water, the weight loss of the monoglycerol initiated at about 150°C, proceeded most rapidly at above 180°C which was caused by the volatilization of monoglycerol, and was finished at 248°C. In the case of the fraction of di- and triglycerol mixtures, the weight loss initiated at 167°C and proceeded most rapidly at about 250°C. This weight loss pattern was a simple, and similar to that monoglycerol. The weight loss of tetra- and pentaglycerol mixture, and octa-, nona-, and decaglycerol mixture initiated at 223°C or 262°C, respectively. On the former mixture, the weight loss behavior from the initial to that with 50% of weight loss proceeded slowly, than those of the monoglycerol and the other two fractions of mixtures. The weight loss of the fraction of tetra- and pentaglycerol mixtures, and the octa-, nona-, and decaglycerol mixtures proceeded slowly after 90% of weight loss, than those of monoglycerol and the fraction of di- and triglycerol mixtures. The weight loss pattern of these fractions were found to be somewhat complicated.

Thus, initial temperature of weight loss and the

Fig.-2 TG curves of commercial polyglycerols.

TG curve of PG were shifted to higher temperature side, accompanied with the increase of the heat resisting temperature, and the increase of degree of polymerization.

Fig.-2 showed the TG curves of the commercial PG. The weight loss of each commercial PG began at a low temperature, which might be caused by the evaporation of water which contained. After the completion of the evaporation of water, the initial temperature of weight loss of each PG was indistinguishable from one another until it was initiated weight loss caused by the volatilization of monoglycerol and polymer of low degrees of polymerization. However, the weight loss behaviors of individual PG were differed by the degree of polymerization. The weight loss of PG-A proceeded rapidly within a temperature range of 250~320°C. On the other hand, the weight loss of PG-B containing a somewhat larger amount of monoglycerol than PG-A became rapidly at about 250°C and proceeded most rapidly within a temperature range of 350~400°C. The weight loss of PG-C containing the smallest amounts of mono-, di- and triglycerol was the slowest until below 300°C and proceeded rapidly in the temperature region about 300°C. The TG curve until the temperature of 50% of weight loss for PG-D containing more mono-, di- and triglycerol than PG-C, was located at lower temper-

ature side when compared with PG-C. However, because of a large amount of components of higher degree of polymerization than PG-C, the TG curve of PG-D in high temperature region over temperature of 75% of weight loss was shifted to higher temperature side.

As mentioned above, the weight loss behavior of individual commercial PG differed characteristically by their water content and polymer composition with one another. The weight loss behavior after the evaporation of water and the temperature of 50% of weight loss were well agreed with the data reported by Shioyama *et al.*¹¹⁾ who examined anhydrides of commercial PG by TG.

3.1.2 Simultaneous determination of water and monoglycerol in PG

The samples by adding 4.0 to 21.7% of water and 9.5 to 24.2% of monoglycerol to the commercial PG-A, were determined the content of water and monoglycerol by TG. **Fig.-3** showed the relationship between the amounts of water added and the ratio of weight loss at the temperature ranges of room temperature to 125, 150, and 170°C. In the dynamic TG of PG with different degree of polymerization, the initial temperature of weight loss and the temperatures of 25, 50, and 75% of weight loss were significantly different from one another. The evaporation of water was not finished at a temperature range of room

Fig.-3 Relationships between the amount of water added and the ratio of weight loss at each temperature range.

Fig.-4 Relationships between the amount of monoglycerol added and the ratio of weight loss at each temperature range.

temperature ~125°C, and therefore the ratio of the weight loss had somewhat lower value. The ratio of weight loss until 175°C had somewhat higher value because of the volatilization of monoglycerol simultaneously occurred. The ratio of weight loss at a temperature range between room temperature to 150°C was agreed well with the amount of the water added. **Fig.-4** showed the relationship between the amount of monoglycerol and the ratio of weight loss above 150°C. Although the ratio of weight loss at each temperature range showed high correlation to the amount of monoglycerol added. It was found that the ratio of weight loss from 150 to 250°C was the most reliable.

Then, this relationship was applied to the commercial PG. As a result, ratio of weight loss until 150°C showed high correlation to the water content ($r=0.986$) and the ratio of weight loss at a temperature range of 150~250°C showed high correlation to monoglycerol content ($r=0.992$). In the similar manner, the ratio of weight loss at a temperature range of 250~300°C or 300~350°C showed high correlation to the sum of di- and triglycerol ($r=0.995$) or the sum of tetra- and pentaglycerol ($r=0.951$).

3.2 Pyrolysis behavior of PGFE in dynamic programmed TG

Fig.-5 showed the TG curve of PG-C16 as an example of PGFE with various acyl groups. The

Fig.-5 TG curve of polyglycerol ester monopalmitic acid.

Fig.-6 TG curves of polyglycerol esters having stearic acid with various degrees of esterification.

weight loss PG-C16 initiated at 201°C, subsequently proceeded rapidly until 350°C and was finished at 490°C. The weight loss pattern in the temperature region above 350°C was complicated than PG with higher degrees of polymerization. The weight loss of PG-C12 and PG-C18 initiated at 197°C and 208°C, and the initial temperature of weight loss were shifted to higher temperature side with an increase of carbon number of acyl groups, though this tendency was not so obvious as that observed in the case of sucrose monoester of fatty acids⁶⁾. After the initiation of weight loss, the weight loss patterns of PG-C12 and PG-C18 were closely similar to PG-C16.

Fig.-6 showed the TG curves of PG-Mo, PG-Tr and PG-He, among the PGFE with different degree of esterification. The weight loss of PG-Mo initiated at 208°C and was finished at 513°C. The weight loss of PG-Tr initiated at 211°C, proceeded rapidly at about 300°C and was finished at 544°C. The TG curve of PG-Tr from 300 to 360°C was located at lower temperature region than that of PG-Mo in spite of initial temperature of weight loss of PG-Tr was higher than PG-Mo. The weight loss of PG-He with

higher degree of esterification initiated at 197°C. Its TG curve was located at lower temperature region than PG-Mo and PG-Tr until about 350°C. However, the weight loss proceeded slowly at a temperature range of 350~400°C and then the TG curve were shifted to higher temperature side than those of PG-Mo and PG-Tr. The weight loss of PG-Di initiated at 209°C and its TG curve was located at the intermediate of those of PG-Mo and PG-Tr. The weight loss of PG-Pe initiated at 207°C and proceeded somewhat rapidly until about 300°C than that of PG-Tr. However, the weight loss pattern of PG-Pe in high temperature region above 300°C was closely similar to PG-He and its TG curve was located at the intermediate position of those of PG-Tr and PG-He.

As mentioned above, the initial temperature of weight loss and TG curves of PG-Mo, -Di and -Tr were shifted to higher temperature side, accompanied with the increase of the thermostability, with an increase of degree of esterification. The initial temperature of weight loss of PG-Pe and PG-He with further higher degrees of esterification were shifted to lower temperature side and the thermostability were decreased. However, TG curves of PGFE with different degrees of esterification at a temperature range of 300~400°C showed characteristic weight loss pattern, and these TG curves from 350 to 400°C were shifted to higher temperature side with an increase of degree of esterification.

3.3 Thermostability of PGFE determined by isothermal TG

The decomposition time from initial to that with 5% of weight loss in isothermal TG was regarded as the heat resisting time, and hence, the thermostability of PGFE could be evaluated by the heat resisting time as described previously⁶⁾. In **Fig.-7**, the heat resisting time of PG-C12, C16 and C18 were plotted against the various temperatures. In each temperature, there were found any significant correlation between the heat resisting time of the samples and their carbon numbers. This tendency agreed well with the temperature with 5% of weight loss determined by the dynamic programmed TG. When the thermostability of these PG monoesters were compared with sucrose monoester of fatty acids with the corresponding acyl groups⁶⁾, the temperature with the same heat resisting time of the former was higher about 50°C

Fig.-7 Plots of heat resisting time vs. heating temperature for polyglycerol monoacyl esters with various carbon numbers of acyl group.

Fig.-8 Plots of heat resisting time vs. heating temperature for polyglycerol esters having stearic acid with various degrees of esterification.

than of the latter, and the thermostability was very excellent.

The heat resisting time of PGFE with different degree of esterification under the various experimental temperatures were plotted against the degree of esterification as shown in **Fig.-8**. The heat resisting time of PG-Mo and -Di at each experimental temperature were also the same with each other, and their thermostability were the most excellent. The temperature with 5% weight loss determined by the dynamic programmed TG showed almost the same tendency with that mentioned above. The temperature with 5% weight loss of PG-Tr, -Pe, and -He determined

by the dynamic programmed TG agreed well with the tendency of the heat resisting time determined by the isothermal TG. However, when compared with the temperature with the same heat resisting time, PG-He, which had the lowest thermostability, was higher about 20°C than that of the monoester which exhibited the highest thermostability among sucrose esters⁶⁾.

From the foregoing, it can be summarized that the TG curves of PG with different degree of polymerization determined by the dynamic programmed TG were shifted to higher temperature side with an increase of degree of polymerization. Thus, from the ratio of the weight loss at various temperature ranges of a commercial PG, it can be determined the water and monoglycerol contents simultaneously, and can be estimated roughly the polymer composition. On the other hand, the initial temperature of weight loss of PGFE was shifted to higher temperature side with an increase of carbon number of the acyl groups. Although the initial temperature of weight loss of PGFE did not correlate with their degree of esterification, their TG curves were shifted to higher temperature side with an increase of degree of esterification in a temperature range of 350~400°C. This weight loss behavior showed characteristic pattern to individual PGFE. These facts suggest that the components of PG, carbon number of acyl groups, and the degree of esterification in PGFE might roughly be estimated by the dynamic programmed TG. When the carbon number of acyl groups and the degree of esterification in PGFE were the same, it is assumed that the initial temperature of weight loss of the PGFE would be shifted to higher temperature side with an increase of degree of polymerization of PG moiety in PGFE. This is because of the fact that the initial temperature of weight loss of PG was shifted to higher temperature side with an increase of degrees of polymerization. Therefore, this technique reported here is expected to be sufficiently utilized in the qualitative control in a production process, though it is inferior to the GLC and HPLC method in the accuracy. The thermostability of PGFE evaluated by the isothermal TG was almost the same with one another, with no influence from carbon number of acyl groups. It showed further that the thermostability of PGFE decreased with an increase of

degree of esterification. When compared the thermostability of individual PGFE with sucrose ester of fatty acids⁶⁾, PGFE showed the same thermostability at higher temperature about 20 or 50°C than the latter at the same heat resisting time. Accordingly, the technique reported here might be useful in the qualitative evaluation of an emulsifier which is used the heating in the preparation of a processed food product.

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ポリグリセリン及びポリグリセリン脂肪酸エステル の熱分解挙動及びその熱安定性

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昇温熱重量測定 (TG) を用いて重合度の異なるポリグリセリン (PG) 及び市販の PG 並びにアシル基炭素数及びエステル化度の異なるポリグリセリン脂肪酸エステル (PGFE) の減量挙動について比較した。さらに PG については各温度間の減量率と組成成分との関係についても検討した。また、昇温 TG による減量開始温度及び恒温 TG による減量開始から 5% 減量するまでに要した分解時間により PGFE の熱安定性を評価した。

1) PG の昇温 TG では、重合度が増加するにしたがって TG 曲線は高温側に移行し、熱安定性は向上した。水分蒸発後の市販 PG の TG 曲線は重合物の組成により特有の減量パターンを示した。

2) PG の昇温 TG において室温から、150°C、150 から 250°C、250 から 300°C 及び 300 から 350°C 間の減量率は水、モノグリセリン、ジとトリグリセリンの和及びテトラとペンタグリセリンの和とそれぞれ相関した。

3) PGFE の昇温 TG では、アシル基炭素数が多くなるにしたがって減量開始温度は高温側に移行した。しかし、エステル化度の異なる PGFE は減量開始温度とエステル化度は相関しないものの、300 から 400°C 間の TG 曲線は特有の減量パターンを示した。

4) 恒温 TG では、各測定温度における PGFE の耐熱時間はアシル基炭素数に影響されずほぼ等しい。しかし、エステル化度が高くなるにしたがって PGFE の耐熱時間は短くなり、熱安定性は低下した。