Investigation of Okposi Brine-based Sodium Hydroxide for Indigenous Manufacturing of Sodium Polyacrylate Absorbent

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DOI: https://doi.org/10.51584/IJRIAS.2024.910014

Received: 20 September 2024; Accepted: 25 September 2024; Published: 07 November 2024

ABSTRACT

Cut-down on importation of essential sodium hydroxide which usually improves absorbency of sodium polyacrylate absorbent (SPAA) determines the success of cost-effective manufacturing of diapers in Nigeria. The sodium hydroxide functions include promotion of hydroxyl groups, which are water loving ions and catalyzing reaction of crosslinker and sodium polyacrylate polymers. Okposi brine-based sodium hydroxide is investigated with N, N'-Methylenebisacrylamide (MBAA) crosslinker for preparation of the sodium polyacrylate absorbent. Different concentrations of sodium hydroxide neutralizer in the solution polymerization reaction were observed for optimal reaction. The samples of synthesized absorbents exhibited hydroxyl groups and amino groups as studied by FTIR spectra. Based on the free absorbency test, the corresponding absorbency and absorption rate are graphically represented and tabulated. The synthesized K-SPAA exhibited high absorbency of 39 wt.% and absorption rate of 8.580 ml/min, translating to capacity of 90 g fluid per gram of K-SPAA in the temperature range of 25 – 32 ℃. In overall, the apparent performance of the Okposi brine-based sodium hydroxide indicates high potential of manufacturing diaper absorbent in Nigeria.

Keywords: Okposi, Sodium hydroxide, Cross-linker, Polymerization, Absorbent

INTRODUCTION

Sodium polyacrylate absorbent type of superabsorbent polymer excellent for voluminous absorption of fluid [1], largely depended on sodium hydroxide and crosslinker [2 – 5]. In terms of absorbency, most diapers constructed with the sodium hydroxide close the gap between polymer and cotton (clothe) absorbents. The polymer performance can vary with respect to concentration of the sodium hydroxide. Recent study shows that the sodium polyacrylate absorbent with sodium ion works more efficiently in liquid absorption [6]. Thus, optimizing the concentration of sodium hydroxide solution potentially enables high absorption rate of the polymer-based diaper.

Manufacturing of diapers in Nigeria will certainly increase with optimized concentration of sodium hydroxide for high quality polymer absorbent. The service groups, babies 42.54 % and aged adults 3.3 % make the national population [7]. In economic view, manufacturers easy access to the absorbent precursors would meet the population demand. Researches show that different sources and preparation methods of sodium hydroxide influences performance of the absorbents [8,9]. In order to ensure sustainable manufacturing of diaper, it is imperative to investigate Okposi brine-based sodium hydroxide to improve absorbency of sodium polyacrylate absorbent. Okposi brine in Ebonyi State Nigeria is naturally endowed Salt Lake that replenishes all year round and serves the community as source of salt used for cooking [10]. The use of Okposi brine-based NaOH can be expanded to synthesis of absorbent for diaper manufacturing in Nigeria.

The degree of neutralization of acrylic acid determines whether the water absorption occurs high, as well as swelling rate of the sodium polyacrylate. The work performed on effect of different degrees of neutralization in crosslinked sodium polyacrylate reported potential increase in water amount with increase in degrees of neutralization of acrylic acid [11]. Meanwhile, Seright et al assert that the crosslinked sodium polyacrylates are insoluble in solvents to uphold more liquid over the non-crosslinked polymer that dissolves in water [12]. Thus, the insolubility of N, N'-Methylenebisacrylamide crosslinker combined with neutralizer of different concentrations remains potential study for obtaining a quality sodium polyacrylate absorbent.

In this work, optimization of Okposi brine-based sodium hydroxide concentration contributes to improving substantial absorbency of diaper absorbent. The varied amount of sodium hydroxide introduced ionic strength in the polyacrylate polymer [13]. Consequently, the sodium ions involved in solution polymerization of sodium acrylate monomers are considerably the active neutralizer. Thus, optimal reaction of cross-linked sodium acrylate absorbent happened at the reaction temperature. The temperature was varied between 10–13 ℃ to observe the effect on polymerization rate. The absorbents with and without neutralizer, crosslinker were investigated of free absorbency and absorbency under load.

EXPERIMENTAL

Preparation of Sodium Polyacrylate Absorbent

Acrylic acid 99 % and N, N'-Methylenebisacrylamide (MBAA) 99 % were purchased from LOBA CHEMIE PVT. LTD, to prepare acrylic monomers. Ethylene glycol di-methacrylate (EGDMA) 98 % from SIGMA ALDRICH chemical company, stored at room temperature were not treated further before use. Initiator, ammonium persulfate 98 % from CENTRAL DRUG HOUSE (P) LTD. chemical company initiates the polymerization reaction. Neutralizer, sodium hydroxide 97 % from LOBA CHEMIE PVT. LTD. chemical company is used to compare with the Okposi brine-based sodium hydroxide. Surfactant, Sodium Dodecyl Sulfate (also known as sodium lauryl sulfate) 91 % from BODI LTD. chemical company helps to control the polymerization process and improve the stability of the reaction mixture. The Okposi brine-based sodium hydroxide was prepared by electrolyzer in chemical engineering laboratory, Nnamdi Azikiwe University, Awka Nigeria.

Neutralization reaction of 30 % v/v acrylic acid (AA) solution and sodium hydroxide solution (100 %, 75 %, 50 %, and 25 % w/v NaOH) was performed in a temperature range of 10–13 ℃. Each 20 ml AA was neutralized with 20 ml NaOH of different concentrations. The temperature was controlled by ice bath. Addition of the neutralizer, NaOH solution was performed dropwise into a 250 ml beaker containing the acid while stirring and the reaction was allowed to complete at room temperature. The sodium acrylate monomer was further reacted with different concentration of crosslinker (0.1 %, 1.0 % and 10 % w/v MBAA) and 0.5 % surfactant in presence of 1.0 % w/v polymerization initiator. The reaction was allowed for 2 hrs. under room temperature and the cooled product was dried at 60 ℃ in a thermostatic oven for 6 hrs. and identified as low crosslinked absorbent (LCA). Moderate crosslinked absorbent (MCA) and high crosslinked absorbent (HCA) were prepared by repeating the polymerization, while varied the crosslinkers, 1.0 % w/v and 10 % w/v represent the moderate and high crosslinked absorbent respectively. Throughout the experiment, while the neutralizer and crosslinker varied, the surfactant and initiator remained constant.

Characterization

Free-absorbency

In this method, a bag made of non-woven fabric, generally a tea bag (that are commonly available), is used [14,15]. The bag is pre-wetted with the test liquid and then placed in another dry cloth to remove excess or weakly bound water or liquid. The bag is then weighed and a calculated quantity of super absorbent polymer (SAP) sample was kept into it. The bag is inserted into the test liquid (usually water or buffer of definite pH or saline solution) for a fixed period of time. Then the bag is hanged to remove excess of water until no liquid drop is dropped off and weighed. The swelling capacity is then calculated by using the following equation [16]

$$S = \frac{W_1 - W_0}{W_0}$$

Where W_0 is the initial weight of tea bag containing sample, and W_1 is the weight of the tea bag after removing excess water.

Swelling Kinetics

To studying the absorption rate of the hydrogels, samples (0.5±0.001 g) were prepared as tea bags, and immersed in 200mL distilled water. At specific time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the above procedure.

Fourier transform infrared (FTIR) technique

The FTIR spectra provides structural functional groups of the samples. The scanning was performed in the frequency range of 500–4000 cm^{-1} and at a resolution of 4 cm^{-1} [18]. By comparing the bands of samples, before and after the adsorption of pollutant, changes introduced by the neutralizer and cross-links can be confirmed.

RESULTS AND DISCUSSION

Figure 1 shows pictures of imported KissKid, SoftCare absorbents and synthesized K-SPAA absorbent (where K is the product unique identifier for sodium polyacrylate absorbent, SPAA). The K-SPAA was dried to form the characteristic grains used in core of diaper. The result demonstrated that Okposi brine-based sodium hydroxide could form diaper absorbent. It is important to note that KissKid and SoftCare absorbents were purchased and have different synthesis methods, thus the three samples have slight difference of color appearance. However, the metric indicated that with solution polymerization, K-SPAA could be scale-up to meet demand of diaper manufacturers in Nigeria. Thus, KissKid and SoftCare companies in Lagos, Nigeria can afford low price of Okposi brine-based sodium hydroxide for synthesis of absorbents.

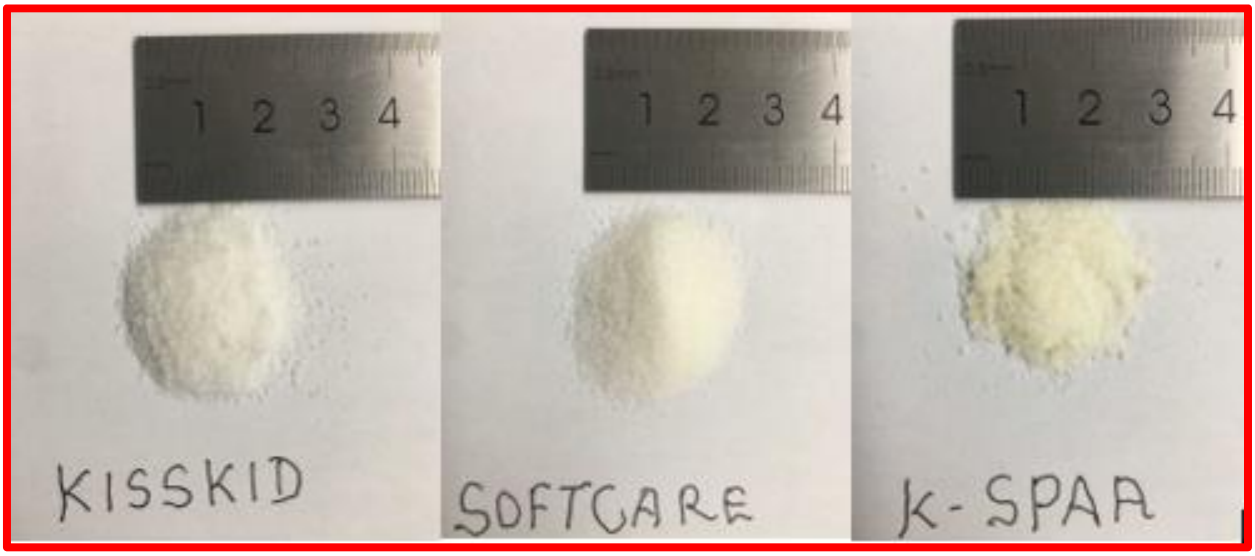

Figure 1. Pictures of imported Kiss Kid (left), Soft Care (middle) absorbents and (right) solution polymerized K-Sodium Polyacrylate Absorbent, K-SPAA

Absorbency tested in compliance with the free absorbency method is considered for the best three samples in **Figure 2**. The test condition, test medium water remains the same and equal for Kiss Kid, Soft Care, and K-SPAA absorbents with absorbency of 76 wt.%, 73 wt.%, and 39 wt.% respectively. In diaper application, K-SPAA absorbency (39 wt.%) is equivalent to 90g fluid/g of absorbent. The performance rating suitably ranks above the post-void residual volume (PVR), usually 43 grams for baby. Thus, few 5 grams of K-SPAA would suitably make baby diaper, which sustains the baby for entire day.

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume IX Issue X October 2024

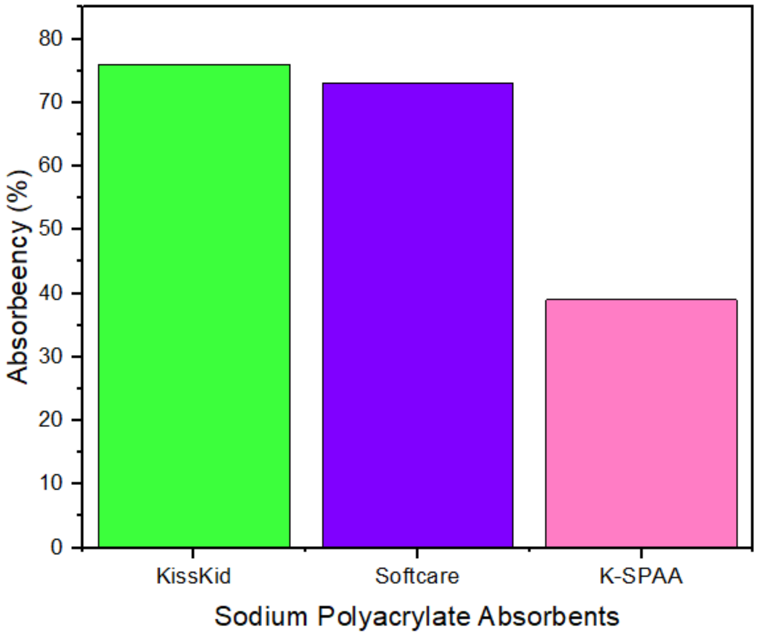

Figure 2. Absorbency of imported absorbents and K-SPAA made from Okposi brine-based sodium hydroxide

Absorption rate, which determines how long a baby can stay in excreted fluid is also a primary concern of end users. **Figure 3** shows the comparison of two imported absorbents and best two synthesized K-SPAA and J-SPAA absorbents (where J is the product unique identifier for sodium polyacrylate absorbent, SPAA). KissKid however displays superior absorption rate of 13.333 ml/min. almost double of SoftCare and K-SPAA absorption rates of 8.570 ml/min and 8.580 ml/min, respectively and more than double of J-SPAA absorption rate of 6.006 ml/min. When the crosslinker (*N*, *N′*-methylenebisacrylamide) changed from 2 w/v% to 1 w/v%, the K-SPAA (renamed J-SPAA) absorption rate lost 30 % of the initial rate. The neutralizer (Okposi brine-based NaOH) was same concentration in both K-SPAA and J-SPAA but the performance changed with change in MBAA. In comparison, the best SoftCare absorbent absorbs the baby PVR in 3min, while the KissKid and K-SPAA absorbents absorb in 5min, which relatively served the fast fluid uptake.

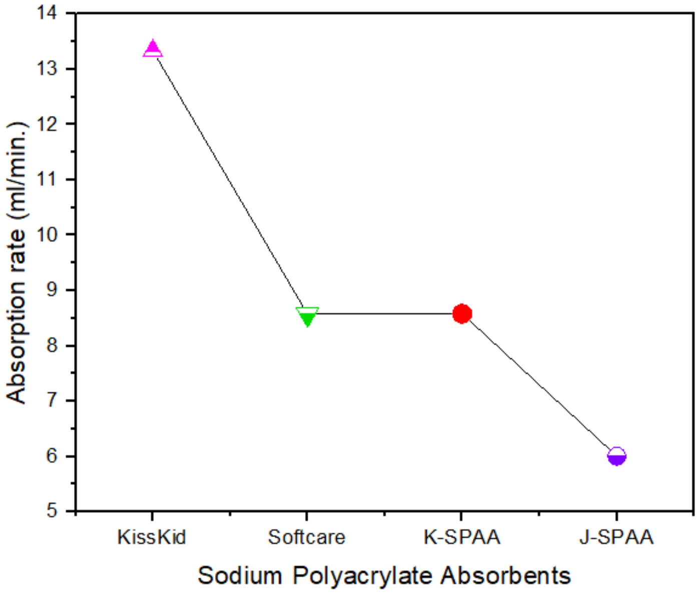

Figure 3. Absorption rate of the imported absorbents verses K-SPAA and J-SPAA (which is MBAA modified K-SPAA absorbent). The MBAA concentration in K-SPAA and J-SPAA are 2.0 w/v% and 1.0 w/v% respectively.

Effect of the Okposi brine-based NaOH concentration on absorbency was investigated. The percentage of NaOH was varied in K-SPAA absorbent and renamed as shown in **Figure 4**. The concentrations below and above the optimum concentration of 10 w/v% NaOH resulted in poor absorbency. C-SPAA absorbent containing 10 w/v% NaOH has a corresponding absorbency of 37 %. The low and high NaOH concentration of 5 w/v% and 100 w/v% in B-SPAA and G-SPAA absorbents correspond to absorbency of 20 % and 16 % respectively. The observed effect aligned to high activity of the as-prepared NaOH, which is promising quality for synthesis of sodium polyacrylate absorbent.

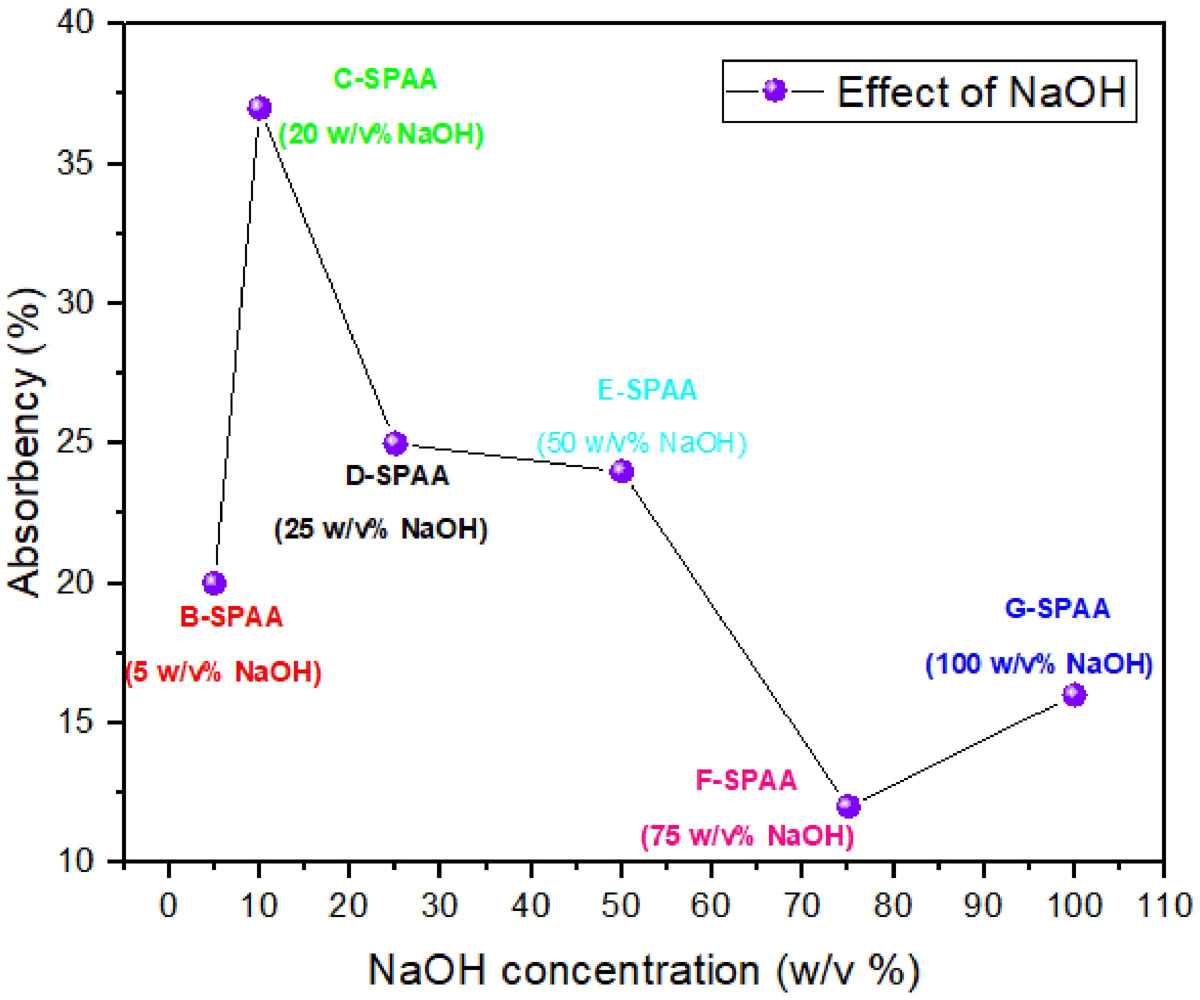

Figure 4. Effect of NaOH (neutralizer) concentrations: 5 w/v%, 10 w/v%, 25 w/v%, 50 w/v%, 75 w/v%, and 100 w/v% on absorbency of as-prepared absorbents with 1.0 w/v% MBAA crosslinker

Functional structures of the absorbents were investigated as shown in **Figure 5**. As expected, the C=O stretching bond at 1700 cm^{-1} [19] exceedingly diminished from the KissKid absorbent. There is also broad presence of newly formed O–H at 3352 cm^{-1} and N–H at 3300 cm^{-1} [20]. The proper breakdown of the carbonyl groups in both N, N′-Methylenebisacrylamide (MBAA crosslinker) and sodium polyacrylate aligned with the newly formed water loving groups. The result validates high absorbency of the KissKid absorbent in Figure 2. The desired hydroxyl and amino functional groups in large quantity will improve hydrogen bonding, which happens between the lone pairs of water and the functional groups to absorb the water. In absorbency test, many presences of these groups in absorbent are associated with the best absorbency of KissKid absorbent.

In **Figure 5 (b)**, the water loving groups have more presence in both stretching and bending bands of KissKid spectrum. The amino groups N–H bending at 1553 cm^{-1} and stretching at 3300 cm^{-1} [21] are quite smaller in the K-SPAA absorbent. Rather the reaction between the sodium polyacrylate and N, N′-Methylenebisacrylamide (MBAA crosslinker) favored more formation of C=O stretching at 1705 cm^{-1}, C–N stretching at 2569 cm^{-1}, and C–H stretching at 2932 cm^{-1}. In the fingerprint region, it is also obvious indication that the C–O rocking at 1163 cm^{-1} reacted weakly with the sodium hydroxide. Further, it is seen

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume IX Issue X October 2024

that only few hydroxyl groups are stretching at 3510 cm^{-1} for the spectrum. The result suggests that the K-SPAA absorbent experienced incomplete reaction, which involved poor formation of crosslinked absorbent, and limited water loving groups. Thus, the K-SPAA spectrum explained why the absorbency dropped significantly in Figure 2.

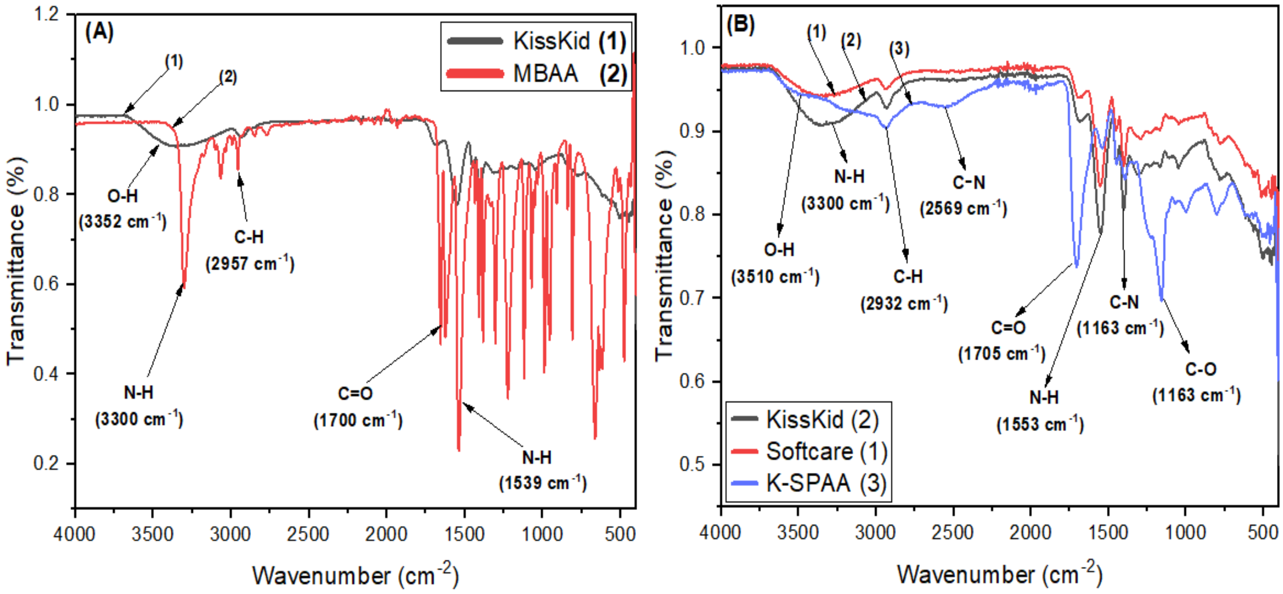

Figure 5. (a) FTIR spectra of imported KissKid and MBAA crosslinker, (b) imported absorbents and K-Sodium Polyacrylate Absorbent, K-SPAA

In order to validate the Okposi brine-based NaOH activity, K-SPAA was prepared without NaOH and renamed as A-SPAA. **Figure 6** shows effect of lack of hydroxide ions in the reaction between the monomer and crosslinker, which resulted in more formation of C–O rocking at 1163 cm^{-1}, C=O stretching at 1705 cm^{-1}, and C–H stretching at 2932 cm^{-1}. More electron distribution arising from the carbonyl carbon and amide carbon described the reaction, which involved the presence of high concentration of acidic compound. Although the polymeric reaction resulted in A-SPAA but heavy lack of O–H and N–H water loving groups explained why its absorbency is only 3 %.

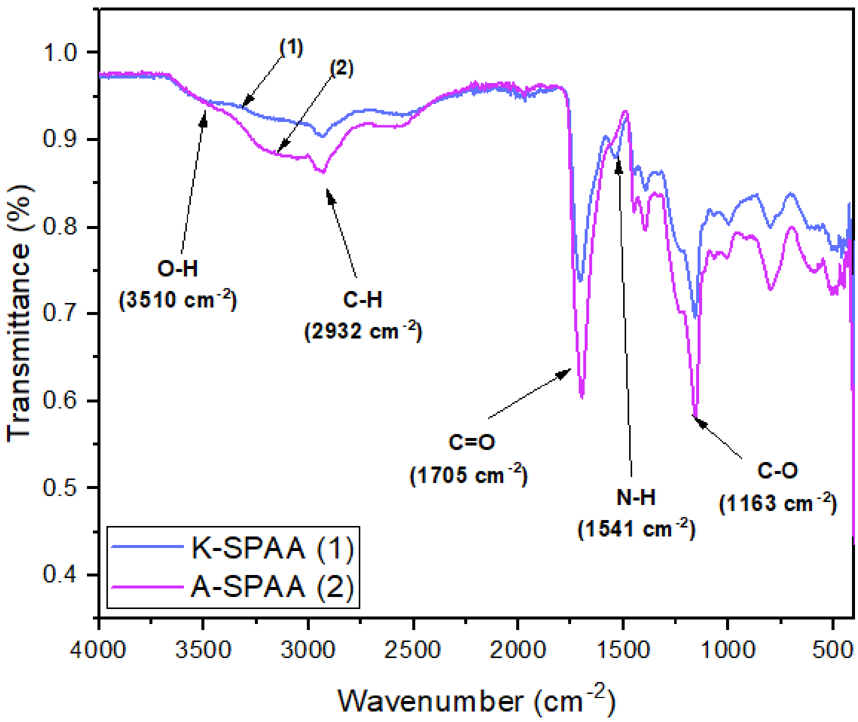

Figure 6. FTIR spectra of K-SPAA (10 % neutralizer) and A-SPAA (prepared K-SPAA without neutralizer)

The effect of NaOH and crosslinker (MBAA) is summarized as shown in **Table 1**. Concentration of monomer was kept constant in all the experiments. Then the Okposi brine-based NaOH was kept constant to understudy the effect of the crosslinker alone. The optimum MBAA concentration of 2 w/v % resulted in superior absorbency of 39 wt.% of K-SPAA, which is the best synthesized absorbent. On the other hand, the crosslinker was kept constant to understudy the effect of NaOH. The C-SPAA showed almost the same absorbency and absorption rate as K-SPAA. The result shows that the optimum reaction condition was found at 2 w/v % MBAA and 10 w/v % NaOH. As shown, the A-SPAA sample without neutralizer helps to know that the Okposi brine-based NaOH contributed 92.31 % to the improved absorbency of K-SPAA.

Table 1. Effect of NaOH and MBAA on absorbency of synthesized absorbents

S/N	**ABSORBENT**	**MBAA (w/v.%)**	**NaOH (w/v.%)**	**ABSORBENCY (wt.%)**	**ABSORPTION RATE (ml/min)**	**REMARK**
1	KISSKIDS	-	-	76	13.333	**Imported best**
2	SOFTCARE	-	-	73	8.570	Imported
3	H-SPAA	0	10	-	-	Synthesized
4	I-SPAA	0.1	10	0.35	-	Synthesized
5	J-SPAA	1	10	37	6.006	Synthesized
6	K-SPAA	2	10	39	8.580	**Synthesized best**
7	L-SPAA	3	10	31	10.309	Synthesized
8	A-SPAA	2	0	3	-	Synthesized
9	B-SPAA	2	5	20	1.847	Synthesized
10	C-SPAA	2	10	37	6.006	Synthesized
11	D-SPAA	2	25	25	4.796	Synthesized
12	E-SPAA	2	50	24	2.500	Synthesized
13	F-SPAA	2	75	12	1.333	Synthesized
14	G-SPAA	2	100	16	4.619	Synthesized

CONCLUSION

Okposi brine-based sodium hydroxide (NaOH) solution was utilized as a precursor for the preparation of sodium polyacrylate absorbent, SPAA. The neutralizer of deferent concentrations produced different effects on functional groups of the absorbent. The optimized solution with 10 w/v% NaOH was polymerized at ambient temperature to form best absorbent (K-SPAA) with high absorbency of 39 wt.%, which is translated to 90g water per gram of absorbent, compared to high 100 w/v% NaOH precursor. K-SPAA showed enhanced rate and the absorption rate reached 8.580 ml/min, which certify fast uptake of the baby PVR volume (15 ml) within 2 min. On the other hand, the imported SoftCare absorbent also showed ability of fluid uptake of the baby PVR volume within 2min. These results will contribute to the development of Nigeria-based sodium polyacrylate absorbents and promote cost-effective manufacturing of diapers in Nigeria.

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