

Mechanical, thermal and flammability properties of nonwoven kenaf reinforced acrylic based polyester composites: Effect of water glass treatment

M S Salim¹, M F Ahmad Rasyid¹, M A Abdullah¹, R Mat Taib¹ and Z A Mohd Ishak^{1,2*}

¹School of Material and Mineral Resources Engineering, Universiti Sains Malaysia, 14300, Nibong Tebal, Pulau Pinang, Malaysia

²Cluster of Polymer Engineering, Science and Engineering Research Centre, Universiti Sains Malaysia, 14300, Nibong Tebal, Pulau Pinang, Malaysia

Email: zarifin.ishak@gmail.com

Abstract. Within this current work, polyester resin on acrylic basis will be modified by the incorporation of environment-friendly sodium silicates (water glass). The modified resin system then was applied on non-woven kenaf fibre (KF) mat via resin impregnation process followed by a compression moulding to prepare the composite samples. The purposes of introducing water glass into the resin system were to improve the fibre-matrix wettability and enhancing the fire resistance in the reinforced composites. Mechanical, thermal and surface morphologies of the composites were examined. The variations in water glass composition in enhancing the flame retardant properties of the composites were evaluated by limiting oxygen index (LOI) and UL94 standard. Significant improvement of fire resistance properties of the composites as amount of water glass increases was observed but reduction in mechanical properties of the composites was recorded.

1. Introduction

The European automotive makers nowadays have extensively use natural fibre within the passenger cars not only for acoustic damping materials but also the interior structural parts in the form of polymer composites. Door trims, spare wheel cover, sun roof, headliners, just to name a few that have been developed commercially by utilizing natural fibre as the reinforcement [1]. The natural fibre reinforced composites have established themselves due to their good mechanical properties, their low production costs, and the good environmental properties [2]. Owing to their low density (approx. 1.3-1.5 g/cm³), natural fibres have a very good lightweight potential. Other features of natural fibre composites are the very good process related and acoustic properties. Additional advantages like good life cycle assessment and easier processability compared to glass fibre materials can also be taken into account [3]. Despite the availability of various types of natural fibre, kenaf fibre, KF (*Hibiscus cannabinus*) are largely cultivated here in Malaysia due to the climate suitability [4]. Realizing the potential of KF in manufacturing industry, Malaysia government has announced that this crop plant could be the third commodity plant of the nation after rubber and palm oil [5].

Conventional thermoset matrices such as polyester and vinyl ester have the ability to be reinforced by natural fibres. However, polyester and vinyl ester matrices tend to suffer from



shortcoming since they emit styrene not only during processing but also from the finished products. The introduction of acrylic based polymer resin in the form of Acrodur resin by BASF has emerged as a new solution in polymer binder technology. This resin is environmentally friendly due to its non-corrosive properties and does not emit styrene during processing and in the final products. The only by product upon the curing process is water. Below its curing temperature, the resin exhibits thermoplastic properties which allow the resin to be processed by means of conventional thermoplastic processing. After being thermally cured, the material shows thermoset properties i.e. resistant to wear and possesses excellent thermal, mechanical and chemical stability [6]. Due to the good features of this resin, it is suitable to be used in automotive industry especially for interior trimmings [7]

One disadvantage of natural fibres is their low chemical compatibility with hydrophobic polymers. This leads to elevated water absorption of natural fibre reinforced composites that can have a significant effect on the mechanical properties of the composites. Another disadvantage of natural fibre reinforced composites is their high flammability that limits their application in many fields including in the automotive industry. Sodium silicate or often referred to as water glass has been considered as a proper modifier for polymeric materials [8]. The incorporation water glass within the polymer resin could provide the solution of both shortcomings i.e. improving the fibre to matrix interaction and the same reduce the flammability. There is similarity in chemical structure between polymerized water glass (polysilicate) and silane. Thus, water glass might act as coupling agent in improving fibre to matrix interaction as shown in the theoretical model by Medina and Schledjewski (2009) (see figure 1). Thongpin et al. (2015) reported that woven mat of jute and abaca fibre treated by sodium silicate significantly increases the tensile strength of the reinforced PLA composites by nearly 25 and 30% respectively. Wang et al. (2010) studied the mechanical properties of sodium silicate treated-moso bamboo particles reinforced polyvinyl chloride composites. They reported an improved tensile strength and Young's modulus of water glass-treated moso bamboo particles. In terms of flame retardant properties, Basak et al. (2014) reported that water glass treatment done to jute fabric by padding method significantly increase the flame retardant properties of the fibre. The LOI value increases from 21 to 43 as a result of 8% water glass treatment onto the fibre.

Based on the literature review, water glass might possess enormous potential as additive to improve the mechanical and flammability properties of the composites. Therefore, the aim of this study is to seek the optimum amount of sodium silicate loading to resin mixture in order to improve fibre matrix interaction and at the same time increase the flame retardant properties of KF reinforced Acrodur composites. The effect of water glass content to mechanical and flammability of the composite will be reported within the current work.

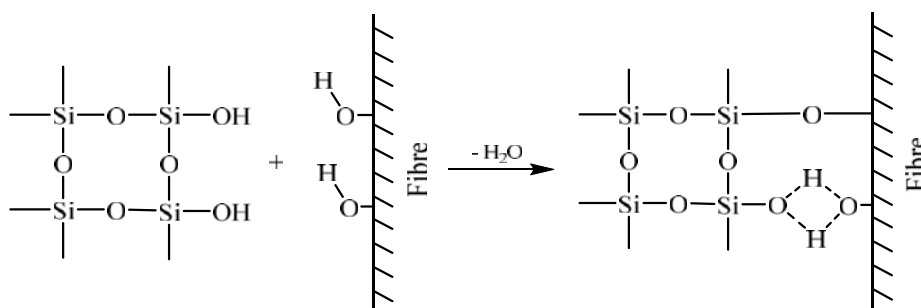


Figure 1. Theoretical model for the surface between water glass and natural fibres.

2. Experimental

2.1 Materials

Kenaf fibre (KF) with an average length of 80 mm was supplied by National Kenaf and Tobacco Board (NKTB), Malaysia. These fibres then underwent a needle punching process to form a non-woven KF mat (NWKF) with an areal density of 1200g/m². The preparation of NWKF is given elsewhere [13]. Acrodur resin 950L used in this study was obtained from BASF. This resin is an aqueous acrylic resin based on modified polycarboxylic acid and a polyalcohol (crosslinking agent) that creates a polyester thermoset material upon crosslinking reaction by esterification at a temperature above 130°C (Figure 2).

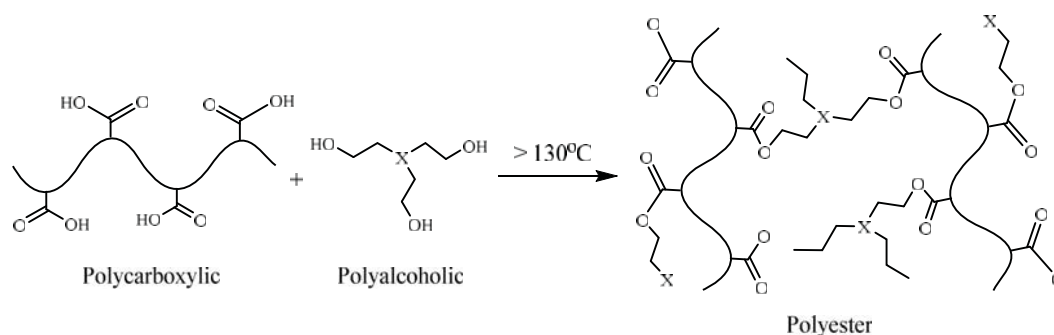


Figure 2. Crosslinking reaction of Acrodur resin.

Sodium silicates belong to the family of soluble silicates, also known as water glasses that represent one of the most versatile inorganic chemicals available. Water glass are manufactured by fusing high purity quartz sand (SiO₂) with sodium or potassium carbonate (Na₂CO₃ or K₂CO₃) in an open hearth furnace at 1100 – 1200°C [8]. The resulting glass is then dissolved using high pressure steam to form liquid silicate or “waterglass” which is clear and slightly viscous. Water glass reacts in aqueous solutions to polysilicates as shown in figure 3 [9]. In this study, sodium silicate solution was obtained from Sigma containing 26 wt.% SiO₂ and 10.6 wt.% Na₂O.

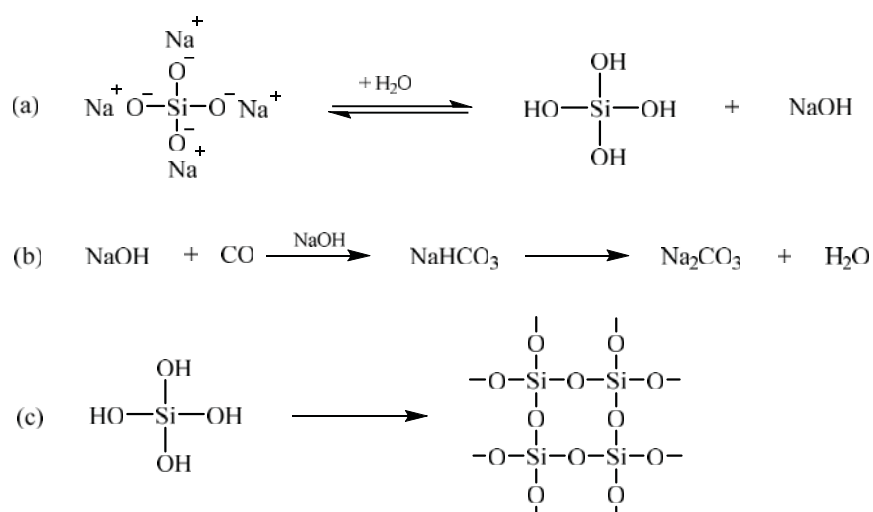


Figure 3. Polycondensation of water glass.

2.2 Viscosity of resin mixture

Different percentage of water glass was added to the Acrodur resin to analyse the compatibility of the resin system with water glass. The stability check of the modified systems was carried out through viscosity measurements and the result is shown in Figure 4. The viscosity of the resin mixture was found to gradually increase from 3900 up to 6000 Pa.s as the water glass content increases from 10 wt.% to 30 wt.%. However, the viscosity increases dramatically to over 14000 Pa.s as 40 wt.% of water glass was added to the resin mixture. High viscosity of resin mixture is not preferable since it might inhibit an adequate impregnation of the NWKF during impregnation process. Therefore, impregnation process was carried out with a maximal 30 wt.% water glass content in the matrix system.

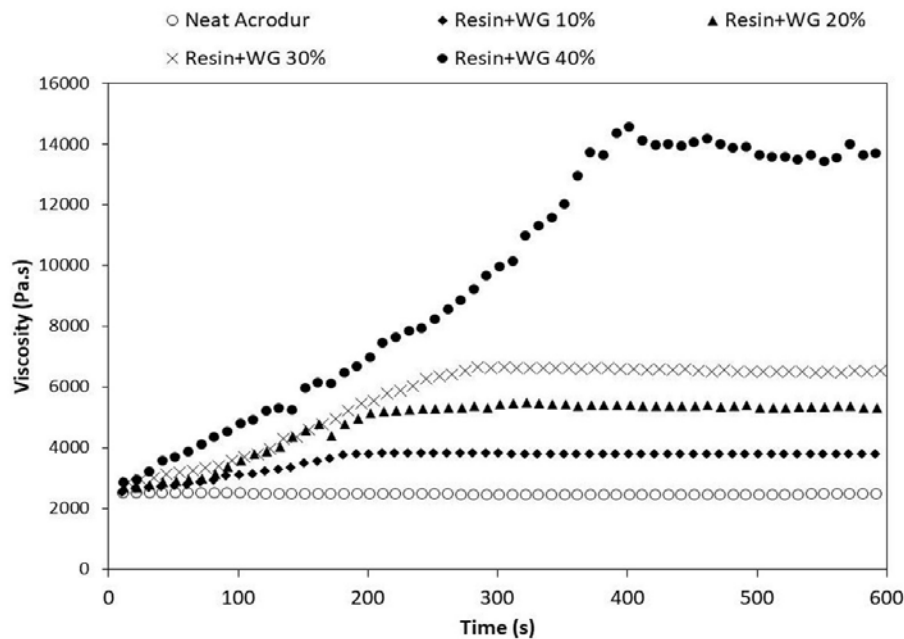


Figure 4. Viscosity of the matrix system mixed with water glass.

2.3 Composite fabrication process

The incorporation of water glass to Acrodur resin yield particles of insoluble polysilicates that increase the viscosity of water glass-Acrodur mixture. Due to this reason, the mixture was properly mixed by electric mixer to segregate these particles into smaller size prior to impregnation process. The impregnation process was carried out by introducing the KF non-woven mat to the fabricated impregnation line consisting of Acrodur and sodium silicate mixture (10, 20 and 30 wt.%). The impregnation process procedure is given elsewhere[14]. After impregnation, the semi-finished material (prepreg) was post-dried inside a vacuum oven at 70°C until the moisture content was approximately 15%. The prepregs were then compression moulded using GOTECH model GT7014-H hydraulic hot press machine at 210 °C for 6 min at 10 bar. Once the pressing process completed, the prepared composites were taken from the mould for characterization. Table 1 depicts the designation of the composites with respect to the water glass content.

Table 1. Designation of KF reinforced Acrodur composites with respect to resin and water glass content.

Designation	Resin content (wt%)	Water glass content (wt%)
WG 0%	100	0
WG 10%	90	10
WG 20%	80	20
WG 30%	70	30

2.4 Mechanical test

The flexural strength and flexural modulus of the composites were determined using the three-point bending test method as per ASTM D790 standard. The span-to-depth ratio of the test specimens was maintained at 16:1. The flexural test was conducted using Universal Testing Machine Instron 5690 (USA). The experimental was carried out at a crosshead speed of 1 mm/min. The average value of flexural strength and modulus were taken from a total of six composite samples according to the machine direction of non-woven mat. Plain-strain fracture toughness of the KF reinforced composites was determined according to ASTM D5045 by single edge notch bending (SEN-B) approach. The sample geometry [i.e., length (L), span length (S), width (W) and thickness (B)] of the specimens satisfies the condition of $2B < W < 4B$, as specified in the standard. The initial crack length (a) was generated by tapping at the centre of the notch of the specimen with a new razor blade. The SEN-B specimens were tested using a 5 kN load cell at a crosshead speed of 1 mm/min. The load–displacement curves generated by the test machine were recorded and the maximum load upon fracture was used to calculate the K_C value of the composite as in Equation 1.

$$K_C = Y \frac{3PS\sqrt{a}}{2BW^2} \quad (1)$$

where P is the maximum load and Y is the shape factor.

2.5 Flammability test

2.5.1 UL 94. The flammability of the different samples was characterized using UL 94-V method. The material classifications are based on the burning behaviour as shown in Table 2.

Table 2. Flammability rating of UL94-V.

	V-0	V-1	V-2
Burning time after flame application (s)	≤ 10	≤ 30	≤ 30
Total burning time (s) for 10 flame applications	≤ 50	≤ 250	≤ 250
Burning and afterglow times of samples after second flame applications	≤ 30	≤ 60	≤ 60
Dripping of burning specimens	no	no	yes
Specimen completely burn	no	no	no

2.5.2 Limiting oxygen index (LOI). The LOI of the composites were determined by FTT Oxygen Index Tester from Fire Testing Technology Ltd. (UK), according to ASTM D 2863. The LOI is the minimum percentage oxygen that is required to maintain flaming combustion of a specimen. The 3mm

in thickness of the composites laminates were cut into 6.5 mm wide and 120 mm long specimens for the LOI tests. The test specimen was ignited at the top. Between individual test specimens of a given sample, the oxygen levels were adjusted upward or downward by approximately 0.2% oxygen depending on whether the specimen continue to burn. The LOI was recorded as the lowest percentage oxygen level that allowed 50 mm of the specimen to be burned or continued flaming for 180s duration. The LOI of the composites for each water glass loading was calculated from the average value of 15 specimens as suggested by the aforementioned ASTM standard.

3. Results and discussions

3.1 Determination of crosslinking percentage

DSC analysis was conducted on the composites to determine the crosslinking percentage of the matrix with the respective amount of water glass content. DSC data was used to detect the enthalpy of residual crosslinking capability ($\Delta H_{\text{residual}}$) in the composites samples and infer the degree of crosslinking by comparing it to the enthalpy of crosslinking reaction (ΔH_{resin}) of an uncured Acrodur resin. The uncured Acrodur resin was first dried under vacuum at 50°C for 3 hours to eliminate the water content without initiating the crosslinking reaction prior to DSC analysis. The DSC scan of dried Acrodur resin at 10°C/min is shown in figure 5 (a). The peak obtained at 200°C corresponds to the matrix curing with a reaction enthalpy of $\Delta H_{\text{resin}} = 140$ J/g. Figure 5 (b-e) show the DSC curves for composites with water glass content of 0, 10, 20 and 30%, respectively. It is important to emphasize that the weight of reinforcement and additive (fibre and sodium silicate) have been excluded in the enthalpy calculation for fair comparison with the uncured resin. The first peak at 100°C is related to the residual moisture within the composite while the second peak at 200°C can be attributed to the post-curing of the Acrodur matrix. The matrix degree of crosslinking was then estimated using Equation 2.

$$\text{Crosslinking percentage (\%)} = \frac{\Delta H_{\text{Resin}} - \Delta H_{\text{Residual}}}{\Delta H_{\text{resin}}} \times 100 \quad (2)$$

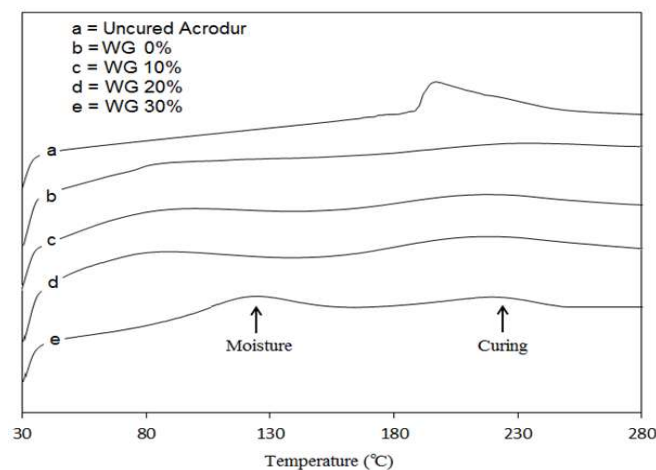


Figure 5. DSC curve for uncured Acrodur resin and composites.

Table 3 summarizes the crosslinking percentage of KF reinforced Acrodur composites with respect to the difference in water glass content. Based on the DSC assessment, incorporation of water glass significantly reduced the degree of the crosslinking. The reduction of degree of crosslinking could significantly affect the mechanical performance of composites [15].

Table 3. Degree of crosslinking of composites.

Composites	$\Delta H_{\text{residual}}$ (J/g)	Degree of Crosslinking (%)
WG 0%	22.26	84.10
WG 10%	31.58	77.44
WG 20%	43.05	69.25
WG 30%	52.23	62.69

3.2 Mechanical properties KF reinforced composites

Figure 6 shows the flexural and fracture toughness of the composites with respect to the water glass content. It can be seen that the flexural strength decrease by increasing amount of water glass content. A reduction by 3%, 16% and 44% for flexural strength were recorded by the incorporation of 10% 20% and 30wt% of water glass, respectively. This tendency can be probably explained by an interference of the reaction between prepolymer substance of polycarboxylic acid and the polyalcohol to form polyester with a reaction of one or even both matrix components with water glass inhibiting the curing process of Acrodur resin. As a consequence, less conversion of the resin into rigid thermosetting polyester occurred, therefore reducing the flexural strength of the composites. In terms of flexural modulus, it is interesting to note that the incorporation of 10wt% water glass (WG10%) imparted a slight increase in flexural modulus by 10%. This is due to the introduction of stiff polysilicate within the composite system as a result of polycondensation reaction between water glass and Acrodur resin (see Figure 3). However, the inhibition of crosslink by the addition of higher water glass content (above 20wt%) gives adverse effect to the flexural modulus of composites. A reduction of flexural modulus by 17% and nearly 47% was recorded by WG20% and WG30% composites, respectively. As mentioned by Galvão et al. (2013), uncured functional groups can act as plasticizers, reducing the mechanical properties of composites. In contrast, the fracture toughness of the composites was found to increase as the water glass content increases (see figure 6a). For instance, incorporation of water glass content by 20% and 30% improved the fracture toughness of composites by 34% and 62% respectively. Due to the lower crosslink percentage, some flexibility properties of uncured Acrodur matrix still remained, contributed the ability of absorbing energy, and therefore increased the fracture toughness.

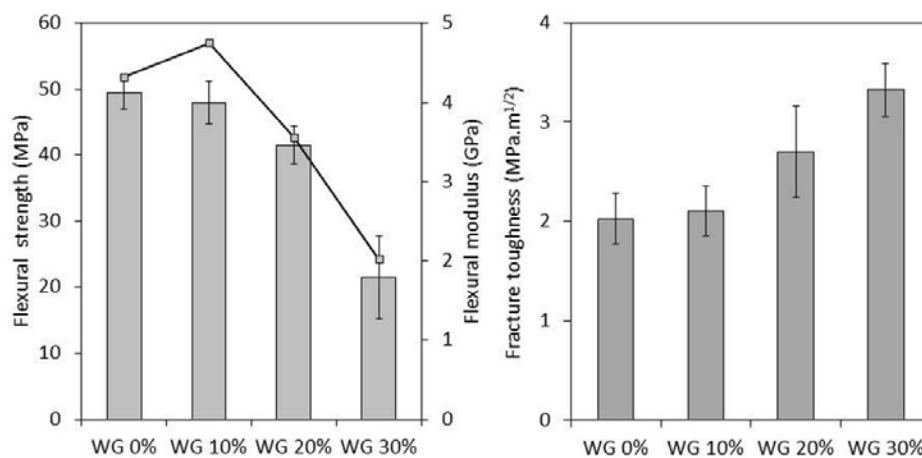


Figure 6. The mechanical properties of Acrodur reinforced KF composites with respect to the water glass content a) flexural properties and b) fracture toughness.

3.3 Flammability properties

Table 4 depicts the UL94 classification and LOI value of the composites with different amount of water glass content. The composites impregnated with solely Acrodur resin and Acrodur with 10% water glass are classified in the category of V-1 due to the burning time exceeding 30s after the application of flame. On contrary, the composites impregnated by Acrodur resin with the additional of 20% and 30% of water glass fall in the best category of V-0 because the flame extinguishes by itself within 10s when the flame is taken away from the specimens. Figure 7 shows that all composites samples containing water glass are not completely burned. It can be deduced that the more water glass content in the resin the better the flame retardant efficiency of the composites. The improvement in the flame retardant of the composite could be evaluated quantitatively by referring to the LOI value which refers to the minimum concentration of oxygen (%) that will support combustion of a material. As expected, the LOI value increase dramatically with the increasing amount of water glass. In the presence of fire, the crystals-like structure of silicates helps to provide an insulating barrier between the product and the flame, and will thus slow down the spread of fire. This result consistent with the study by Cheng and Zhou (2016). They reported an increase in LOI value from 24.5% to 39.5% as the amount of sodium silicate loading increase in the polyurethane.

Table 4. UL94 classification and water absorption value of composite with different amount of water glass content.

Composites	UL94 Classification	LOI
WG 0%	V-1	24
WG 10%	V-1	33
WG 20%	V-0	38
WG 30%	V-0	46

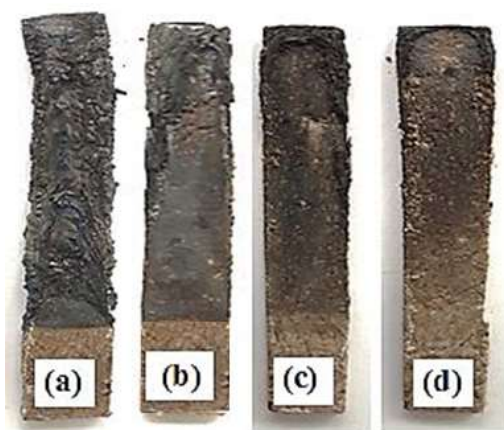


Figure 7. UL 94 tested sample (a) WG 0%, (b) WG 10%, (c) WG 20% and (d) WG 30%

3.4 SEM and EDX analysis

Figure 8 shows the SEM image of composites surface with different amount of water glass content. By increasing the amount of water glass in the matrix system, fewer polymers can be observed in the composite's surface as a very open surface can be perceived. Composites with thermoset resin (WG 0%) polymer shows a smooth, homogeneous surface (Figure 8a), while the compound with 30wt% water glass (WG 30%) exhibits an irregular structure with many air gaps (Figure 5d). This is due to the evaporation of uncured resin during composite fabrication process by compression moulding.

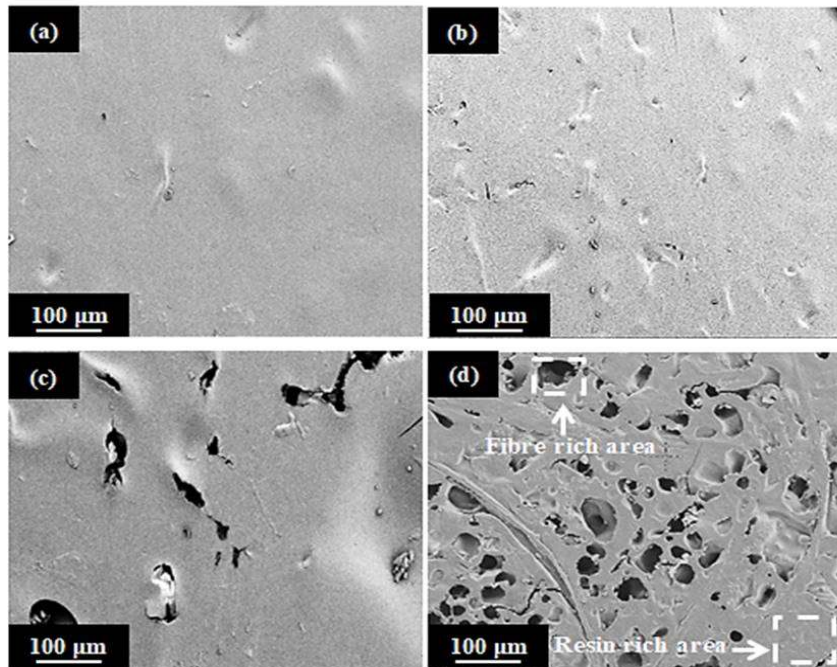


Figure 8. SEM microscope images of composites surfaces (a) WG 0%, (b) WG 10%, (c) WG 20% and (d) WG 30%.

In this research, work Energy Dispersive X-Ray (EDX) analysis was applied on the surfaces of the SEM-samples. The results were shown in figure 9. By using the EDX technique, the composition of the compounds could be detected. Samples impregnated just with thermoset matrix showed only carbon and oxygen signals (Figure 9a), the samples impregnated with sodium water glass showed a small peak for carbon and sodium, a middle signal for oxygen, and a significant signal for silicon (Figure 9b-d). The presence of water glass on the composites surface explains the good behaviour of suppressing flame during the flammability test. It can also be perceived that the decreasing of the carbon signal takes place by increasing the water glass amount on the composite. This could again be a sign of the decreasing of the thermoset polymer amount in the composite due to the interference of water glass on the curing reaction of the polyester system. The EDX analyses on the resin rich area and fibre rich area for WG30% were shown in figure 9(d) and (e), respectively. It is interesting to note that the silicon peak was observed not only on the polymer but also on the fibre surface. The presence of this peak on the fibre rich area might approve the hypothesis where the incorporation of water glass could improve the fibre-matrix bonding by silane coupling mechanism. This is consistent with the study by Thongpin et al. (2015) where sodium silicate treatment on jute and abaca fibres could enhance the fibre-matrix bonding thus improving the tensile strength of the composites. In this study however, the increase in composite strength due to the improved fibre-matrix bonding was constraint by the inhibition of resin curing.

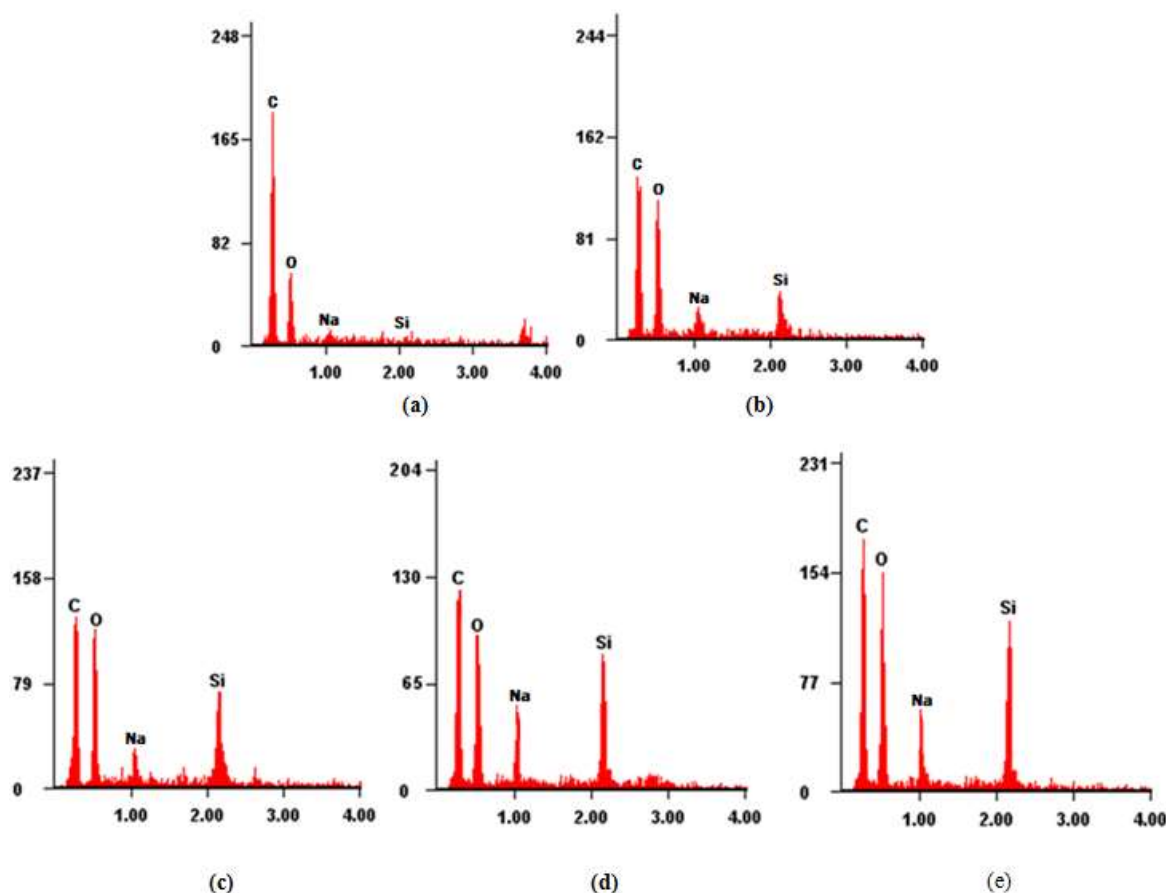


Figure 9. EDX analysis of KF reinforced Acrodur resin with different amount of water glass content a) WG0%, b) WG10%, c) WG20%, d) WG30% (resin rich area) and e) WG30% (fibre rich area).

4. Conclusions

Within this research work sodium water glass was used as environment friendly inorganic additive in a thermoset matrix system. Water glass should act in the composite as a binder as well as a flame retardant system. However, the improvement of fibre to matrix bonding was constrained by the interference of water glass on the curing reaction of the polymer avoiding the generation of the rigid polyester. The fracture toughness somehow increased as the water glass content increases. The presence of uncured functional group within the resin Acrodur imparts ductility, contributed the ability of absorbing energy thus increased the fracture toughness. Very promising is therefore the flame retardant effectiveness of composite due to the water glass loading. The flame extinguished by itself during the fire testing when the flame was taken away from the sample containing as low as 20% water glass content giving an excellent UL94 classification of V-0. The improvement in flame retardant efficiency of the composites containing water glass content was quantitatively verified by the increasing LOI of the composites as amount of water glass in the composites increase. In order for the developed composites to be used in automotive industry, the amount of water glass content should be appropriately selected to ensure a good compromise between flame retardant properties and strength of the composites is achieved.

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