

Dissolution Properties of Phosphate Glasses with Trace Elements

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(Received May 3, 2005; Accepted June 10, 2005)

ABSTRACT

Phosphate glasses were prepared by melting quenching process, and glass formation and dissolution properties were studied. The glass forming region in the K_2O - CaO - P_2O_5 system is quietly agreed with the report by Mazurin OV *et al.* with M_2O - $M'O$ - P_2O_5 system (M : monovalent cation, M' divalent cation). Conditionally these glasses have solubility from absorbing the moisture or water and then release elements with trace elements, and the thermal and chemical properties were controllable by the CaO , K_2O , P_2O_5 contents. In the abnormal glass properties, this paper showed the possibility the present glasses can be a good candidate for one component of the slow released agriculture fertilizer.

Key words : Environment conscious, Glass fertilizer, Dissolution, Phosphate glasses, Slowly-effective fertilizer

1. Introduction

Since conventional phosphate glass has hygroscopic property and poor chemical durability caused by the glass structure, its application has been limited. Thus many efforts have been focused on to increase the chemical durability.^{1,2)} However, the new applications for phosphate glasses were proposed by Drake³⁾ and Knott⁴⁾ and are lately emerging for environmental materials such as glass fertilizer, anti-bacterial, far-infrared radiation, dental, and biomedical materials. Bunker *et al.*⁵⁾ studied the dissolution properties and mechanism of the M_2O - CaO - P_2O_5 glass (M: Li, Na). They reported that the dissolution rate is controlled by the glass composition. The other studies of the water soluble phosphate glasses were reported by Motohiro Uo *et al.*⁶⁾ and Shin *et al.*⁷⁾ with P_2O_5 - CaO - Na_2O glasses and P_2O_5 - Na_2O - CuO glasses respectively. Even though there are several achievements in soluble phosphate glasses, the most of them are focusing on the not glass fertilizer but biomaterials.

As the requirements for glass fertilizer, the glass, which should be easily formed and contain other elements by melt-quenching process, should have solubility from absorbing the moisture or water on earth and then release elements from glass structure. Also, the solubility and duration of each element should be controllable and not have environmental problems by the soil acidulation. The currently used chemical fertilizers in agriculture have immediate effect so that it offered excess nutrition than those plants needed or release to the soil. Resulting in not only the great waste of

fertilizer but environmental problems due to the soil acidulation. Thus, the controllable released glass fertilizer that could offer the nutrients as much as the plants needed for months or years is needed. The phosphate glass is the most suitable glass system for that purpose because the solubility of the phosphate glasses already has been shown by other researchers and can be controlled by composition design if the composition was modified.

Therefore, in this study, we made many glass compositions with chemicals such as potassium, calcium and phosphate to can supply nutrients (K^+ , Ca^{2+} , P^{5+}) included in 5 elements of chemical fertilizers and needed for growth to the plants, and the glass formation and dissolution properties has been studied. And the trace elements such as B, Mg, Zn, Fe, Cu, Co, and Mo doped K_2O - CaO - P_2O_5 glass was studied by ICP-MS, pH meter, and FT-IR.

2. Experimental Procedure

As inorganic fertilizer components, K_2O - CaO - P_2O_5 system⁸⁾ was selected, and melting procedure was performed for stable glass. Three compositions, the 40, 50, 60 mole% P_2O_5 , as a representative inorganic fertilizer composition, were selected, and trace elements doped K_2O - CaO - P_2O_5 glasses were prepared. For the raw materials, K_2CO_3 (Junsei, 99.5%), $CaCO_3$ (Junsei, 98.5%), H_3PO_4 (Duksan Chemical, 85%), B_2O_3 (Junsei, 99.0%), MgO (Duksan Chemical, 98%), Fe_2O_3 (Junsei, 98.5%), ZnO (Junei, 99.0%), CuO (Junsei, 99.0%), MnO (Duksan Chemical, 99.0%), MoO_3 (Aldrich, 99.0%) were used for batch mixing. The raw materials were mixed with distilled water for one hour and kept for 12 h in dry oven. Then the batch was melt in porcelain crucible at 700~1300°C for one hour and poured into water bath. And then glasses were dried in the dry oven at 120°C to prevent the glass reaction with water. Thermal stability was deter-

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mined by TG-DTA at a heating rate of 10°C/min in air (TG 8110, Rigaku). Samples were grounded in mortar and subsequently sieved to obtain a powder with a particle size ranging $500 > d > 250 \mu\text{m}$ and then 70% of the powder had a mean particle size of 400–450 μm measured with a linear-intersection method. In the water solubility (pH=6.64) test with closed system, 1.25 g of samples were placed in a plastic container full with distilled water with 25 ml and were kept at 30°C without stirring in the temperature and humidity chamber. The pH and ICP-MS (Shimadzu Co., ICP 7500) were used to observe dissolution behavior at various time points. Fourier transform infrared (FT-IR) spectra with remained powder after dissolution test were obtained on an infrared spectrophotometer (FTS-3000MX, Bio-rad) to analyze structure change by dissolution time.

3. Results and Discussion

3.1. $\text{K}_2\text{O-CaO-P}_2\text{O}_5$ Glasses

The glass forming regions of $\text{K}_2\text{O-CaO-P}_2\text{O}_5$ system is shown in Fig. 1. The transparent glass formation region is (0~40 mole%) K_2O , (20~50 mole%) CaO , and (40~60 mole%) P_2O_5 . These glass forming regions are quietly agreed with the report by Mazurin OV *et al.*⁹⁾ with $\text{M}_2\text{O-M'O-P}_2\text{O}_5$ system (M : monovalent cation, M' divalent cation). The basic structural unit of phosphate glass is the PO_3^{-4} group, which can be attached to a maximum of three neighbour PO_3^{-4} groups to produce a cross-linked structure. The first addition of alkali or alkaline earth oxide such as K_2O or CaO to P_2O_5 glasses results in conversion of the cross-linked structure to linear phosphate chain. This chains structure results in cleavage of P-O-P linkages and the creation of non-bridging oxygens as shown in Fig. 2(a). Also, the estimated average chain length is an important factor to decide the glass forming region.⁶⁻⁸⁾

The Ca^{2+} ions can serve as ionic cross-links between the non-bridging oxygens of two different chains as shown in Fig. 2(b). Such a cross-link is assumed to strengthen the phosphate network, and this means that the glass contain-

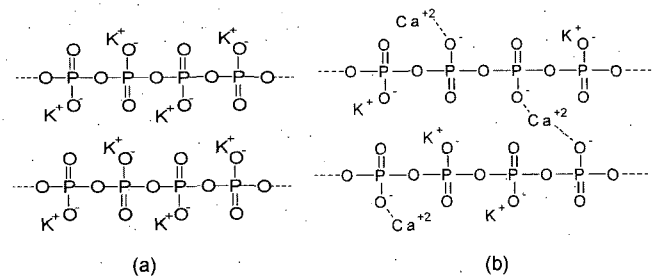


Fig. 2. Schematic representation of phosphate glass; showing the chain structure and cross-link formation by Ca^{2+} ion.

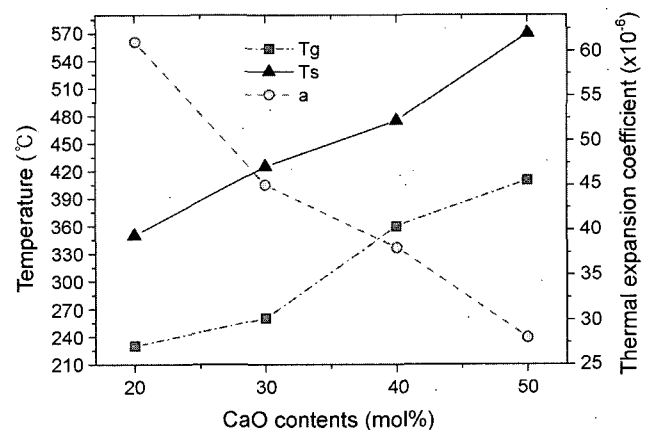


Fig. 3. Thermal properties of the glasses according to CaO contents.

ing CaO has cross-link formation by Ca^{2+} ions and effects on the thermal property and solubility

The thermal properties of mother glasses are shown in Fig. 3. In each P_2O_5 glass, glass transition and transformation temperature increase while thermal expansion coefficient decreases with CaO increasing. It suggests that the CaO exits at Ca^{2+} in the glass and makes the cross-link formation between chains. Therefore, we assume that the dissolution property should be concerned with the contents of each component and controllable by them.

Fig. 4 shows the data obtained from pH measurements in the 4P3C (40 mole% P_2O_5 , 30 mole% CaO , 30 mole% K_2O), 5P3C (50 mole% P_2O_5 , 30 mole% CaO , 20 mole% K_2O), and 6P3C (60 mole% P_2O_5 , 30 mole% CaO , 10 mole% K_2O). Generally, the unstable phosphate glass attracts water and occurs the reaction of depolymerization to transfer to stable state. In the case of 6P3C containing large amount of P_2O_5 , the pH value decrease to the acid range because the network of phosphate glass was broken by attracted water, and released phosphorus reacted with water and changed to HPO_3 resulting in decreases in pH value. Such change in pH values is similar with 5P3C. Therefore, the lower pH values were expected for the higher phosphate containing composition, due to the breakdown of more PO_4 groups thus creating more acidic species in the solution. In case of 4P3C, however, since this glass contains less amount of P_2O_5 than

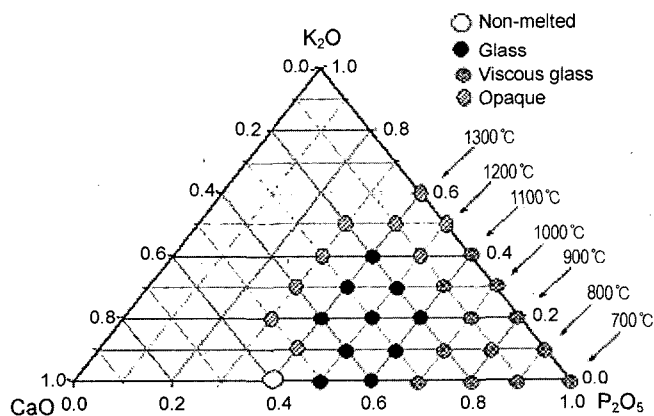


Fig. 1. Glass formation region in ternary $\text{K}_2\text{O-CaO-P}_2\text{O}_5$ glass system.⁹⁾

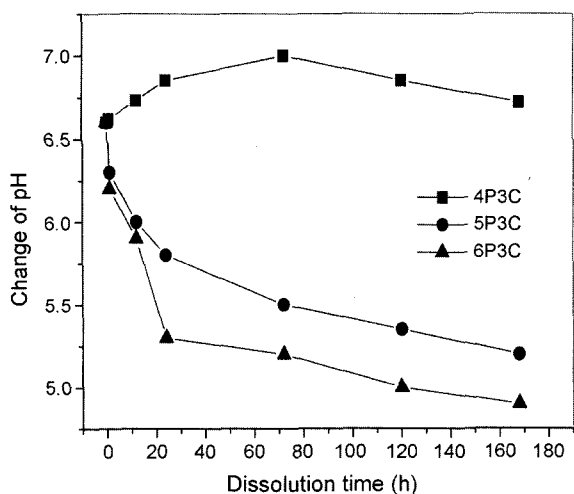


Fig. 4. Variation of pH versus dissolution time of (60-40 mol%)P₂O₅-30 mol% CaO-(10-30 mol%) K₂O.

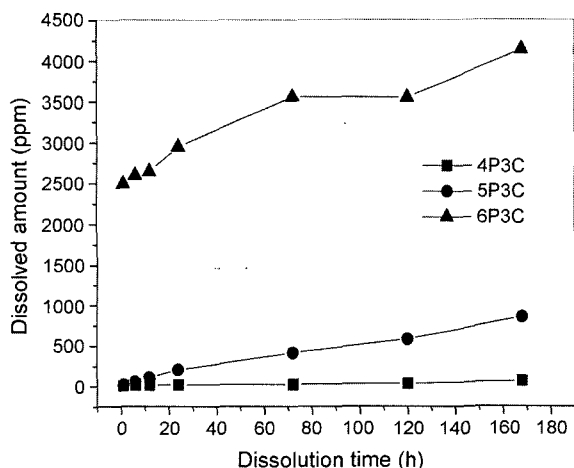


Fig. 5. Variation of dissolved P ion amount according to dissolution time of (60-40 mol%)P₂O₅-30 mol% CaO-(10-30 mol%) K₂O.

others, the glass is stable and shows quietly different result in pH value. The case could be considered by that pH value depends on the dissolute alkali ion from glass as silicate glass in the water bath.^{11,12} However, if consider a long period, it can be expected that the pH value will finally move onto acid range.

Dissolution mechanism in the phosphate glasses could be explained by the anti-branching rule.¹³ By this rule, because PO₄ group in the phosphate glasses is unstable, it attracts water and occurs the reaction of depolymerization (P-O-P + H₂O → P-OH + OH-P) to transfer to stable state when the value of MO (M₂O)/P₂O₅ (M = Ca, Mg, K, Na, etc.) is smaller than 1. Therefore, the pH of 5P3C and 6P3C containing lots amount of P₂O₅ was a continual decrease with time to values of around pH 5. This was expected as the gradual breakdown of the higher phosphate containing compositions probably released HPO₄ and PO₃⁻⁴ ions into solu-

tion.⁸) On the other hand, 4P3C glass shows an initial increase in pH measurements by 7.0, and the values decline over time to a around pH 6.75. The 4P3C glass of the value of MO (M₂O)/P₂O₅ is larger than 1 and stable state so, it is considered to be similar with silicate glasses which have the alkali dissolution. Thus, alkali ion is firstly released into water until the value of MO (M₂O)/P₂O₅ is smaller than 1 and then followed above-mentioned mechanism.

Fig. 5 shows variation of dissolved P ion amount according to dissolution time. With increasing amount of P₂O₅ and dissolution time, the dissolved amount increases. Especially, 6P3C shows that the change is the highest of them. It means that amount of P₂O₅ can control the dissolution velocity and easily collapse the network. Also, we can assume that lots of released P ion changes the pH value to acid range.

Figs. 6 and 7 show the change of dissolved Ca and K ion according to dissolution time in 50 mol% P₂O₅. Fig. 6 shows that the dissolution amount of Ca ion is inversely proportional to the quantity of CaO. In Fig. 8, the dissolved

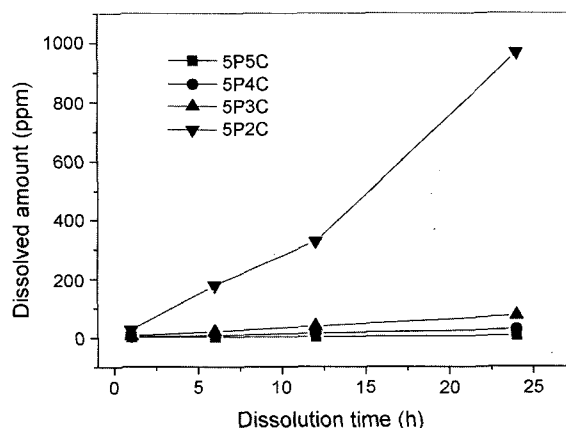


Fig. 6. Variation of dissolved Ca ion amount according to dissolution time of 50 mol% P₂O₅-(50-20 mol%) CaO-(0-30 mol%) K₂O.

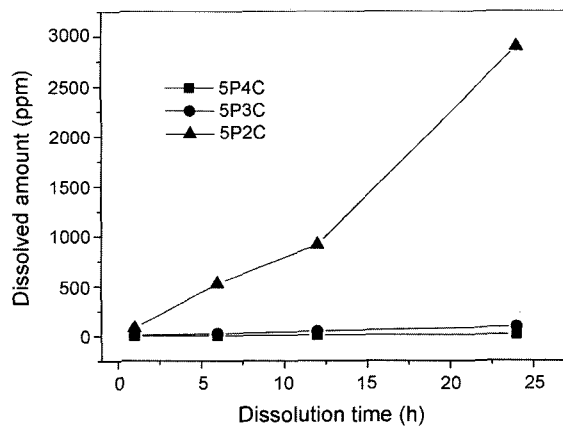


Fig. 7. Variation of dissolved K ion amount according to dissolution time of 50 mol% P₂O₅-(40-20 mol%)CaO-(10-30 mol%) K₂O.

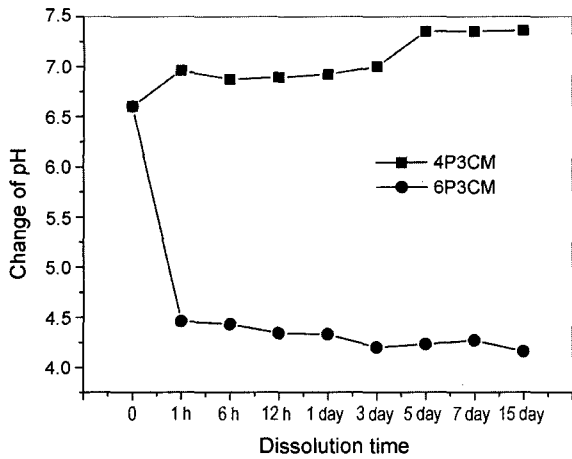


Fig. 8. Variation of pH versus dissolution time of 4P3CM and 6P3CM.

K ion amount is proportional to quantity of K_2O . From Figs. 5, 6, and 7, therefore, we know that the dissolved amount of each ions could be controlled by the quantity of each glass oxide and dissolution velocity also controlled by the composition change as follows ; the glass structure substitute (-O-) P-O-Ca for (-O-)P-O-...K+ when the quantity of K_2O increases.

3.2. Trace Elements Doped K_2O -CaO- P_2O_5 Glasses

The change of pH value in the 4P3CM (93.92 wt% 4P3C containing 6.08 wt% trace elements; 5 wt%MgO, 0.322 wt% B_2O_3 , 0.179 wt% Fe_2O_3 , 0.516 wt%MnO, 0.028 wt%ZnO, 0.0188 wt%CuO) and 6P3CM ((93.92 wt% 6P3C glass containing 6.08 wt% trace elements) is shown in Fig. 8. The 6P3CM and 4P3CM also followed the 6P3C, 4P3C respectively. Consequently, these results demonstrate that the doped trace elements haven't significant effects on stability and pH.

Figs. 9, 10. show that the dissolution amount of 6P3CM is larger than 4P3CM, and the dissolution amount of 6P3CM and 4P3CM were measured by the order as follow; Mg > Mn > B > Fe > Zn > Cu > Mo, Mg > Mn > B > Fe > Cu > Zn, Mo and Mo was not detected until 15 days respectively.

Fig. 11 shows the percentages of long-term dissolution in 4P3CM and 6P3CM glasses. The 6P3CM has a dissolution amount of above 80% within 30~45 days and almost released after 100 days. However, the 4P3CM shows slow-released dissolution property and the percentage is below 40% until 120 days. Therefore, the author expect that the 6P3CM is suitable for seedbed or slow release compound fertilizer of upland crop rather than a cultivation medium, and 4P3CM is suitable for soil substances need extremely slow-release.

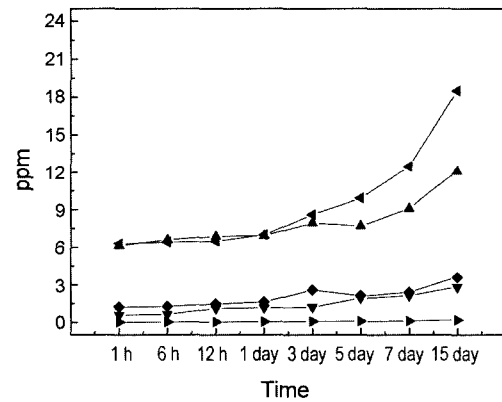
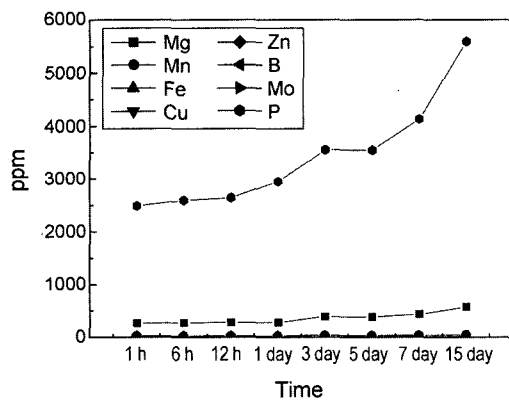


Fig. 9. Dissolved amount of chemical element contained in 6P3CM glass in distilled water measured by ICP-MS.

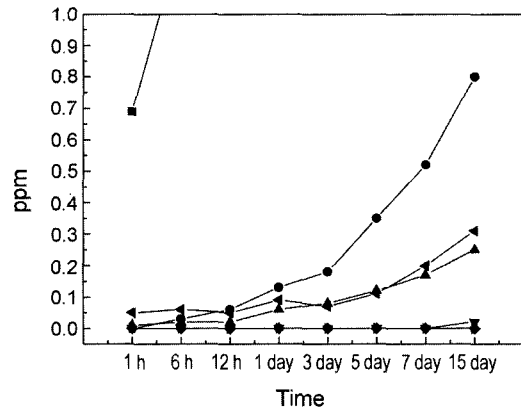
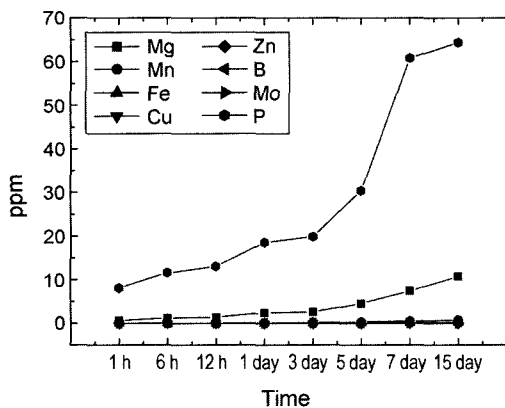


Fig. 10. Dissolved amount of chemical element contained in 4P3CM glass in distilled water measured by ICP-MS.

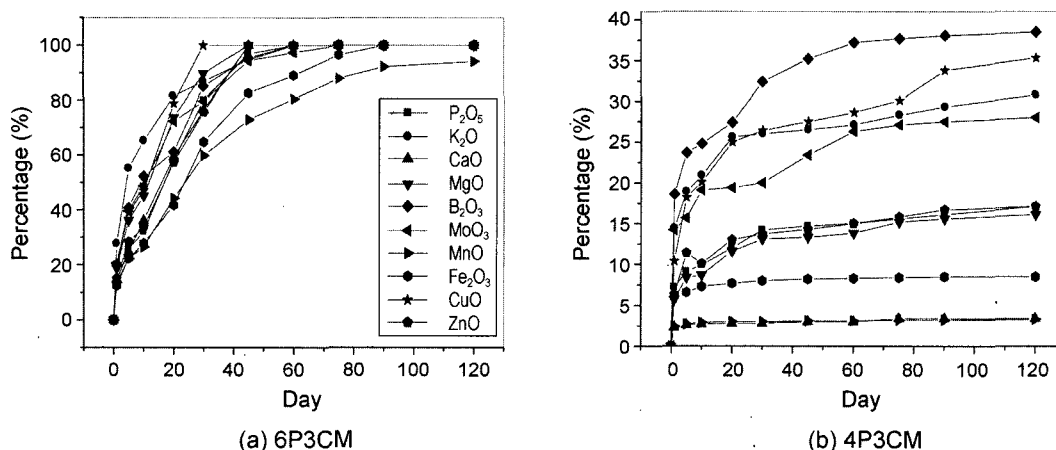


Fig. 11. Percentages of long-term dissolution amount of chemical element contained in glasses in distilled water.

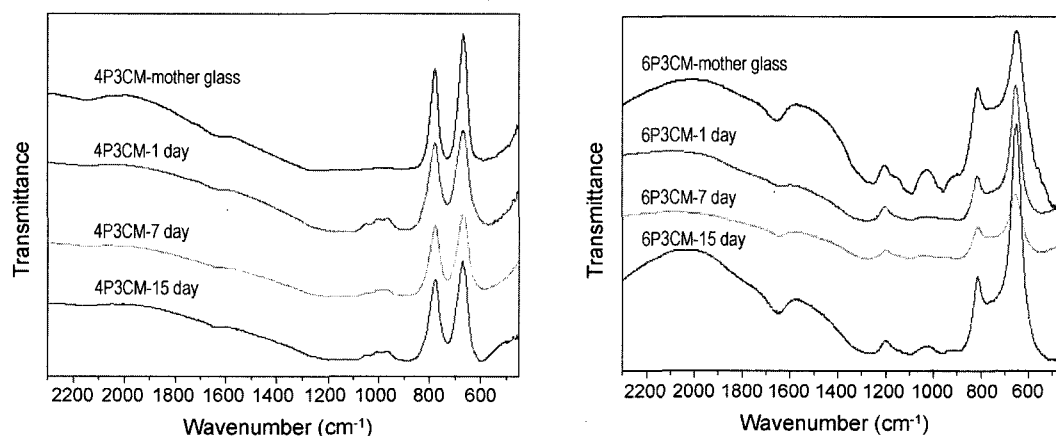


Fig. 12. FT-IR spectra of 4P3CM and 6P3CM remained powder before and after dissolution for 1, 7, and 15 day.

The structure change with remained powder before and after dissolution test was shown in Fig. 12. The 4P3CM in comparison to the mother glass, the intensities of some absorption peaks ranged from 450 to 600 cm^{-1} and from 900 to 1100 cm^{-1} were reduced due to the chemicals leaching out of the glass matrix with the leaching time increasing. The band in the region 450 – 600 cm^{-1} shows that the band becomes narrower with increasing the dissolution time. This band attributed to the bending vibrations of bridging phosphorous such as O-P-O and/or O=P-O.¹⁴⁾ The peaks at 980, 1020, 1060 are assigned to the $(\text{PO}_3)_{\text{as}}^{3-}$ anion, (P-O-P)_{as} bridge, $(\text{PO}_2)_{\text{sy}}^-$ terminal group, respectively. And the intensity of peak at 700 assigning to (P-O-P)_{sy} bridge is also reduced due to the decrease in content in the mother glass. The change in the amount of the bridges may reflect the dissolution in the glass structure due to the depolymerization of phosphate matrix.

For the sample 6P3CM, the IR spectra of mother glass has many absorption peaks when it is compared with 4P3CM. We expect that such differences came from the glassy process. It means that the dissolution behavior already has started as soon as the unstable 6P3CM was poured on the

quenching water due to comparably poor bonding. The peaks in the region 850 – 1350 cm^{-1} are assigned to mostly (P-O-P)_{sy} bridge, $(\text{PO}_4)_{\text{sy}}^{3-}$ anion, $(\text{PO}_2)_{\text{sy}}^-$ terminal group, and $(\text{PO}_3)_{\text{as}}^{2-}$ terminal group. After dissolution for 1 day in water, the peaks in the rang from 900 – 1100 cm^{-1} were disappeared due to the chemical leaching out and it may be considered why the pH change 6P3CM was so fast. With immersion time increase to 15 days, absorption peaks were observed.

From the Fig. 12, we assume that the 6P3CM easily reach out the chemical because it has poor bonding structure by P_2O_5 . On the other hand, the 4P3CM shows the strong bonding and these facts are already demonstrated by thermal analysis and pH changes.

Many research reported that the phosphate glasses have solubility and can be a good candidate for bio-medical materials. However, we carried out the experiment focusing on agriculture fertilizer, especially glass compositions to supply needed nutrient to plants and dissolution properties of them. The phosphate glasses consisted of potassium, and calcium included in 5 elements needed for growth to the plants and trace elements doped phosphate glasses were

prepared and evaluated for usage as a glass fertilizer. The stable glass forming region of K_2O - CaO - P_2O_5 system is (0~40 mole%) K_2O , (20~50 mole%) CaO , and (40~60 mole%) P_2O_5 , and this region is quietly agreed with Mazurin OV *et al.* report.⁹⁾ The CaO in the glass network tends to form polymeric chain structure increase bonding strength, and this phenomenon was confirmed by thermal analysis. The pH change depend on the amount of P_2O_5 dissolution, and the dissolution and velocity of each chemical depend on the initial contents contained in batch. In case of CaO , it has a role of limiting the dissolution behavior from increasing bonding energy and forming polymer chain. On the other hand, P_2O_5 and K_2O are attributed to increase dissolution rate. The phosphate glasses containing trace elements show similar behavior with phosphate glasses. So we find the trace elements don't give significant effect on the mother glasses. But the trace elements as well as mother glass components leach out according to the time, and such leaching amount also depend on the mother glass and initial contents of trace elements. From FT-IR analysis with remained powder after dissolution test, the 4P3CM, which showed slow dissolution behavior, shows a little change from 900 to 110 cm^{-1} , and the 6P3CM, which showed fast dissolution behavior, shows much change according to time. This result is agreed with the result of pH and ICP analyze.

Therefore, finally, this study showed the possibility that the K_2O - CaO - P_2O_5 system is a good candidate for environment conscious inorganic fertilizer, and the dissolution properties is designed by the compositions (or structure) of mother glasses. We thought that the product process such as complex fertilizer or compound fertilizer for application would be need because these glasses could not supply needed nutrients, the nitrogen or chlorine, for plants.

4. Conclusions

We fabricated the phosphate glasses with chemicals needed for growth to plants, and glass formation and dissolution properties were studied. The stable glass forming region of K_2O - CaO - P_2O_5 system is (0~40 mole%) K_2O , (20~50 mole%) CaO , and (40~60 mole%) P_2O_5 and this region makes stable glass even though containing trace elements. The CaO has a role on connecting the each chain structure and increase the thermal property and reduce the dissolution rate. The change of K_2O and P_2O_5 was another factor to control chemical durability and physical properties. The ICP analysis confirmed that the dissolution amount of mother glass components as well as trace elements is proportional

to the initial quantities of chemicals and could be controlled by mother glass composition or structure. Consequently the paper showed the possibility the present glasses can be a good candidate for agriculture fertilizer.

Acknowledgement

The present research was conducted by the research fund of Dankook University Alumni Association in 2004

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