

# Geopolymers Using Rice Husk Silica and Metakaolin Derivatives; Preparation and Their Characteristics

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## Abstract

The effect of the amorphous silica derived from biomass rice husk (RH) in the alkaline activating solution on the properties was investigated in geopolymerization process, when metakaolin was used as the aluminum source from metakaolin (MK). With changing a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$  and  $10$ , the curing in the preparation of geopolymers was carried out at  $85^\circ\text{C}$ ,  $100^\circ\text{C}$  and  $200^\circ\text{C}$ . Viscoelastic properties of the geopolymer pastes including  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  components suggested that the alkaline activation was found in higher RH silica source. The mineralogical and micro-structural characteristics of the cured products were evaluated to be amorphous aluminosilicate.

## Keywords

Rice Husk, Silica, Metakaolin, Geopolymer

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## 1. Introduction

Geopolymerization is an effective manner to process and reuse silicates, aluminates or aluminosilicates in mineral waste. It is known that geopolymers are alkaline activated aluminosilicates consisting of reactive species of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to produce high-strength materials that can effectively immobilize other industrial by-products, and even hazardous waste. Generally, the formula of the geopolymers is  $\text{M}_n(-(\text{Si}-\text{O})_z-\text{Al}-\text{O})_n \cdot w\text{H}_2\text{O}$ , where M is an alkaline cation (Na, K or Ca), z is generally assigned a value of 1, 2 or 3 and n is the degree of polymerization [1]. Geopolymers are interesting materials formed by polycondensation of the silicon and aluminum species resulting from the dissolution of their raw materials found in fly ash, slag, metakaolin in alkaline solution condition [2]. Usually, the geopolycondensation depends of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and alkali concentration [3] [4]. Geopo-

lymerization is affected by the reactive precursor, meaning that OH-concentration and curing conditions finally produce three-dimensional networks that comprise geopolymer matrices at different time and temperature [5].

Therefore, the advantage is the proven durability and erosion resistance of both ancient mortars and cements and modern geopolymer cements. It was known that a great number of minerals-industrial wastes were studied as raw materials for geopolymer synthesis, including pozzolana [6], natural aluminosilicate minerals, metakaolin, fly ash, granulated blast furnace slag, fly ash and kaolinite mixture, red mud and metakaolin mixture [3] [7]-[12].

More importantly, the starting raw materials play a significant role in the geopolymer reaction and affect the mechanical properties and microstructure of the final geopolymeric products [3] [11] [13]. It would be expected that silica from rice husk (RH) is an excellent pozzolanic material, but that has not been extensively studied in geopolymerization. RH silica can be generated by the combustion process of RH [14], itself is biomass and to be an issue for sustainability environment, due to its abundant amount and capability to resist natural degradation. RH silica therefore is an alternative material with good pozzolanic reactivity, to be included in the geopolymer mixture to complete the ratio of modulus of  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . In the present study, the effect of the RH silica was determined on the resultant geopolymers as a function of curing time and temperature. It was investigated that the rheometry properties of the geopolymer pastes and properties of resultant geopolymers were compared at different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios at different cure temperature in addition with their bulk characteristics. Since such biomass resource was attractively interesting in point of view of sustainability, this paper focused on the detail in the geopolymerization.

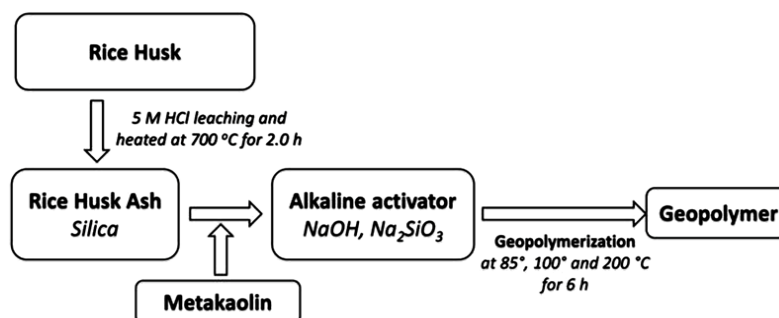
## 2. Experimental

### 2.1. Materials

Silica was obtained from by leaching of rice husk in dilute HCl (5 M) and burned at  $700^\circ\text{C}$  to produce pure amorphous white silica. The chemical composition of obtained silica was determined by XRF reveals at 99.5% of  $\text{SiO}_2$  with a surface area calculated from BET method of  $207.5\text{ m}^2/\text{g}$ . Obtaining Metakaolin was carry out by dehydroxylation of kaolinite at  $750^\circ\text{C}$  by 20 h according to reference [15] [16]. The chemical composition of metakaolin was measured by XRF for 52% of  $\text{SiO}_2$  and 42.1% of  $\text{Al}_2\text{O}_3$ . The surface area of metakaolin calculated from BET method was  $11.5\text{ m}^2/\text{g}$ .

### 2.2. Preparation of Geopolymer

Geopolymers were prepared by changing a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$  and  $10$  for GP-3 and GP-10, respectively. For NaOH and  $\text{Na}_2\text{SiO}_3$  molar ratio,  $\text{Na}_2\text{O}/\text{SiO}_2 = 0.25$  was used. The preparation procedure is as followed as described in **Figure 1**. The powders of RH silica were mixed with NaOH solution until dissolution. Then, metakaolin (MK) powders were added and mixed together for 15 min in the silica solution. The paste samples were cast in plastic molds with a diameter of 20 mm and height of 40 mm. The curing time for preparation of geopolymers was carried out at  $85^\circ\text{C}$ ,  $100^\circ\text{C}$  and  $200^\circ\text{C}$  in a conventional oven at open mold(). Before the curing process, rheological measurements of the paste samples were performed using a controlled stress rheometer (Anton PaarPhysica MCR 301 Rheometer), as operated in controlled strain mode. The geopolymer paste was prepared manually outside the rheometer and then introduced into the rheometer disk after mixing. Transferring the geopolymer to the measurement cell generates residual stresses, when the sample was prior to



**Figure 1.** Protocol of geopolymerization synthesis.

each rheological measurement. This was done before each test by applying a strain at frequency of 1 Hz. Characterization of the geopolymers was obtained by infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM).

### 3. Results and Discussion

Figure 1 presents synthesis protocol of RH silica-MK geopolymerization. In this process, the RH silica and MK were produced by sintered rice husk and kaolin at 700°C and 750°C, respectively, before the provided.

Figure 2 shows the strain sweep at a frequency of 1 Hz for raw material activated by NaOH and geopolymer paste with a satisfactory repeatability. It was observed in the viscous elastic rheometer that the deformation of the geopolymers pastes (a) was higher than that of RH silica and MK (b). It was understanding that the linear viscoelasticity region was due to nondestructive to the geopolymerization of the silica-alumina component in the

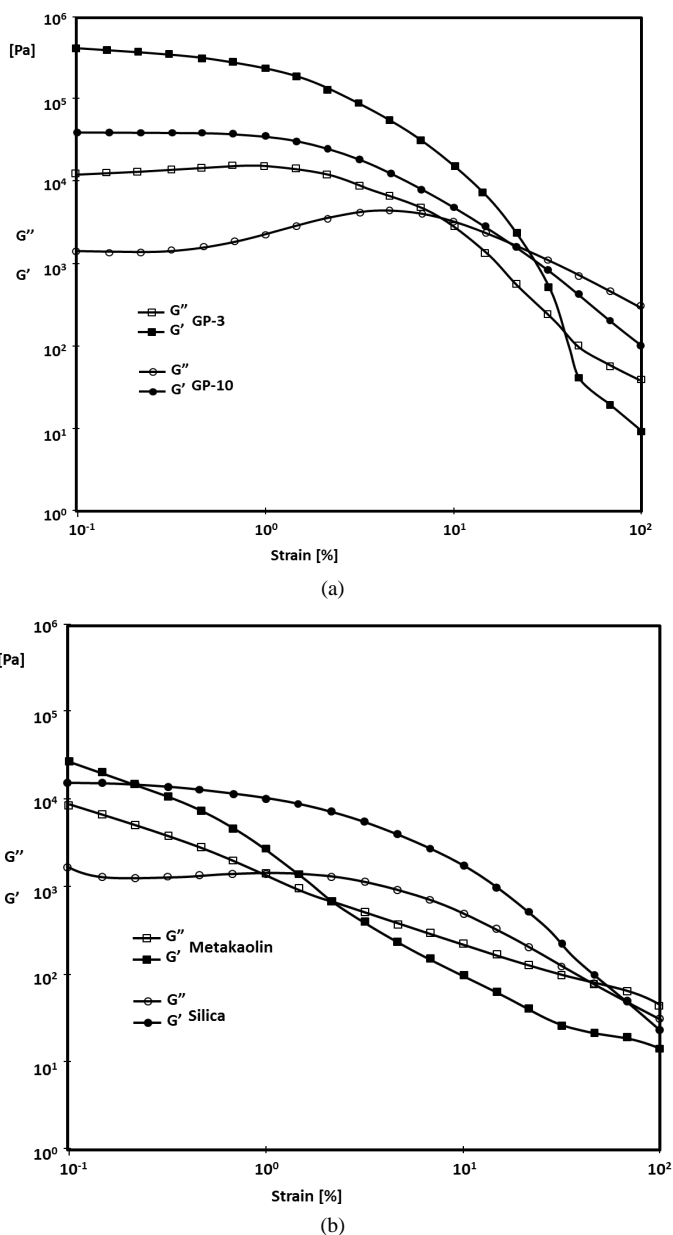
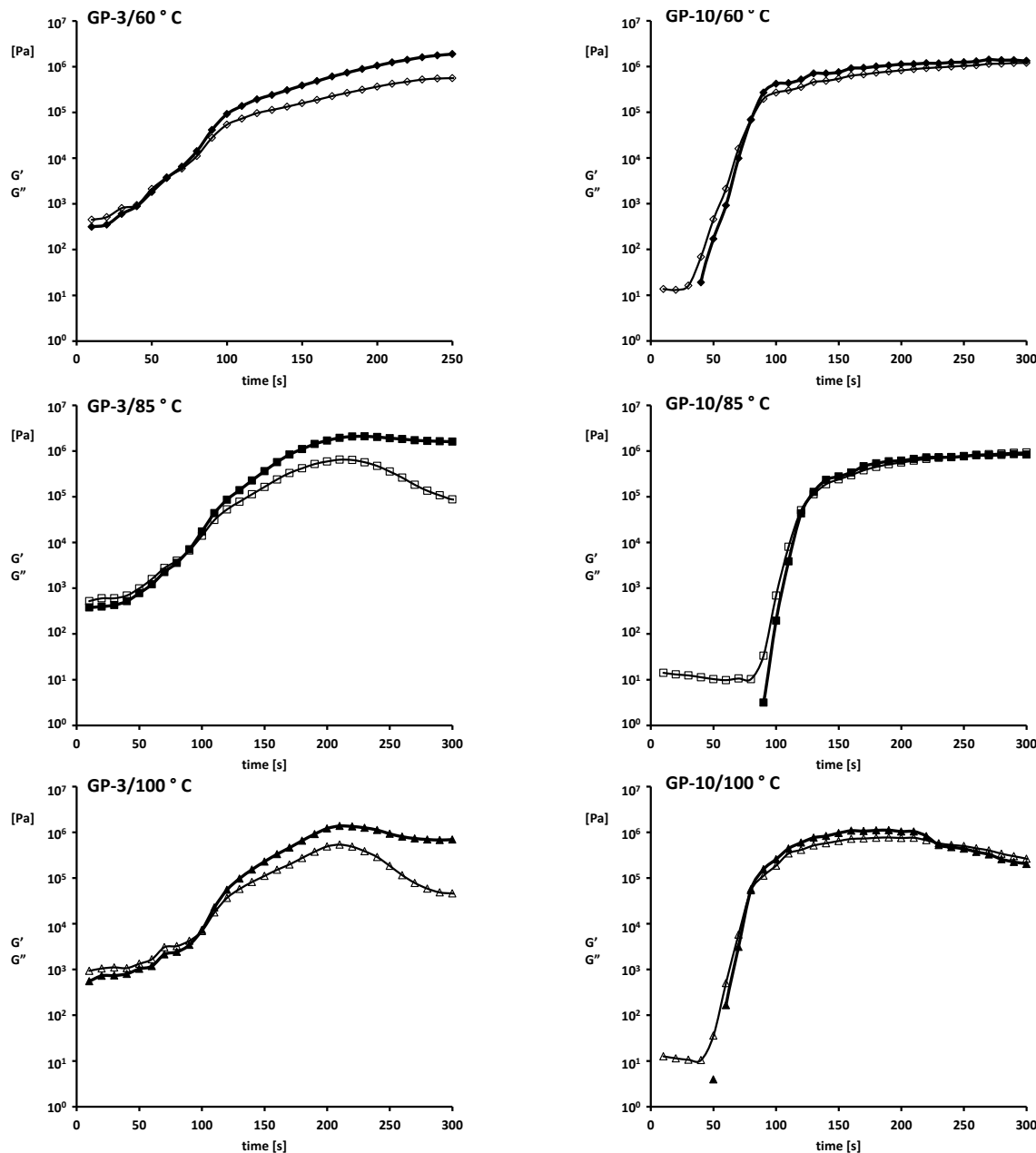


Figure 2. Strain sweep test for (a) geopolymer paste of GP-3 and GP-10 at 25°C, and (b); silica from rice husk and metakaolin activated by NaOH.

activated paste, when a critical strain  $\gamma_c$  was applied. Strain was generally taken as the strain value at the storage modulus equal to 90% of the plateau modulus. In both cases for GP-3 and GP-10, the elastic modulus ( $G'$ ) came to be higher than that of viscous modulus ( $G''$ ). That meant that the paste was considered in the gelation for solid.

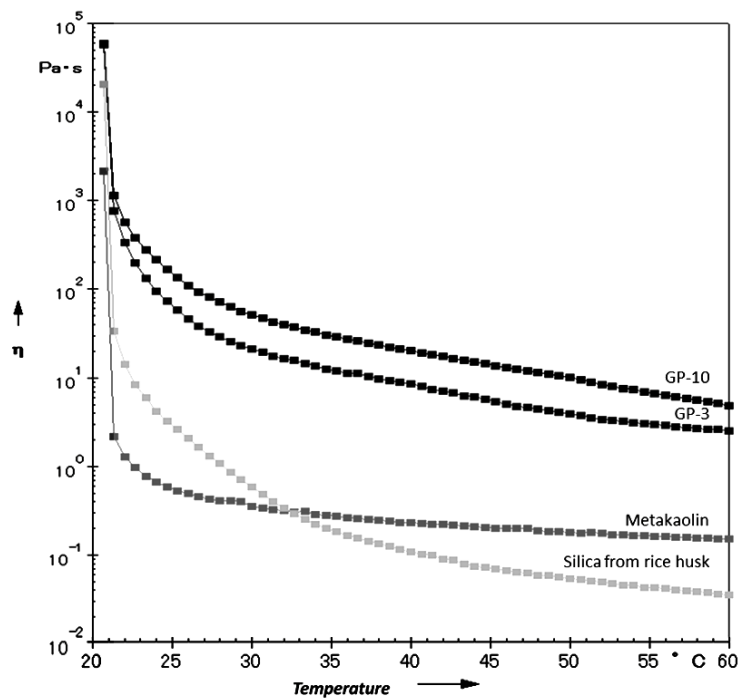
When comparison made between the paste of GP-3 and GP-10, high values of  $G'$  and  $G''$  for geopolymer pastes were observed, indicating that the geopolymerization in the activator condition was easily occur at the point of  $G''/G' = 1$ , GP-3 containing higher alumina and higher strain. This means that the high MK content was better for the polycondensation reaction.

**Figure 3** show time curves of  $G'$  and  $G''$  at different temperature. It was also observed at fixed temperature of 60°C, 85°C and 100°C for GP-3 and GP-10. The both  $G'$  and  $G''$  were increased with increasing time and then

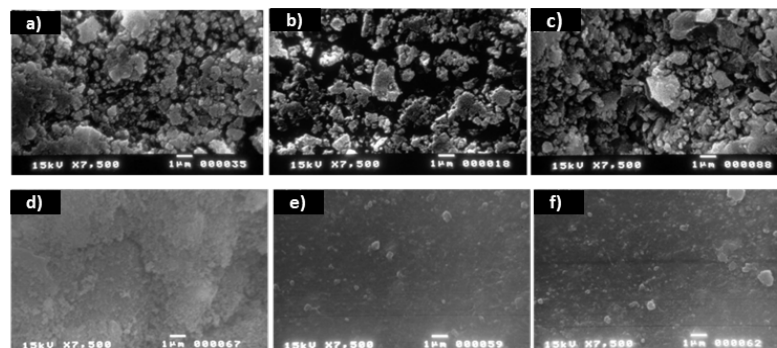


**Figure 3.** The  $G'$  and  $G''$  as a function of time and maintaining a constant temperature at 60°C, 85°C and 100°C for GP-3 and GP-10 [ $\blacklozenge$  for elastic modulus ( $G'$ ) and  $\diamond$  for viscous modulus ( $G''$ )].

became to be constant at about 250 seconds. The comparison between GP-3 and GP-10 meant that the cure ability of the activated paste was higher in GP-10. The time curves suggested that the curing was finished at about 2 min heating. But, the GP-3 increased the  $G'$  and  $G''$  values near 200-250 seconds and then was cured in the geopolymer solidified. Due to that the polycondensation reaction occurs, the geopolymer paste loses viscosity, while the paste became a solid material, the elastic modulus became constant at the longer time. This change was exactly observed after 250 s for GP-3 at 60°C and 210 s for GP-3 at 85°C and 100°C. At a high amount of  $Al_2O_3$  for GP-3, it was less to be on geopolymerization. However, the GP-10 registered a constant modulus  $G'$  and  $G''$  for all the cases due to with a high content of RH silica on the geopolymer pastes which made a very elastic and viscous material even after 250 s. **Figure 4** shows viscosity of the pastes of GP-3 and GP-10 at different temperature. It was noticed that the viscoelasticity of the paste decreased, when the temperature was high. The resultant viscosity of the GP-10 was higher than that of GP-3, due to the increment of the  $SiO_2$  in geopolymer composition resulted in a decrease of the viscosity of the pastes. After polycondensation reaction for GP-3 and GP-10, the microstructures of geopolymers at different curing temperature were observed. **Figure 5** shows



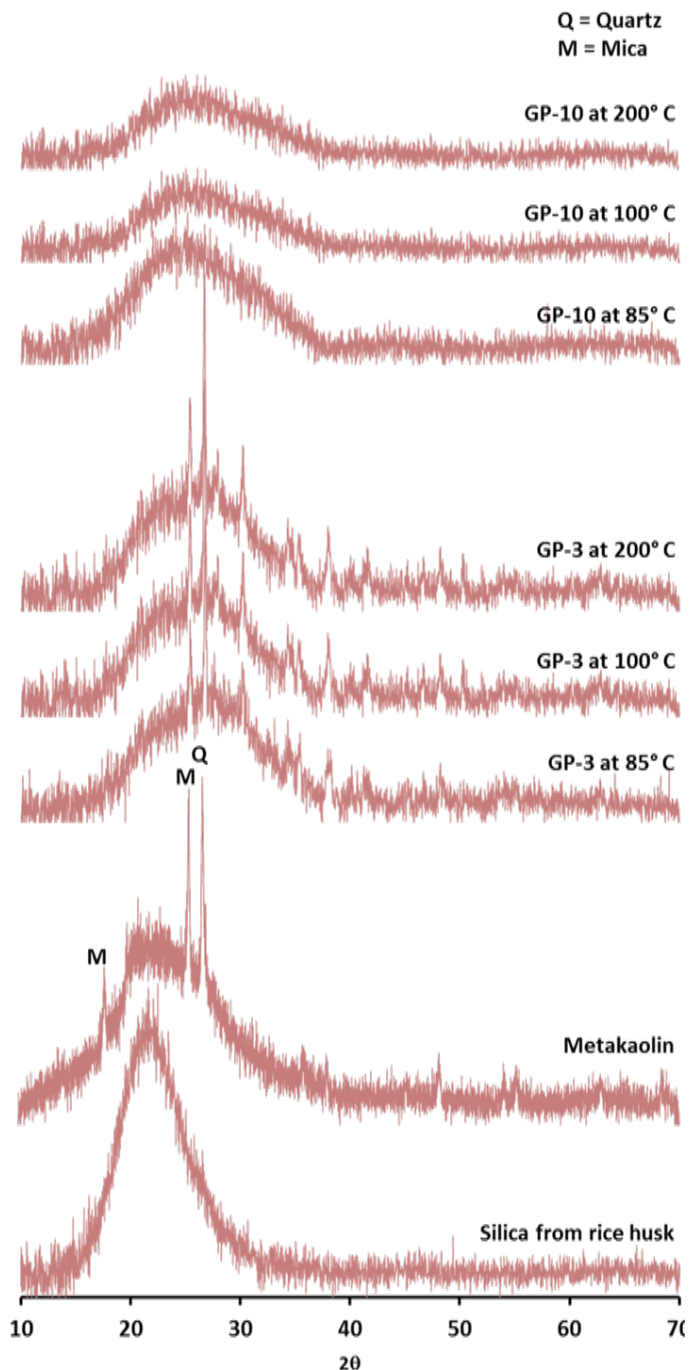
**Figure 4.** Viscosity test for silica from rice husk, metakaolin activated by NaOH and geopolymer paste of GP-3 and GP-10 from 20°C to 60°C.



**Figure 5.** SEM images of (a) GP-3 at 85°C; (b) GP-3 at 100°C; (c) GP-3 at 200°C; (d) GP-10 at 85°C; (e) GP-10 at 100°C and (f) GP-10 at 200°C.

microscope picture for the resultant geopolymers. The pictures showed the formation of the heterogeneous matrix after the polycondensation of raw material. It was seen that the geopolymers of the GP-3 became to be more porosity matrix. Their porosities of the geopolymers decreased at the GP-10 containing higher RH silica contents. It was seen that with the increment of the temperature, changing into a homogeneous phase was found in the geopolymer matrix, wich was condensed at 200°C of the geopolymer matrix.

The XRD patters of the geopolymers of GP-3 and GP-10 at different curing temperature are shown in **Figure 6**. It was seen that the peak shift toward higher 2θ side was significant in the cases of GP-3. This meant that the



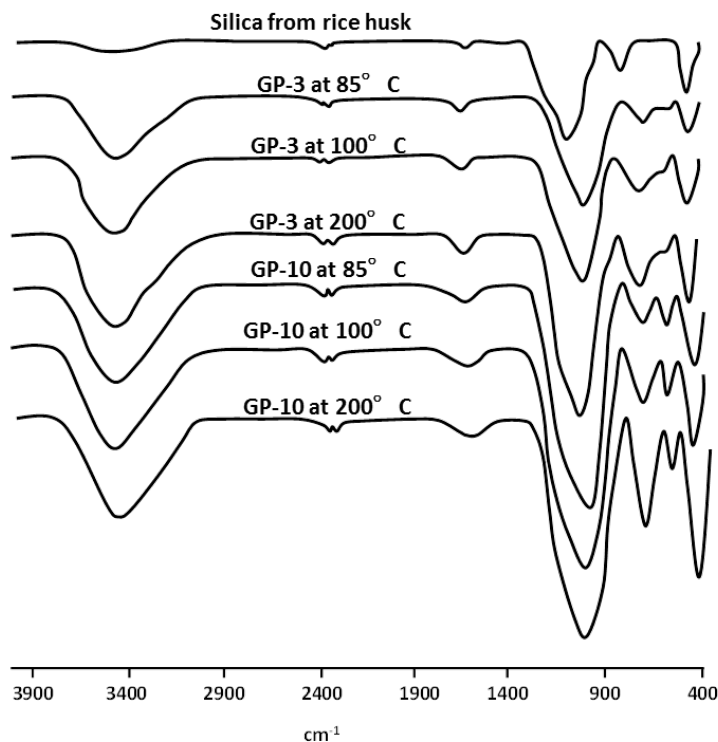
**Figure 6.** X-ray diffraction of geopolymers synthesized by alkali activation of silica from rice husk and metakaolin different curing time.

reconstruction of silica-alumina order in the paste was highly observed at the polycondensed GP-3. This was strongly demonstrated geopolymerization with the amorphous nature of the samples. In addition with the XRD results, the alteration and restructuring of materials during geopolymerization were also suggested in the diffraction pattern by the marked shift in the scattering diffraction peak for each samples. When the starting materials were activated with an alkaline solution, the scattering diffraction peak shifted from  $\sim 20^\circ$  to  $\sim 25^\circ - 28^\circ$  in  $2\theta$ . This suggested that the local bonding environment was changed during the geopolymerization process [17]. Apparently, an increase of the temperature from  $85^\circ\text{C}$  to  $200^\circ\text{C}$ , no influence of the amorphous structure of the geopolymers was observed.

The data suggested that the silica/alumina component was affected to the reconstruction. In order to confirm this from chemical reaction of RH silica and MK we measured FT-IR spectra of the resultant GP-3 and GP-10. **Figure 7** shows the infrared spectra of the geopolymer matrixes. The band around  $460\text{ cm}^{-1}$  was related to Al–O and Si–O in plane and bending modes,  $730\text{ cm}^{-1}$  with octahedral Al and  $820\text{ cm}^{-1}$  with tetrahedral Al–O stretching and, the peak  $1030\text{ cm}^{-1}$  was assigned with asymmetric Si–O–Al stretching [18] [19]. The change in the intensity of the IR peaks was associated with the structural reorganization by the geopolymerization of RH silica and MK. In the geopolymer samples prepared using the RH silica, there was an increase and broaden in the IR intensity of IR peaks indicating higher polymerization, when the content of the RH silica was high. The IR peak around  $1030\text{ cm}^{-1}$  meant that overlapping of the IR peaks related to  $\text{SiQ}_n$  ( $n = 0 - 4$ ) structural units [20]-[24] was caused and became broaden, especially a higher temperature. In addition, the spectral data has broadening peak at  $3400\text{ cm}^{-1}$  for OH stretching of Si–OH and Al–OH. It was apparent that the GP-10 system contained broadening tendency on the OH stretching peak. This meant that higher RH silica content easily occurred in the geopolymerization with MK.

#### 4. Conclusion

Based on the result of these analyses, it could be concluded that silica obtained from rice husk combustion at  $700^\circ\text{C}$  became to be raw material for geopolymers and significantly contributed to the formation of geopolymer



**Figure 7.** Infrared spectra of geopolymers synthesized by alkali activation of silica from rice husk and metakaolin at different curing time.

matrix with MK. The presence of the RH silica was an important during the geopolymerization reaction due to sodium hydroxide activation. The evolution of the viscoelastic parameters of the geopolymers GP-3 and GP-10 were performed by dynamic rheology method for pastes. In general, the elastic modulus quickly exceeded the viscous modulus regardless of the geopolymer studied, indicating that both materials was on the process of solidified geopolymerization having reconstructed Si and Al species.

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