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Preface

We would like to present, with great pleasure, the inaugural volume-7, Issue-9, September 2021, of a scholarly journal, *International Journal of Engineering Research & Science*. This journal is part of the AD Publications series *in the field of Engineering, Mathematics, Physics, Chemistry and science Research Development*, and is devoted to the gamut of Engineering and Science issues, from theoretical aspects to application-dependent studies and the validation of emerging technologies.

This journal was envisioned and founded to represent the growing needs of Engineering and Science as an emerging and increasingly vital field, now widely recognized as an integral part of scientific and technical investigations. Its mission is to become a voice of the Engineering and Science community, addressing researchers and practitioners in below areas

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Each article in this issue provides an example of a concrete industrial application or a case study of the presented methodology to amplify the impact of the contribution. We are very thankful to everybody within that community who supported the idea of creating a new Research with IJOER. We are certain that this issue will be followed by many others, reporting new developments in the Engineering and Science field. This issue would not have been possible without the great support of the Reviewer, Editorial Board members and also with our Advisory Board Members, and we would like to express our sincere thanks to all of them. We would also like to express our gratitude to the editorial staff of AD Publications, who supported us at every stage of the project. It is our hope that this fine collection of articles will be a valuable resource for *IJOER* readers and will stimulate further research into the vibrant area of Engineering and Science Research.

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Table of Contents

Volume-7, Issue-9, September 2021

Effect of Processing Method of Kidney Beans (*Phaseolus Vulgaris*) on Carcass Quality, Organ Weight and Organoleptic Properties of Broiler

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Abstract— *Effect of processing method of kidney beans (phaseolus vulgaris) on carcass quality, organ weight and organoleptic properties of broiler was studied using one hundred and twenty day-old chicks (Arbo acre strain). Raw, dehulled and boiled KB were used for treatment 2, 3 and 4, respectively. Prior to grinding of KB, 50kg was boiled at 100 ^{0}C for 1 hour, 10kg was dehulled by immersing in cool water for 20 hours, and seed coat removed. The work was carried out using completely randomized design, with four treatments and three replicates of 10 birds per replicate. Data collected were analyzed using SPSS version 22. The relative weight of liver, spleen and heart had no significant effect ($p>0.05$) within the dietary treatment. The weight of the liver was smaller in birds fed raw kidney beans meal and the liver was characterized by marked coagulative necrosis. The weight of the gizzard was significantly ($p<0.05$) higher in birds fed control diet. Furthermore there were no significant differences ($p>0.05$) in birds fed boiled, dehulled and control diets on the breast weight but significantly smaller in those fed raw diet meal. There were also no significant differences on the drumstick, thigh, neck and head size. Tenderness was not significantly affected by the dietary treatments. Juiciness, taste, and flavour intensity showed significant differences within the dietary treatment while overall acceptability showed a significant increase with the boiled kidney bean meal. Consequently, birds fed with BKD performed better in the organoleptic properties, while those on dehulled kidney beans meal gave better result for organ weight and carcass yield. In conclusion, sensory characteristics, organ weight, and carcass yield is an indication that kidney beans especially the boiled and dehulled one can serve as a feed ingredient in broiler ration would have no adverse effect.*

Keywords— dehulled kidney beans, organoleptic properties, sensory characteristics.

I. INTRODUCTION

According to Dipeolu *et al.* (2004) poultry industry has been described as the fastest means of ameliorating the animal protein deficiency in third world countries particularly in Nigeria, due to the high turnover rate associated with poultry production and consequent economic efficiency. Feed, which accounts for 60-80% of the total cost of production of most livestock species, is by far the major factor limiting the growth and expansion of the livestock industry (Ogundipe, 1992; Ikani *et al*., 2001). Currently, the convectional protein ingredient for monogastric animal feed production such as soyabean and groundnut cakes are often scarce and expensive due to the high demand for them for human consumption. Consequently, animal nutritionists in developing countries such as Nigeria have resorted to exploring other potential and hitherto neglected feed resources in order for the monogastric animal feed industry to have a wider range of alternatives to choose from. The availability of alternative sources of nutrient will encourage a shift to the sources for which there is less competition. Efforts have been made to use the vegetable protein sources such as pigeon pea (Amaefule and Obioha, 2001; Lorgyer *et al*., 2009; Lorgyer, 2010), *Mucuna pruriens* seeds (Emenalom and Udedibie, 1998; Tuleun *et al*., 2011) and Jack beans (Esonu *et al.*, 1998) in monogastric diets with encouraging results. There are however, many other legumes whose seeds can be explored

for their nutritional value for monogastric animals (Bawa, 2003); one of such legumes is the kidney beans (*Phaseolus vulgaris*).

Kidney beans (*Phaseolus vulgaris*) also referred to as common bean belong to the genus phaseolus in the legume family Fabaceae and is botanically classified as dicotlydeons (Uebersax, 2006). Kidney bean is a potential feed source for pigs and poultry because of its high content of protein, energy. The amino acid profile is similar to that of soyabean, expect for lower level of methionine (Laurena *et al*., 1991).

However, like other grain legumes, the usefulness of kidney beans as a feed factor ingredient for monogastric animal may be limited due to the presence of some anti-nutritional factors which include trypsin inhibitor, hydrocyanic acid, tannin, phytic acid, oxalate and lectin (Olomu, 2011). It has been established that heat treatment and other processing methods exert beneficial effects on the nutritional quality of the seed of grain legumes by destroying the anti-nutritional factors inherent in them (Balogun *et al.*, 2001). Some of the anti-nutritional factors are, however thermostable. Thus different processing method should be applied either alone or in combination with heat treatment. This is needful because some researchers have reported that the effectiveness of heat treatment in detoxifying tannin, phytate and oxalate in kidney beans is low (Emiola *et al.*, 2007).

Thus, emphasis has been placed on the various ways of inactivating the anti-nutritional factors in the kidney bean and improvement of its nutritive value. However, little attention has been given to the evaluation of the effect of sun drying, or dehulling or aqueous heating of kidney beans (*Phaseolus vulgaris*) prior to inclusion in poultry feed. Consequently, we aimed at evaluating the effect of feeding sun dried, dehullied and aqueous heated kidney beans on the carcass quality, organ weight and organoleptic properties on broiler chicken. Specifically, the study determines:

- The weight of the heart, gizzard, liver, spleen and intestine of broiler fed raw, dehulled and aqueous heated *Phaseolus vulgaris* seed based meals.
- The carcass quality via drumstick, thigh, neck, head, breast, shank, wing of broiler fed raw, dehulled and boiled *Phaseolus vulgaris* based diet.
- The juiciness, tenderness, taste, flavour intensity and overall acceptability of broiler fed raw, dehulled and boiled *Phaseolus vulgaris* based diet.

II. MATERIALS AND METHODS

The research was undertaken at the Poultry unit of the Department of Animal Science and Technology, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria. Awka is the Capital of Anambra State and it is in the tropical rainfall zone of Nigeria. The mean annual temperature, rainfall and humidity are 27.0 ^{O}C, 1828 mm and 80 %, respectively. The driest month is December with a rainfall of 7mm and the highest is September having an average of 306mm. Rainy season last for six months, occurring from April to July and September and October. It is locate within the latitude of 6^{o}12’25”N and longitude, 7^{o}04’04”E.

The Kidney bean (*Phaseolus vulgaris*) used in the study was procured from Eke Awka Market in Awka, Anambra State. They were divided into three equal parts for the respective processing method before inclusion in the diet. For the boiled, the dry seeds were cleaned from dust and dirty materials, weighed and then poured into a cooking pot with water boiling at 100 ^{o}C and left for a period of an hour after which it was sundried for 4 days using empty rice bag before milling. For the dehulled, the dry beans was cleaned from dust and dirt materials and soaked in cool water for between 18-24 hours after which the seeds were removed using grinding machine; then the seed coats were separated from the beans. The beans were then rinsed and sundried using empty rice bag until they were sufficiently dried. The raw kidney bean together with the aqueous heated kidney beans were them grinded using a grinder.

One hundred and twenty day old broiler chicks of the breed Arbo Acre were procured from Fidan hatchery, Ibadan, Oyo State for the experiment. The birds were reared in a deep litter system, and acclimatized for one week and fed with commercial broiler starter (vital feed) bought from Eke Awka market for one week. On the 8th day, the chicks were weighed individually and distributed into the four treatment group and replicates. The treatments were: T1- Control diet; T2- Birds fed

raw kidney bean meal diet; T3 – Birds fed dehulled kidney bean meal diet; T4 – Birds fed aqueous kidney bean meal diet. So, the experimental design was a one way classification in a completely randomized design (CRD) with the following model.

$$X_{ij} = \mu + \alpha_i + \varepsilon_{ij} \quad (1)$$

Where X_{ij} is the observed value of each of the response variables (carcass characteristics, organ weight and organoleptic quality characteristics) arising as a result of:

μ = the overall population mean

α_i = observed effect of the dietary treatment

ε_{ij} = random or residual error due to the experimentation

Brooding was done with the chicks in the four treatment group and adequate heat provided. Light was set out at night for enhanced growth. Each treatment was separated into three replica with 10 birds in each replica and the birds were fed their respective experimental diet daily. By the end of the starter phase at 4 weeks, the finisher experimental diet was given to the birds as in the starter phase. The chicks were given an anti-stress formulation in their drinking water (Milk and sugar) on the first day to relieved transportation stress. They were given Lasota vaccine on the first day of arrival. Feed and water were provided *ad libtum*. The chicks were vaccinated against Gumboro and Newcastle disease at 2 and 3 weeks of age, respectively. Prophaltytic doses of cocidiostat, (Ancoban), vitamin and antibiotic were regularly provided in their drinking water at a dose of 1ml liter of water. Litters were being changed weekly.

The feeding trial was carried out in two phases; the starter and the finishes phase. 100kg starter diet were formulated for the four treatment. Diet 1 (treatment 1) with no inclusion of *Phaseolus vulgaris*, Diet 2 (treatment 2) with the inclusion of 10% raw *Phaseolus vulgaris*, Diet 3 (treatment 3) with the inclusion of 10%. dehulled *Phaseolus vulgaris* and Diet 4 (treatment) with the inclusion of 10% boiled *Phaseolus vulgaris.* The finisher diet was adjusted to suit the required broiler finisher phase of lesser protein and higher carbohydrate. Thus a 500kg finisher was formulated.

Iso nitrogenous and iso calorific diets were compounded using zero percent (T1), 10 % raw (T2), dehulled (T3) and aqueous (T4) kidney bean meal.

At the end of the metabolism trial, 12 birds from each replicate of different treatments were starved over night to empty their gut contents, weighed and slaughtered. They were left to bleed completely then scalded in hot water and defeatered; their weight after defeathering and evisceration were taken. The cut up parts which include thighs, drumstick, shank, wing, neck, breast, and head were weighted and expressed as percentage of the eviscerated weight. The organ such as heart liver, spleen and gizzard were also weighed using a sensitive electronic scale.

Samples were collected from the breast of the experimental bird and cut into small size and cooked for approximately 20minutes with 5g of salt. Thereafter, they were presented in dishes under bright light to an untrained panel of 15 tasters. The panellists Include student of Unizik and staff of Ezi Awka Community Secondary School. A structural questionnaire was designed to solicit responses about juiciness, tenderness, tenderness, taste flour intensity and overall acceptability of the meat (see appendix I) using 5 point hedonic scale as described by Barylko-Pikielna (1975) with one being the least favourable of each parameter and 6 being its best condition. The scale was thoroughly explained to the panellists prior to the tasting session. Warm water was provided with which panellists rinsed their mouth between samples tasted.

Data collected were subjected to analysis of variance (ANOVA) using SPSS-22 release 7.2 statistical software. The differences between treatment means were separated using the least significant different (LSD) test.

III. RESULTS

Table 1 presents the effect of raw, dehullled and boiled kidney beans based meal on the organoleptic properties of broiler chickens.

TABLE 1

THE EFFECT OF RAW, DEHULLLED AND BOILED KIDNEY BEANS BASED MEAL ON THE ORGANOLEPTIC PROPERTIES OF BROILER CHICKENS

	Treatment diets			
Parameters	**T1(control)**	**T2(RKB)**	**T3(DKB)**	**T4(BKB)**
Juiciness	3.53^{b}	3.82^{ab}	3.69^{ab}	3.95^{a}
Tenderness	3.36^{a}	3.76^{a}	3.69^{a}	3.86^{a}
Taste	3.36^{b}	3.33^{b}	3.51^{b}	4.08^{a}
Flavor intensity	3.15^{b}	3.18^{b}	3.27^{ab}	3.96^{a}
Acceptability	3.42^{b}	3.56^{b}	3.30^{b}	4.20^{a}

Means bearing different superscripts along the same row were significantly different at p<0.05.

According to the Table there were no significant differences (p>0.05) in the juiciness of the birds fed T2, T3 and T4. There were also no significant differences in the juiciness of birds fed T2, T3, and T1. However, there was a significant difference (p<0.05) in the juiciness of birds fed T1 and T4. The result showed no significant differences (p>0.05) in the tenderness and taste of the chicken fed the different treatments, except in taste of birds fed T4 and T2 (p<0.05). Flavour intensity of birds fed T1, T2 and T3 were similar (p>0.05), while significance difference was observed between the birds fed T3 and T4 diets. But no significant differences (p>0.05) were recorded in the overall acceptability of birds, except for T4.

Table 2 presents the carcass yield of broilers fed raw, dehulled and boiled kidney bean seed meal based diet

TABLE 2

THE CARCASS YIELD OF BROILERS FED RAW, DEHULLED AND BOILED KIDNEY BEAN SEED MEAL BASED DIET

	Treatment diets			
Parameters	**T1(control)**	**T2(RKB)**	**T3(DKB)**	**T4(BKB)**
Breast	210.67a	129.00^{b}	195.00^{a}	189.00^{ab}
Drumstick	214.00^{a}	191.00^{b}	215.00^{a}	205.67^{a}
Thigh	160.33^{b}	171.00^{ab}	198.33^{a}	197.33^{a}
Wings	173.33^{ab}	166.00^{b}	181.00^{a}	166.00^{b}
Neck	94.67^{b}	95.67^{ab}	100.67^{a}	103.00^{a}
Head	57.67^{a}	50.00^{b}	54.00^{a}	53.00^{a}
Shank	91.67^{a}	80.33^{ab}	71.33^{b}	94.67^{a}

Means bearing different superscripts along the same row were significantly different at p<0.05.

No significant differences (p>0.05) were recorded in the breast weight and drumstick of all the birds, except for bird fed RKB. Birds fed RKB were similar to all the groups (p>0.05), whereas birds in control group were significantly different (p<0.05) from those in DKB and BKB. Wing size was significantly higher (p<0.05) in DKB than other treatment groups except for control; similarly, the size of the neck was smaller in control group than other groups except for those fed RKB. Except for birds fed RKB, the size of the head was uniform (p>0.05) in all the groups. There were no significant differences (p>0.05) in shank weight between birds fed control diet, BKB and RKB. There is also no significant difference in the shank weight of birds fed RKB and DKB.

Table 3 presents the organ weight of broilers fed raw, dehulled and boiled kidney bean seed meal based diet

TABLE 3

THE ORGAN WEIGHT OF BROILERS FED RAW, DEHULLED AND BOILED KIDNEY BEAN SEED MEAL BASED DIET

	Treatments			
Parameters	**T1(control)**	**T2(RKB)**	**T3(DKB)**	**T4(BKB)**
Heart	11.00 ± 1.73^{a}	10.33 ± 0.58^{a}	12.67 ± 2.08^{a}	12.00 ± 1.57^{a}
Gizzard	89.677 ± 2.08^{a}	64.67 ± 10.79^{b}	77.00 ± 21.38^{ab}	67.00 ± 2.65^{ab}
Liver	50.67 ± 6.66^{a}	45.67 ± 8.50^{b}	52.33 ± 4.51^{a}	52.33 ± 11.68^{a}
Spleen	2.00 ± 0.00^{a}	2.00 ± 0.00^{a}	3.00 ± 1.00^{a}	2.33 ± 0.57^{a}
Intestine	19.33 ± 4.04^{a}	18.67 ± 3.22^{a}	19.67 ± 3.51^{a}	18.67 ± 2.04^{a}
Live weight	2008.33 ± 95.7^{a}	1877.33 ± 107.83^{a}	2061.67 ± 229.44^{a}	2000.00 ± 52.51^{a}
Plucked weight	1887.33 ± 163.5^{ab}	1678.00 ± 23.26^{b}	1901.00 ± 157.87^{ab}	1993.00 ± 173.85^{a}

Means bearing different superscripts along the same row were significantly different at p<0.05.

The study observed similar ($p>0.05$) heart, spleen, intestine and live weight across all the treatment groups. Smaller liver, gizzard, and plucked weight were recorded in birds fed raw kidney beans ($p<0.05$), however, the gizzard and spleen of birds fed raw kidney beans did not vary with those fed DKB.

IV. DISCUSSION

There were no significant differences on the weight of the heart, liver, spleen and intestine indicating that the three methods used in processing of KB had no deleterious effect on the internal organs of the broilers. Wafar *et al*. (2017) reported a similar result on the organs (liver and gizzard) while working with pumpkin seed based meal on the performance and carcass characteristics of broiler chickens. They maintained that the increasing level of the pumpkin seed in the diet did not affect the internal organs. Again, Soultan (2009) observed that 5% inclusion of palm kernel cake in broiler diet had no significantly effect on spleen and live weight. However, Fasuyi (2007) and Tamburawa *et al.* (2016) reported increase in weight of heart and liver while feeding some supplements.

Yakubu (2017) also gave similar result that *Jatropha curcass* seed meal increased heart weight which according to him might have be caused by increased metabolic requirement. There is also a significant difference in the weight of the gizzard across the dietary treatment. This could be as a result of extra muscular activity in breaking down ingesta which have high fiber. Richard (2012) reported a similar result and attributed a higher gizzard weight obtained to increase in frequency of contraction of this organ to reduce fiber particles. There is a significant difference between bird fed treatment diet two and other treatments. This could be as result of toxic substance. The result is in line with the report of Emiola *et al*. (2007) who equally observed that the liver was characterized by marked coagulative necrosis and degeneration of the hepatocytes of bird when fed raw and dehulled seed meal. Ortiz *et al.* (1994) also observed a degeneration of the hepatocytes in the liver which he said was due to the high tannin content of the diet.

No significant differences in the breast weight of birds fed boiled, dehulled and control diet implies that either processing method is ideal as long as breast weight is concern. Thus the treatments did not exhibit any detrimental effect on breast weight. The difference observed on the breast weight of birds fed raw kidney bean with others indicate insufficient nutrient for tissues synthesis in the group. This result correlates with that of Tuleun *et al*. (2011) who in their study reported a decreased in the breast weight of bird fed fermented Mucuna seed meal. He claimed that the nutrients required for tissues synthesis was not sufficient and this could be attributed to poor utilization of protein due to the presence of ant nutritional factors possibly tannin. Muhammad (2017) reported a high breast weight and better feed utilization when fed 20% pigeon pea boiled with potash diet in birds because of the improved palatability with inclusion of boiled pigeon pea seed in diet.

The drumstick, thigh, neck and head of the different dietary treatments were not significantly similar. This may be that the carcass was not influenced by the treatment. This result concurs observation of Aletor (1992) who reported from his study on the effect of different processed soybeans on the performance, organ weight, carcass yield on the economic producing broiler that the carcass were not significantly influenced by the dietary treatments. The differences observed in the shank weight and this result is in agreement with Aletor (1992).

There were no significant difference on the juiciness, tenderness and flavor intensity of the broiler fed the different dietary treatment. This may be due to the age of the bird at slaughter, adequate water in the meat and similar fat level in the meat. This result agrees with Teye *et al.* (2011). The juiciness in meat arises from the moisture relaxed by the meat during chewing (Howard, 1976; Christens *et al*, 2000). According to Lowrie (1976) and Ledward (2006) fat in meat improves the appearance, juiciness and other sensory qualities of meat. The taste and overall acceptability of the dietary treatment four were significantly higher than other treatment groups. Boiled kidney bean was observed to be most preferred in terms of taste, overall acceptability, flavor intensity in addition juiciness and tenderness.

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UHPLC-DAD-ESI-MS/MS of Ethanolic Extract of the Flowers from *Spathodea Campanulata* Beauv. in Cuba

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Abstract— *A sample of ethanolic extract of the flowers from Spathodea campanulata Beauv. was scrutinized using a UHPLC-DAD-MS/MS Thermo scientific Dionex Ultimate 3000 RS coupled to a Thermo scientific LTQ XL mass spectrometer. In addition, about nine different chemical compounds were tentatively identified in this species based on chromatography retention time (Rt), UV and MS/MS spectra and compared with those of isolated authentic compound and literature data in our country for the first time. Information obtained from these studies can be used as biomarkers in the identification and standardization of this flower as an herbal remedy and also towards monograph development on the plant*.

***Keywords— UHPLC, Flowers, Chemical compounds, Ethanolic extract, Spathodea campanulata*.**

I. INTRODUCTION

Spathodea campanulata P. Beauvais tree is native to Africa. In tropical Africa it is planted as an ornamental plant, e. g. in Cape Verde, Zimbabwe and Madagascar. It is widely grown in tropical and subtropical regions outside Africa [1]. This plant is also commonly found in India as an ornamental plant. This plant is also called as African tulip tree or Flame tree, *Spathodea campanulata* P. Beauv is the botanical name. It is a single species of the monotypic genus Spathodea in the flowering plant family Bignoniaceae which is composed of around 800 species distributed in 112 genera [2].

The flowers are used as diuretic and anti-inflammatory, while the leaves are against kidney diseases, urethra inflammations and as an antidote against animal poisons [3]. Several phytochemical studies were performed with different parts of *Spathodea campanulata* including stem barks, leaves, flowers and fruits. The leaves contain spathodol, caffeic acid, other phenolic acids and flavonoids, while fruits contain polyphenols, tannins, saponins and glycosides [4]. The plant leaves reported to have antiplasmodial, analgesic, anti-inflammatory and anti-larvicidal activity. The stem bark decoction of *Spathodea campanulata* have been displayed hypoglycemic, anti-complementary, antimalarial and anti-HIV activity [5].

The large, orange-red flowers are arranged in dense clusters (8-10 cm long) at the tips of the branches. The reddish-orange colored petals are also fused together and are shaped somewhat like a tulip flower i.e. tubular (Figure 1). Flowering occurs throughout the year, but usually peaks during spring [6].

FIGURE 1: Flowers of *Spathodea campanulata* Beauv

Preliminary phytochemical screening of *S. campanulata* revealed the presence of alkaloids, reducing sugars, carbohydrates, flavones, glycosides, and phenolic compounds **[7**]. Several compounds have been isolated from different parts of the plant. From the flowers has been isolated 1,1-diethoxy-3-methyl-butane, N-hexadecanoic acid, 1,2-benzenedicarboxylic acid diisooctyl ester, and oleic acid [**8**]. Phytol, *α*-methyl cinnamaldehyde, *β*-sitosterol-3-acetate, naringenin, catechin-3-*O*-*α*-rhamnopyranoside and 5, 6, 4'-trihydroxy flavonol-7-*O*-*α*-rhamnopyranoside, and anthocyanins [**9**].

The floral nectar contains a complex mixture of triterpenoids and steroids [Rev. Bras. Pl. Med., 2012. (**10)**]. The aim of this study therefore, was to isolate and characterize the active phytochemical(s) of *S. campanulata* flowers ethanolic extract.

II. MATERIAL AND METHODS

2.1 Sample Collection and Processing

The flowers were freshly collected in the morning between 9 and 10 AM during five days in April of 2018 in the gardens of the Faculty of Pharmacy and Foods at Havana University. Authors are waiting for identification at the herbarium of National Botany Garden of Havana, where the voucher specimen number will be deposited.

2.2 Extract and Samples Preparation

The flowers used were dried in an oven with controlled temperature at 40˚C, during 5 days. The extracts were prepared with the ground material (100 g), using a Soxhlet apparatus and 95% ethanol (675 mL) for 20 hours, by triplicated. The ethanolic extracts were concentrated and rotoevaporated under vacuum to 200 mL at 120 rpm, 70˚C, and 500 mbar. The concentrated extract was put on to the Lab table at room temperature until an abundant solid appear and it was recuperated by filtration.

2.3 UHPLC-DAD-ESI-MS/MS Procedures, Instrumentation, and Parameters

The LC system consisted of an UPLC/DAD/MS Thermo scientific Dionex Ultimate 3000 RS with quaternary pump, autosampler, DAD (diode array detector) Dionex with a UV-VIS at 200 nm (UV1), 250 nm (UV2), 280 nm (UV3), and 330 nm (UV4) coupled to a mass spectrometer Thermo scientific LTQ XL with ESI (ion trap analyzer) in negative ionization mode. Conditions of detection were optimizing with a Tune archive based on the behavior of quercetin. Temperature: 225˚C, Voltage 5 KV, Capillary voltage 50 V. Column: Accucore RP-MS (100 × 2.1 mm × 2.6 µm). Temperature: 35˚C. Chromatographic system: eluent CAN (5%): HCOOH (0.1%). Isocratic 20 min. Flow: 0.4 mL/min (Table 1). Nitrogen gas flow: 34, auxiliary gas: 16, barrier gas: 3. Induced fragmentation gas: Helium. Was realized an experiment Full Scan in independent mode to identify the principal ions (TIC) and get the MS and MS^2. The sample was dissolved in methanol HPLC grade at 1 mg/mL filtered by a nylon filter of 0.20 µm. Injection volume: 2 µL. Mass scan between 200 - 700 u.m.a.

TABLE 1
CHROMATOGRAPHIC CONDITIONS USED IN THE STUDY

Time (min)	ACN	Formic acid 0,1 %
0	12	88
2	27	73
3	27	73
5	30	70
6	30	70
9	35	65
10	95	5
11	12	88
17	12	88

III. RESULTS AND DISCUSSION

3.1 MS-ESI Identification of phytocompounds in S. campanulata flowers from Cuba

Several phytochemical components in *S. campanulata* flowers were detected and tentatively identified using UHPLC with UV-visible data and ion trap electrospray mass spectrometry (IT-ESI-MS). Figure 3 shows the TIC chromatogram fingerprint at 250 nm. All of them were analyzed in negative ion mode between 0.17 and 11.38 min of retention time.

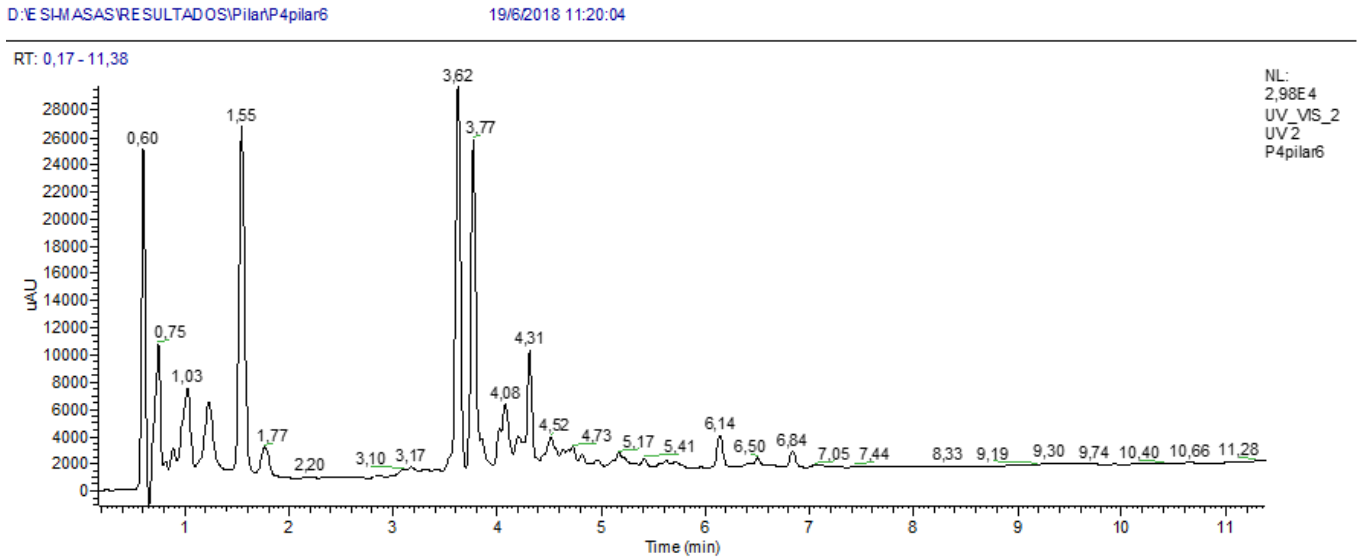


FIGURE 3: Current chromatogram at 250 nm of ethanolic extract from *S. campanulata*.

Fifteen chemical components were detected after sample running, but among them, only 9 compounds were tentatively identified, mainly glycosylated flavones, glycosylated flavonols and alkaloids (Table 2). Below is the detailed explanation and identification of the compounds using UHPLC and DAD-ESI and MS^n analysis.

TABLE 2
HPLC-DAD-ESI-MS^n DATA OF *S. CAMPANULATA* ETHANOLIC EXTRACTS

Peak No.	Retention time	UV Max	[M−H]	Other ions	Identification
1	0.61	322, 208	–	–	Unknown
2	0.74	296, 206	–	–	Unknown
3	1.02	218, 258	–	–	Unknown
4	1.22	326, 301, 247	–	–	Unknown
5	1.54	256	–	–	Unknown
6	1.77	318, 246, 222	–	–	Unknown
7	3.62	260	481	319, 205	Flavonoid glucoside
8	3.78	327, 245	523	361, 179, 163	Flavonoid glucoside
9	4.31	315, 247	523	361, 179, 163	Flavonoid glucoside
10	4.14	–	593	327, 285, 257	Flavonoid glucoside
11	4.54	–	507	345, 231, 163	Flavonoid glucoside
12	5.02	–	507	345, 231, 163	Flavonoid glucoside
13	6.65	–	582	462, 342	Alkaloid
14	6.88	–	582	462,342	Alkaloid
15	7.09	–	612	492, 466 (462), 342	Alkaloid

According to the data reported by the technician.

3.2 Flavonoids and Derivatives

Explanation was done taking into account the retention times, spectral data and the grouping order in which the phytochemicals were reported by the technician. The three first chemical components were registered at 3,66; 3,81 and 4,35 minutes of retention time, respectively, as is showed in Figure 4, two of them with a molecular mass of 523 Da, but with different retention times, at 3.81 and 4.35 min, respectively, indicating that both chemical components are closely related or perhaps they are isomers.

The first compound detected at 3.66 min have a molecular mass of 481 Da, having a similar molecular mass of flavonoids related with some of the four gossypetin glycosylated derivatives isolated and characterized from spices that belong to Hibiscus and Taliparitiгenders, but the confirmation is still pendant by NMR spectroscopy (data not shown here). We are assuming that only two aglycon moieties in nature have a MM of 318, there are gossypetin and hibiscetin. The first one is a flavonol and the second one a flavone.

As is known, four gossypetin glucosides have been isolated and characterized from different plants like *Hibiscus vitifolius* and *Hibiscus sabdariffa* L. (Gossypetin-8-*O*-glucoside or gossypin); from *Hibiscus sabdariffa* L., *Taliparitielatum* (Sw.) and *Taliparitiтiliaceum* (Sw.) (Gossypetin-7-*O*-glucoside or gossypitrin or gossypetrin); from *Hibiscus sabdariffa* L. and also from *Taliparitiтiliaceum* (Sw.) (Gossypetin-3-*O*-glucoside or gossytrin) and finally from *Abelmoschus manihot* (initially *Hibiscus manihot*) and *T. elatum* (Sw.) in Martinica and Cuba (Gossypetin-3'-*O*-glucoside) (11, 12, 13).

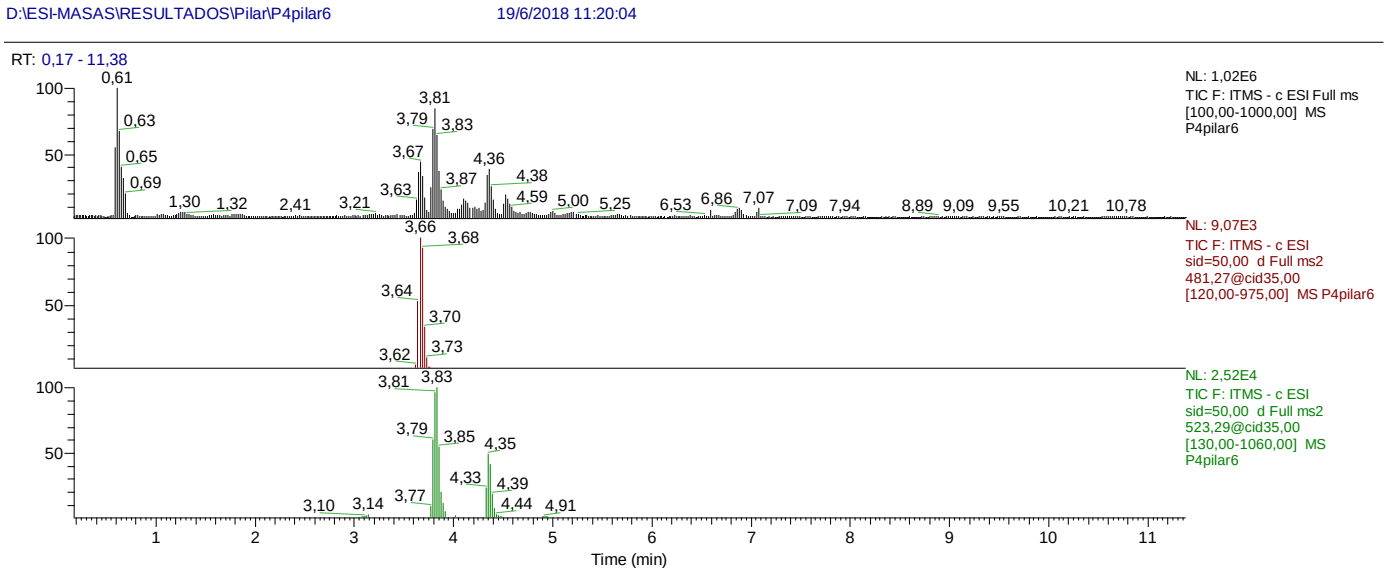


FIGURE 4: Full mass chromatogram of the three first chemical components registered.

Beside the retention time, both chemical compounds with the same molecular masses of 523 Da, showed different fragmentation pathway suggesting the presence of two isomeric forms from the same chemical component as is represented in Figure 5.

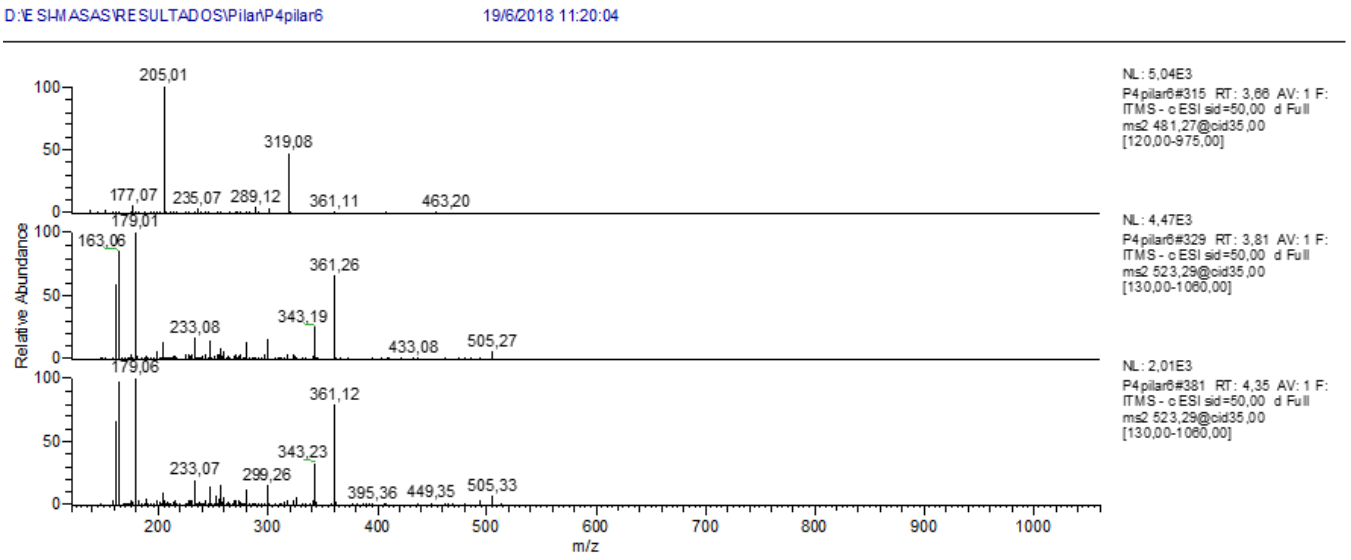


FIGURE 5: MS/MS spectrums of the three first chemical components registered.

Both compounds with MM of 507 amu have a little different behavior in their fragmentation pathway, but with the same daughter ions at m/z 345, 231 and 163. Seems to indicate that they are glucoside derivatives from 5,7-dihydroxy-3',4',5'-trimethoxyflavone with m/z 344 and $[M-H]^-$ 343, with the glucose moiety in C8 in both isomeric forms: α and β. So, we are

proposing the structure of 8-α-D-glucopiranosyl-5,7-dihydroxy-3',4',5'-trimethoxyflavone ($[M]^+$ 524; $[M-H]^-$ 523) or instead, the structure of 8-β-D-glucopiranosyl-5,7-dihydroxy-3',4',5'-trimethoxyflavone ($[M]^+$ 524; $[M-H]^-$ 523).

Three second chemical components were then registered between 4.14 and 5.02 min, keeping the same behavior like previous case, the first one of them at 4.14 min with a molecular mass of 593 Da, following by another two compounds at 4.52 and 5.02 min, respectively, but with the same molecular masses of 507 Da and different fragmentation pathway, so we can consider that both phytochemicals are isomers too (Figures 6 and 7).

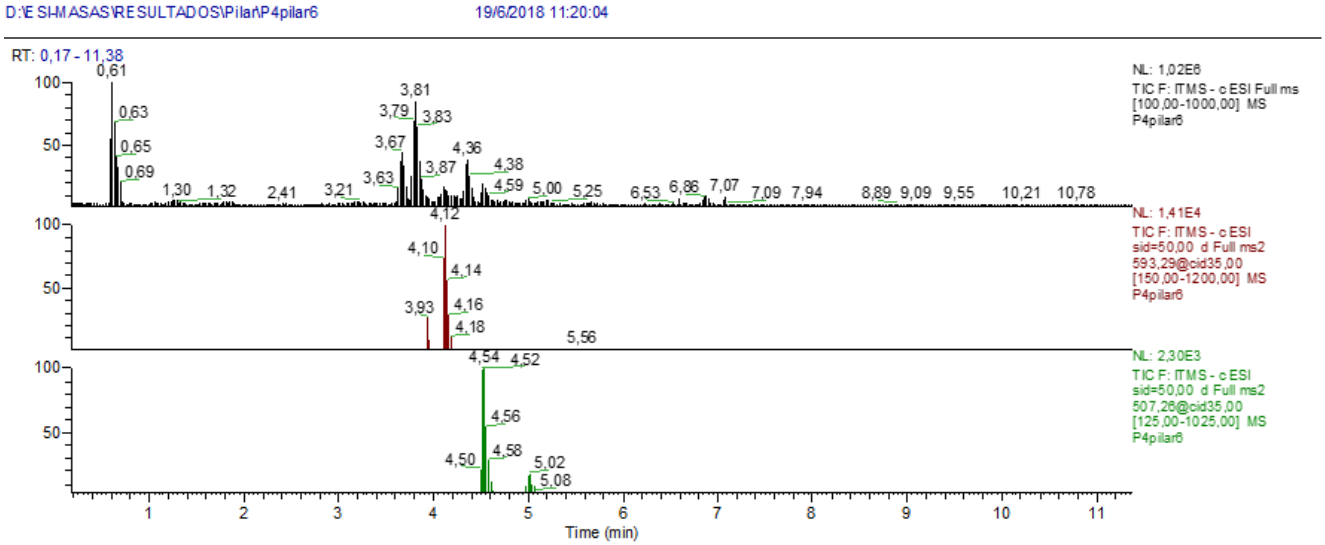


FIGURE 6: Full mass chromatogram of the three second chemical components registered.

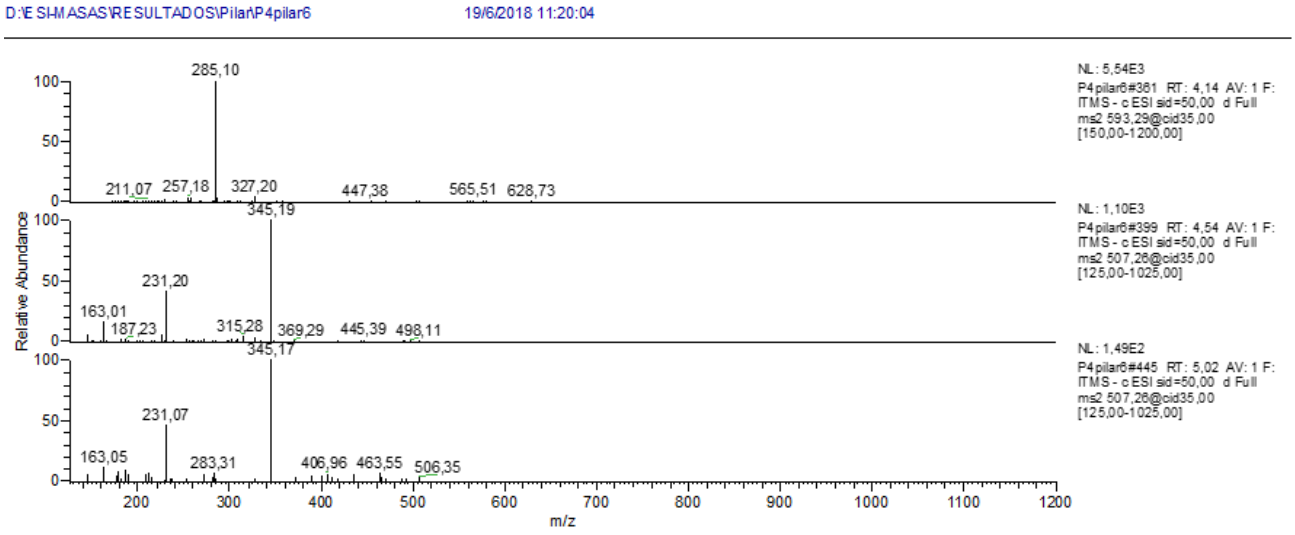


FIGURE 7: MS/MS spectrums of the three second chemical components registered.

Four different secondary metabolites in nature produce a parent ion at m/z 593: luteolin-7-*O*-rutinose, kaempferol-3-*O*-rutinoside, kaempferol-3(*p*-coumarylglucoside) and glycosylated sitosterol, this one, identified in the bark and flowers extracts of *S. campanulata* by Heim et al., 2012. According to Rodriguez et al., 2009 **[14]**, we are tentatively proposing the structure of kaempferol-3(*p*-coumarylglucoside) for the component at 4.14 min of retention time, because of its present the same fragmentation pathway of that phytocompound analyzed and daughter ions at m/z 447 and m/z 285 $[M-H-\text{coumarylglucoside}]^-$.

Both chemical components with parent ion at m/z 507 are closely related with 3-hydroxy-4',5,7- trimethoxyflavone that have a parent ion at m/z 328 to be the precursor moiety to those compounds. In such case, both structures keeping the stereochemical configuration α or β, but in this case, having one OH group attached at the flavone moiety. They presented a pseudomolecular ion at m/z 507, which experienced a hexoside loss (162 u) to produce a flavone ion at m/z 327 and, thus, was identified as 8-α-D-*O*-glucosyl-3-hydroxy-4',5,7-trimethoxyflavone (or its isomeric form β).

3.3 Alkaloids

Finally, the three third chemical components were detected at 6.65; 6.88 and 7.09 minutes, respectively. The first and second one with a molecular mass of 582 Da, probably two isomeric forms of the same phytochemical compound, and the third one with a molecular mass of 612 Da (Figures 8 and 9).

Obviously, those three phytocompounds perhaps belong to alkaloids group due to them impair molecular masses, according to Brindha et al., 2012, who previously reported that preliminary phytochemical screening of *Spathodea campanulata* P. Beauvais revealed the presence of alkaloids.

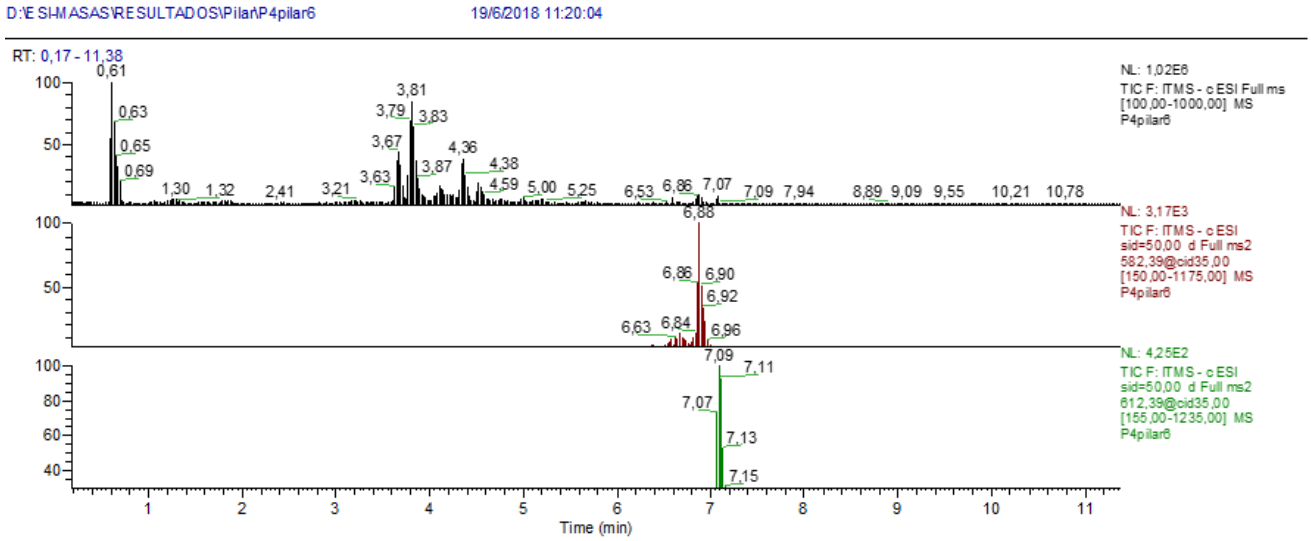


FIGURE 8: Full mass chromatogram of the three third chemical components registered.

Compounds with pseudomolecular mass at m/z 582, producing daughter ions at m/z 462 and 342, exhibit the same molecular formula $C_{35}H_{38}N_2O_6$, $[M]^-$ m/z 582. They both carry a secondary amino function. According to Fournet et al., 1987 **[15]**, two *bis*-benzylisoquinolines were isolated and characterized from *Abuta pahni*, belonging to the genus Abuta (Menispermaceae, Anomospermae) spreads widely throughout tropical America. *A. pahni* is part of Amazonian curare mixtures.

The parent ion at m/z 582 are in correspondence with those both chemical components found out in this research but more experiments will be needed to confirm their presence in ethanolic extracts from the flowers of *S. campanulata* in our country.

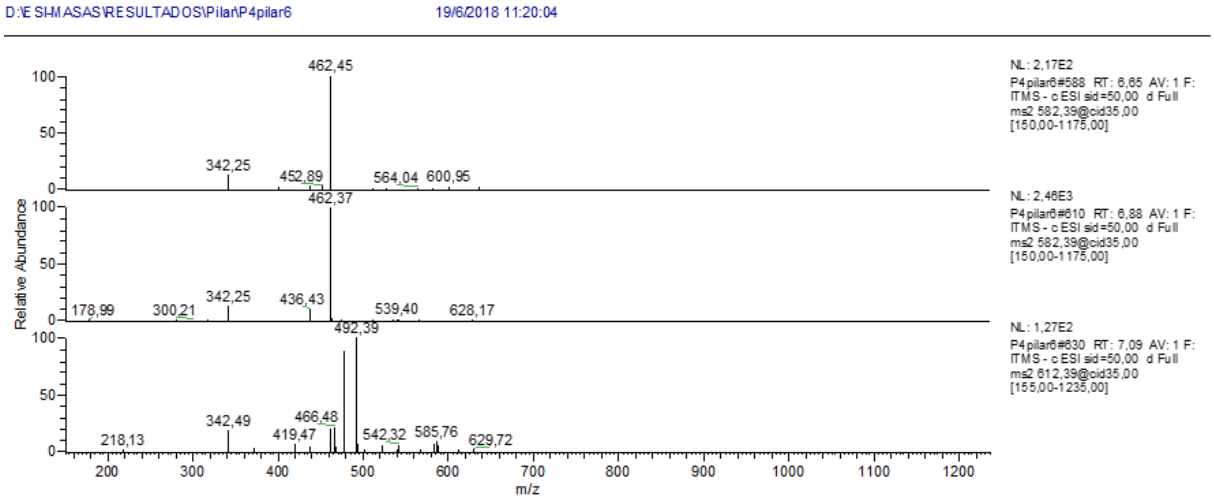
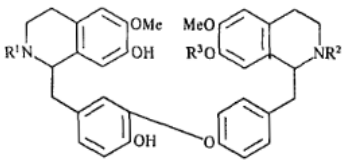


FIGURE 9: MS/MS spectrums of the three third chemical components registered.

Figure 10 shows the structures of both *bis*-benzylisoquinolines. They are in correspondence with structures **4** and **5**, identified by comparison with authentic samples and the respective positions of the secondary amino and tertiary amino groups in alkaloid **4** are determined through NOE measurements (cf. values in the Experimental). It can then be given the structure 2-*N*-methyllindoldhamine. Consequently, alkaloid **5** corresponds to 2'-*N*-methyllindoldhamine.



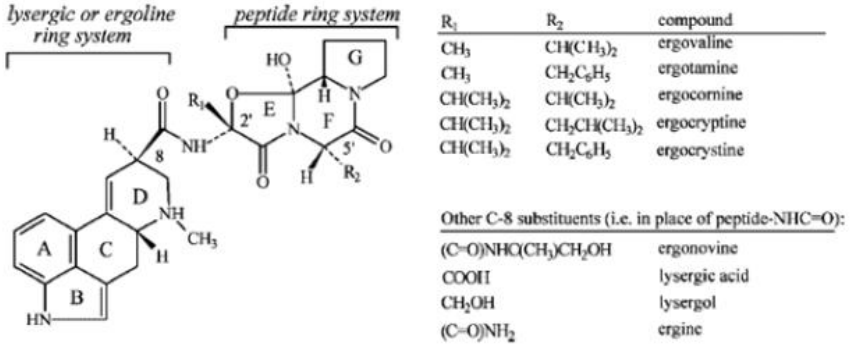
1 R^1 = Me, R^2 = Me, R^3 = Me
2 R^1 = Me, R^2 = H, R^3 = Me
3 R^1 = H, R^2 = H, R^3 = H
4 R^1 = Me, R^2 = H, R^3 = H
5 R^1 = H, R^2 = Me, R^3 = H
6 R^1 = Me, R^2 = Me, R^3 = H

FIGURE 10: Structural representation of *bis*-benzylisoquinolines from *Abuta pahni*.

Surprisingly, another two chemical components belonging to alkaloid group are in correspondence of those molecular masses: ergotamine (m/z 582) and ergocrystine (m/z 610). They were found in Ergot (*Claviceps purpurea*). Ergot alkaloids are mycotoxins generated by grass and grain pathogens such as *Claviceps*, for example. Ergot alkaloid–poisoning syndromes, such as tall fescue toxicosis from endophyte-infected tall fescue grass, are important veterinary problems for cattle, horses, sheep, pigs and chickens, with consequent impact on food, meat and dairy industries. Damage to livestock is of the order of a billion dollars a year in the United States alone (Lehner et al., 2005 **[16]**).

HPLC with UV and fluorescence detection are the predominant means of ergot alkaloid. Lehner et al., 2005, demonstrated the facility of using electrospray(+) mass spectrometry with multiple reaction monitoring (MRM) detection during chromatographic examination of ergot alkaloid standards of lysergic acid, lysergol, ergonovine, ergovaline, ergotamine, ergocornine, ergocryptine and ergocrystine by HPLC.

Figure 11 shows the general structure of Ergot alkaloids. The ergocrystine dehydrate was studied with settings similar to those of parental ergocrystine.



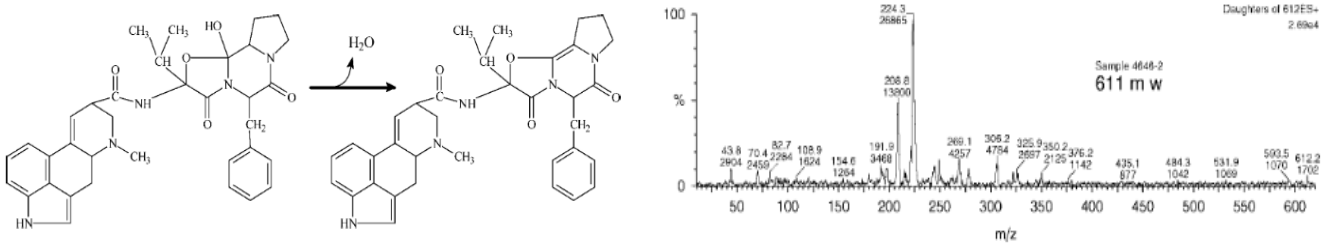
R_1	R_2	compound
CH_3	$CH(CH_3)_2$	ergovaline
CH_3	$CH_2C_6H_5$	ergotamine
$CH(CH_3)_2$	$CH(CH_3)_2$	ergocornine
$CH(CH_3)_2$	$CH_2CH(CH_3)_2$	ergocryptine
$CH(CH_3)_2$	$CH_2C_6H_5$	ergocrystine

Other C-8 substituents (i.e. in place of peptide-NHC=O):

$(C=O)NHC(CH_3)CH_2OH$	ergonovine
COOH	lysergic acid
CH_2OH	lysergol
$(C=O)NH_2$	ergine

FIGURE 11: Ergot alkaloid general structure, including stereochemistry and crucial position numbering and ring labeling (rings A–D constitute lysergic or ergoline; E–G, peptide ring systems). R1 and R2 alkyl and aralkyl substituents are listed in tabular form with corresponding compound names (taken from Lehner et al., 2005).

According with that, our results are in concordance with those authors when explained the presence of ergocrystine (m/z 612) and its dehydrated form (dyhydroergocrystine, m/z 592) due to the loss of 18 u.m.a. [M-18] (Scheme 1).



SCHEME 1: Dehydration of the ergocrystine 12'-hydroxyl group in the peptide ring system (from Lehner et al., 2005)

Mass spectrum of chemical compound detected at 7.07 min shows that the phytocompound identified in *S. campanulata* in Cuba have the same fragmentation pathway of that one found in perennial ryegrass (*Lolium perenne*) and tall fescue grass (*Festuca arundinacea* Schreb) (Figure 12). For that reason, we are proposing the structure of ergocrystine that showed a $[M - H]^-$ ion at m/z 612 and MS^1 ion at m/z 592 ($[M - H - H_2O]^-$) that belongs to the dehydrated product dyhydroergocrystine.

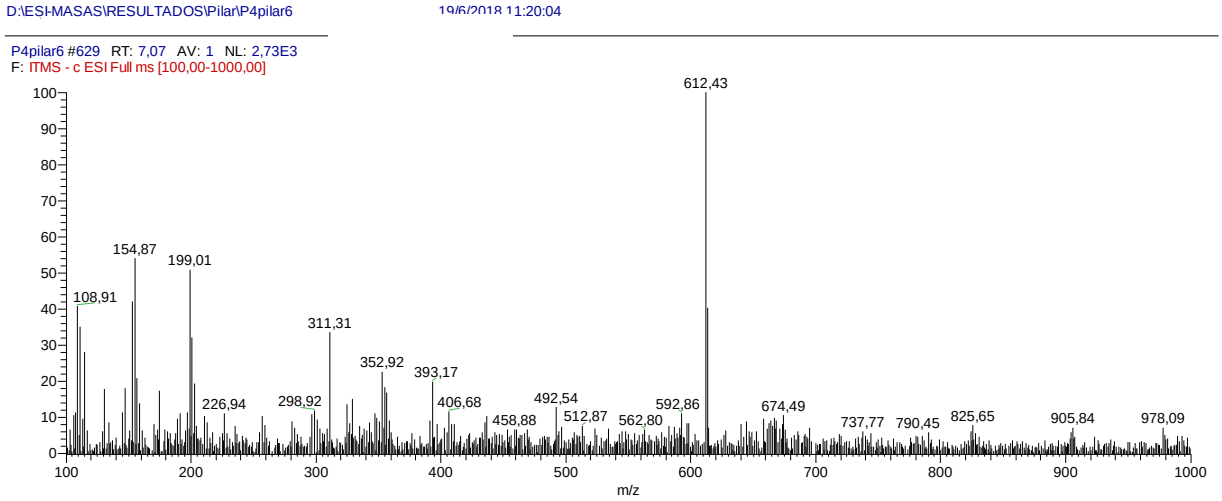


FIGURE 12: Full mass spectrum of compound with m/z 612 at 7.07 min.

Probably, degradation products in the spectrometric measurement carry out to obtain another ergot alkaloid component: ergocornine, after the loss of 30 u.m.a ($[M-30]^-$, m/z 562). Those losses are typically of alkaloids (NH_2CH^-, CH_2O, NO). Obviously, parent ion at m/z 582 $[M-H]^-$ could be assigned to 9,10-dyhydroergotamine or ergotamine (m/z 581), and consequently, the peak at m/z 462 correspond to ergocornine after the same loss of 30 u.m.a.

Summarizing, Table 3 relate the chemical compounds proposed to be present into ethanolic extracts of flowers from *S. campanulata* in our country. Further experiments will be done to increase the information about the existence of such phytocomponents in ethanolic extracts of the flowers of this plant, including the use of NMR spectroscopy.

TABLE 3

PROPOSAL COMPONENTS IN ETHANOLIC EXTRACTS OF THE FLOWER FROM *S. CAMPANULATA*

Compound	Ret. time	Parent ion	Daughter ions	Identification
1	3.62	481	319, 205	Gossypetin glucosides derivatives or Hibiscetin-3-*O*-rhamnopiranoside*
2	3.78	523	361, 179, 163	8-α-D-glucopiranosyl-5,7-dihydroxy-3',4',5'-trimethoxyflavone
3	4.31	523	361, 179, 163	8-β-D-glucopiranosyl-5,7-dihydroxy-3',4',5'-trimethoxyflavone
4	4.14	593	327, 285, 257	Kaempferol-3-(*p*-coumarylglucoside)
5	4.54	507	345, 231, 163	8-α-D-glucopiranosyl-3-hydroxy-4',5,7-trimethoxyflavone
6	5.02	507	345, 231, 163	8-β-D-glucopiranosyl-3-hydroxy-4',5,7-trimethoxyflavone
7	6.65	582	462, 342	2-*N*-methylindoldhamine *9,10-dyhydroergotamine
8	6.88	582	462,342	2'-*N*-methylindoldhamine *9,10-dyhydroergotamine
9	7.09	612	592, 562, 466, 342	Ergocrystine

more probably expected.

IV. CONCLUSIONS

The present study point outs the essentiality of collecting similar data for different plants and their flowers, as well as other parts. For the first time in our country nine different chemical compounds were tentatively identified using UHPLC-DAD-ESI-MS/MS experiments. Six of those components belong to flavonoid group (flavones and flavonol subgroup) and 3 of them to alkaloid group. All stretching related with biological activities associated to this part of the plant (antioxidant, anti-

solar, diuretic and anti-inflammatory activity). Further investigation to explore the therapeutic action of the individual phytochemicals and their mechanism of action can be encouraged.

CONFLICT OF INTEREST

Authors declare that we have not conflict of interest.

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Comparison of different Poly vinyl chloride (PVC) /Calcium Carbonate ($CaCO_3$) blends and their properties

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Abstract— *The effects of micro and nanoscale calcium carbonate ($CaCO_3$) particles on the mechanical properties of polyvinyl chloride (PVC) were investigated. Type of (PVC S5070) were used as the matrix in this study, hydrocarb 95T $CaCO_3$ as a micro size particles, and SOCAL 312 $CaCO_3$ as a nano size particles with different phr (0 wt%, 10 wt% and 20 wt%). The nano-$CaCO_3$ particles were observed by FT-IR spectras. Nano- $CaCO_3$ increased the tensile strength and affected the tensile strength of PVC more than micro-$CaCO_3$ particles. The raise in hardness shore (A) is more considerable in nano-$CaCO_3$ filled PVC compared to that of micro-$CaCO_3$. TSDC test investigated that nano-$CaCO_3$ in PVC samples have greater electrical resistance, and the maximum volume resistivity in micro-$CaCO_3$ in PVC samples which mixed by ultrasonic. Thermal characterization of PVC samples were tested by DMA. Storage modulus and loss factor (tan δ) examined and showed that the storage modulus of PVC decreased as a function of temperature. The storage modulus can be increased concurrently by the presence of $CaCO_3$. The glass transition of nano-$CaCO_3$ sample mixed by ultrasonic has higher glass transition than other samples which mixed by normal mixing.*

Keywords— Calcium carbonate, Polymer composites, PVC, Micro-$CaCO_3$, Nano-$CaCo_3$.

I. INTRODUCTION

Poly (vinyl chloride) as well known as PVC is one of the most using polymers around the world because of being in low cost [1-4], durability [5-7], flexibility [8-10]. However, they need to enhance their mechanical properties [11-13] such as toughness, morphological, thermal, and processing properties to work properly in widely and different range fields [14-17]. The mechanical properties of blends change as per various fillers [18]. Much improvement of the poorer properties of PVC has been carried out by the combination of additives such as plasticizers [19-20], antioxidant [21], and flame-retardant fillers [22-24] higher thermal stability [25] copolymerization, fillers and heat stabilizers with other monomers. Calcium carbonate ($CaCO_3$) nanoparticles are one of the viable nanofillers that enhance the thermo-mechanical properties of the polymer matrix composites [26-28].

PVC is the most common used to produce pipes, windows, entryways, and others in the development business [29-34]. The utilization of nanoparticles of calcium carbonate, not just improves the relentlessness, but also enhances electrical properties, heat opposition, radiation obstruction and different properties [35-39], yet in addition lessens the expense of the mixes [40-43], also in medical uses PVC have roles [44-48]. The mechanical properties of $CaCO_3$ microstructural additive on PVC are totally dependent on the interaction between the fillers [49-51], the polymeric matrix and the filling ratio, and the surface attributes [52-56].

The effects of the loads on the microstructure and on the properties of the PVC compounds are depending on the magnitude size and shape of the particle, combined size, surface treatment of the polymer and $CaCO_3$ filler. Therefore, by adding some low-cost additives to the PVC to develop it and create new formulation, it will be more affective and widely uses in more ways and application [57-59]. So as to acquire higher been utilized to treat nano $CaCO_3$ particles to improve the interfacial bond between the PVC lattice and the nano $CaCO_3$ molecule. The most regularly utilized adjusting operators

to treat nano $CaCO_3$ molecule are stearate and titanate coupling specialists, and the last is noted to have a higher hardening and strengthening impact [60].

It is notable that calcium carbonate ($CaCO_3$) is a characteristic happening and bountiful mineral involving around 4% of earth crust [61-63]. Lately, many tests and exams have been committed to the calcium carbonate particles [64-67]. By adding some amount of calcium carbonate, tensile strength and impact strength will be improved [68-70]. $CaCO_3$ can be created by different ways, including precipitation, dry grinding, and wet grinding, and essential evaluations of $CaCO_3$ can be separated by size of particles, surface area and morphology [71-74].

In this research different amounts and percentages of the calcium carbonate ($CaCO_3$) and DIDP plasticizer added to the PVC blends to make samples, and studying the mechanical behavior for the samples. The samples made in Borsod-Chem at Miskolc-Hungary. The samples going through some tests and measurement. First of all, hardness mechanical test (shore A), then tensile strength test to know mechanical properties of new PVC including (elongation at break, tensile stress, tensile strain, and young modulus), electrical property by TSDC electrical test, FT-IR spectroscopy, then thermal characterization test by (DMA). After all measuring, the results will be comparing with the previously works of literatures. The aim of project is to investigate the new PVC composites with a better mechanical property for further application.

II. MATERIALS AND METHODS

2.1 Applied Materials

2.1.1 Type of: PVC S5070:

$(C_2H_3Cl)n$ with a melting range between 140°C to 200°C. The glass transition temperature is between 75°C to 85 °C and flow temperature is 140°C.

2.1.2 Plasticizer: DIDP

Diisodecyl phthalate (DIDP: increase flexibility of plastic and workability.

2.1.3 Heat Stabilizer ADVASTAB TM181

Advastab TM181 is performances as a heat stabilizer.

2.1.4 WAX E

Wax E is a classified class of natural mixtures: softening.

2.1.5 Hydrocarb 95T $CaCO_3$

Micro sized calcium carbonate which is extremely fine, size between 0.7 -100 µm.

2.1.6 SOCAL 312 $CaCO_3$

Ultrafine calcium carbonate is near to nano size. The particle size is below 0.01 µm. 3.2 Preparation of Samples.

The detail of all PVC samples shown in Table.1

TABLE 1
PVC SAMPLES WITH DIFFERENT AMOUNTS OF FILLERS AND MIXING. $CaCO_3$ (1) IS MICRO SIZED PARTICLE OF CALCIUM CARBONATE, $CaCO_3$ (2) IS NANO PARTICLE SIZED OF CALCIUM CARBONATE

Material /Sgn	ST0	ST1-10	ST1-10U	ST2-10	ST2-10U	ST1-20	ST1-20U	ST2-20	ST2-20U
PVC S5070	100	100	100	100	100	100	100	100	100
DIDP	50	50	50	50	50	50	50	50	50
Advastab-TM181	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Wax E	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
$CaCO_3$ (1)		10	10UH			20	20UH		
$CaCO_3$ (2)				10	10UH			20	20UH

2.2 Characterizations and Experimental Part

2.2.1 Fourier Transformation Infrared Spectrometry (FTIR)

Fourier-Transformation-Infrared spectroscopy (FTIR) is a scientific system used to checking the surface of PVC, and the comprehend the design of individual particles and the structure of molecular combinations. The machine was used for testing the samples for the FT-IR test was BRUKER TENSOR27 in the Institute of Ceramic and Polymer Engineering. The software that was used in computer for reading and analyzing the measurement data from the machine is called OPUS. First of all, the plate cleaned by ethyl-alcohol (Ethanol, C_2H_5OH) to make waves more accurately, also the sample should be cleaned before the testing. Then putting the sample on the plate and fix it under 65 scans measurements and wait until the data and result will be import to the computer, and repeating the same procedure for all the samples.

2.2.2 Tensile Properties Test

Tensile strength test was carried out on testing machine INSTRON 5566 speed of 100 mm/min. and room temperature 20°C as shown in figure 6. All of samples were cut and divided to 3 parallel measurements with size (length: 60 mm, thickness:2 mm, and width:10 mm) for each sample as shown in figure 7. In tensile test four measurements will be study which is the stress, strain, elongation at break and young modulus.

2.2.3 Hardness Test- Shore (A)

The shore A hardness of the PVC samples was measured using a machine named by Zwick Roell (type: H04.3150) as shown in figure 8. The indenter was pressed with sufficient band force for 5 seconds into the plastic specimen vertically with room temperature 20°C, and repeated the same procedure for each sample 10 times, each time in different point on the surface of sample as shown in figure 9. The results recorded and the average of hardness and standard deviation will be calculating. The shore (A) hardness scale measures the hardness of flexible mold rubbers that scope in hardness from very soft and flexible, toward medium and rather flexible, and toward hard with almost no flexibility at all.

2.2.4 TSDC Electrical Properties Test

PVC samples will examine under electrical direct current. In terms of their electrical properties, specific volume resistivity (ρ) will be measure with standard (IEC 93) for each PVC sample. Direct current (DC) is electrical current which flows consistently in one direction. The current that flows in a flashlight or another appliance running on batteries is direct current. Selecting DC voltage on the multimeter will be (voltage Um=500V) and electrode area ($A=44.15cm^2$). Thermal stimulated depolarization current (TSDC) is use to define the varying rules of charge distribution within insulation structure when it reaches the thermal equilibrium state and the specific parameters [112].

2.2.5 Thermal Characterization Test: Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a method for characterizing thermal behavior of PVC samples as a function of temperature, time, frequency, stress, atmosphere or an arrangement of these limits [74]. DMA measures stiffness and damping, these are reported as storage modulus and loss factor (tan δ) [26,40,43], and also describe the relaxation behavior of the PVC [4,6,22,44,53,69,72]. The DMA tests were measured by (Metravib 1Db DMA 25) machine. Tension and compression over a temperature range (-60 °C to 120°C) with heating rate of 2°C per minute at frequency 10Hz. The dimensions of PVC samples for DMA test are (length: 15 mm, width 12 mm, and thickness 1.2 mm).

III. RESULTS AND DISCUSSIONS

3.1 FT-IR Test Results and Discussion

FTIR procedures usually look at the PVC resin carbon- chlorine bond and plasticizer groups. The results of FT-IR spectras for all the samples was shown in Fig.1.

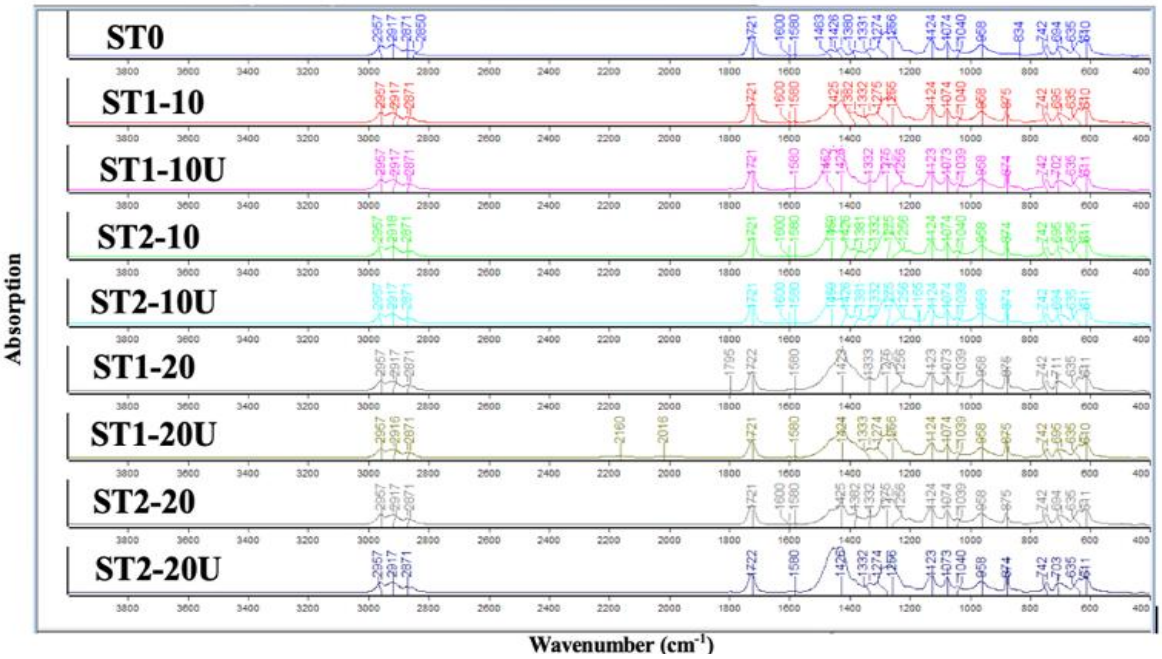

FIGURE 1: FT-IR spectras result for PVC samples.

FT-IR spectra of the plasticizers and the PVC samples were acquired. The main absorption bands in the infrared are shown in Table 2. Each sample can be obverse the peaks of 2957 cm^{-1} which is related to CH_3 stretching and at the peaks of 2916-1918 cm^{-1} can be observe the CH_2 stretching which is a behavior of PVC polymer [80,84,101,102,104]. CH_2 angular deformation mode at 1331-1333 cm^{-1} [101,102], and C-Cl stretching mode at 834-610 cm^{-1} [84, 96, 101-104]. The difference between the pure PVC which is sample (ST0) and sample (ST2-20U) can be seen from the FT-IR spectra that the sample (ST2-20U) is more sensitive comparing to the pure PVC (ST0), and the ST2-20U sample is extra homogenous and the plasticizer on the surface is not obvious, but its inside sample everywhere and well mixed, that is make it the best one among all of the samples.

TABLE 2
MAIN INFRARED ABSORPTION BONDS OF THE PLASTICIZERS AND PVC

Wavenumber (cm^{-1})	Assignment	References
2957	Asymmetric Stretching CH_3	84,101,102,104
2916-2918	Stretching CH_2	101,102,104
2871	Symmetric stretching CH_3	102
2850	CH_2 Symmetric stretching	102,104
1795	C=O stretching	103,80
1721-1722	C=O stretching	102,80
1580-1600	C=C aromatic stretching	102
1423-1463	Deformation (Wagg), CH_2-Cl	101,104
1380-1382	CH_3 Symmetric angular	102
1331-1333	CH_2 Angular deformation	101,102
1255-1275	Cl-CH Out of plane angular deformation	102,104
1123-1124	C-H aromatic	102
1039-1074	Rocking, CH_2	101,104
958	C-H or C-C aromatic	102
874-875	Stretching, C-Cl	84,103
834	Chain stretching	102,104
694-610	Stretching, C-Cl	96,101,102,104

3.2 Tensile Properties Test Results and Discussion

3.2.1 Tensile Stress and Strain Results

It can be ascertained from the figure 2 that the tensile strength is maximum at (13.71 MPa) in sample named (ST2-10U) which is contain 10 wt% of nano- $CaCO_3$ particle, by ultrasonic mixing, the results of tensile stress is shown in Fig.2.

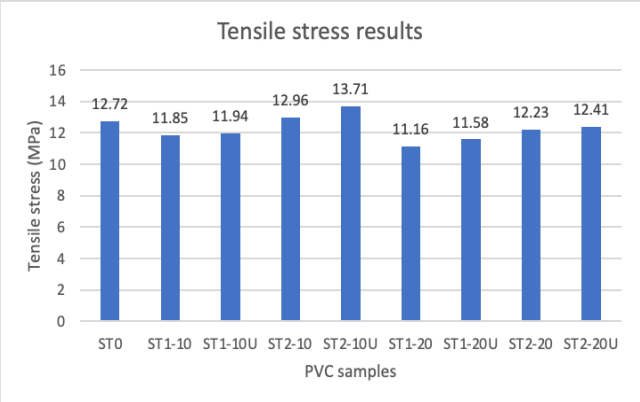

FIGURE 2. Tensile stress results

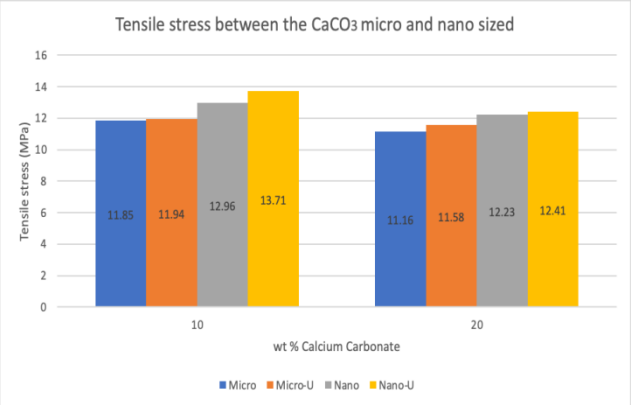

FIGURE 3. Comparing tensile strength between the $CaCO_3$ micro and nano sized particles

The reason behind increasing the tensile strength in the nano particle of $CaCO_3$ as shown in Fig.3 is that nano particles have excellent mechanical properties and unique properties that are not found in micro particle and nanocomposite products contain reinforcing or fillers in nanoscale. Most of the mechanical properties can be enhanced using nano scale particles this might be ascribed to the incredible similarity between nano $CaCO_3$ and PVC matrix.

The result of tensile strain is shown in Fig.4, the highest tensile strain is (428.33) which can be seen in two samples (ST2-10U and ST2-20U).

The results showed that the tensile strain of nano particle of $CaCO_3$ is higher than micro sized particle of $CaCO_3$.

Nano particle of calcium carbonate affected and increasing in tensile strain of the PVC more than the micro particles. The results of growth could be recognized to the huge boundary area between nano-sized particles and matrix.

3.2.2 Elongation at Break Results and Discussion

The maximum elongation is (6.97) which can be seen in sample (ST2-10U) which contain 10 wt % nano particles of $CaCO_3$. Elongation at break initially increases and then decreases quickly when the quantity of $CaCO_3$ amount is greater than 10 wt % as shown in Fig.5. Comparing the PVC samples contain micro size of $CaCO_3$ particles to pure PVC, the pure PVC has higher elongation which increases in homogeneity and reduces the elongation

The nano particle affects more in raising the elongation at break of the PVC sample PVC samples filled nano particle of $CaCO_3$ have higher elongation than micro.

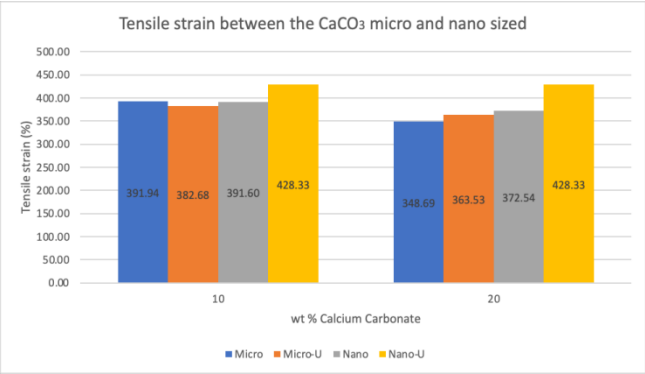

FIGURE 4. Tensile strain results

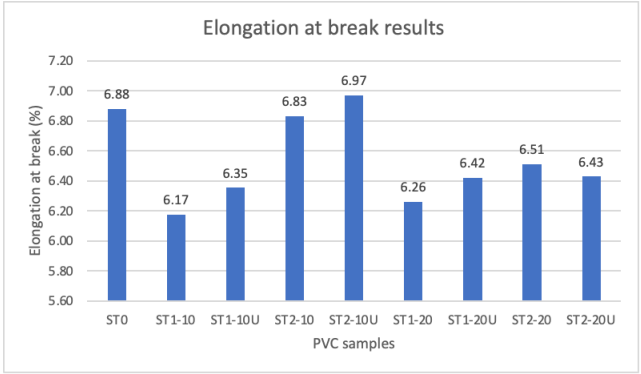

FIGURE 5. Elongation at break results

3.2.3 Young Modulus Results and Discussion

The results showed that young modulus increase by increasing the amount of $CaCO_3$ as shown in Fig.6 and it reached the highest value in 10 wt % of $CaCO_3$, but above 10 wt % young modulus gradually decreasing. Comparing the micro to nano $CaCO_3$ particle in PVC samples, the results showed that using nano sized particles of $CaCO_3$ in PVC sample have more positive affect than micro sized $CaCO_3$ particles.

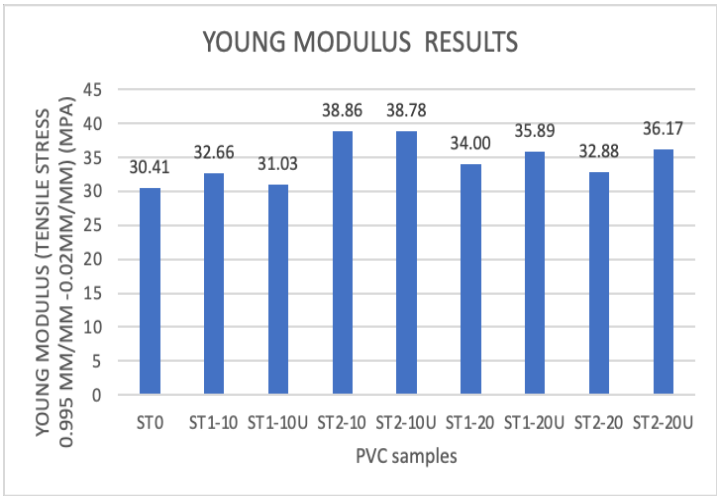

FIGURE 6: Young modulus Results

3.3 Hardness (Shore A) Results and Discussion

The highest value is (93.52 °Sh) for sample (ST2-10U) which contain 10 wt % nano particles of $CaCO_3$. The results showed in Fig.7. PVC samples have great resistance to indentation and they are hard materials. The raise in hardness is more considerable in nano $CaCO_3$ filled PVC compared to that of micro $CaCO_3$. The way of mixing also affected the raise of hardness, obviously the PVC samples with ultrasonic mixing results are much higher than the normal mixing of PVC sample.

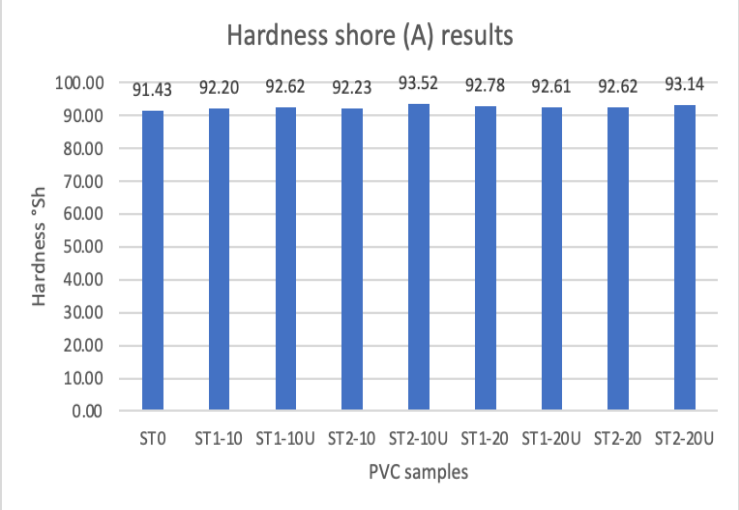

FIGURE 7: Hardness (shore A) results

3.4 TSDC Electrical Test Results and Discussion

The smallest electrical resistance: (ST1-10U) which is (0.9 MΩ), highest electrical resistance: (ST2-20U) which is (6.1 MΩ). The maximum volume resistivity : (ST1-10U) with value (3.34×10^{12} Ωcm) which is a PVC refilled with micro particles of $CaCO_3$ ultrasonic mixed as showed in Fig. 8 and Fig. 9. The specific volume resistivity in PVC micro sized $CaCO_3$ normal mixing is reducing by increasing the amount of $CaCO_3$ to 10 wt %, and slowly increase in 20 wt%. The specific volume resistivity in PVC micro sized $CaCO_3$ ultrasonic mixing is rapidly growth by increasing the amount of $CaCO_3$ to 10 wt %, and slowly decrease in 20 wt%. The PVC with nano $CaCO_3$ particles showed improvement in insulation resistance when compared to unmodified PVC.

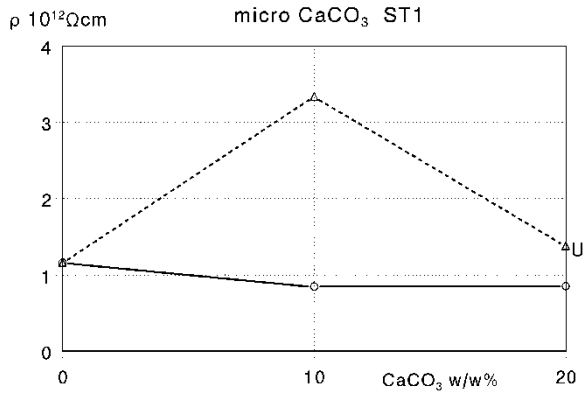

FIGURE 8. Result of electrical resistance and specific volume resistivity of micro sized $CaCO_3$ filled in PVC

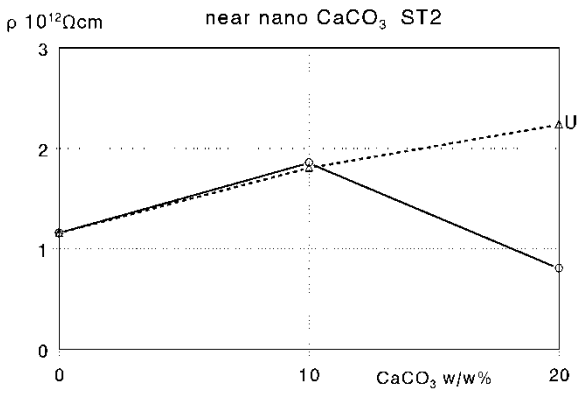

FIGURE 9. Result of electrical resistance and specific volume resistivity of nano sized $CaCO_3$ filled in PVC

IV. RESULTS AND DISCUSSION

4.1 Thermal Characterization Test (DMA)

The storage modulus of PVC decreased as a function of temperature that indicated that samples became in the rubber mood by increasing temperature. The storage modulus can be increased concurrently by the presence of $CaCO_3$ as showed in Fig. 10 and Fig.11.

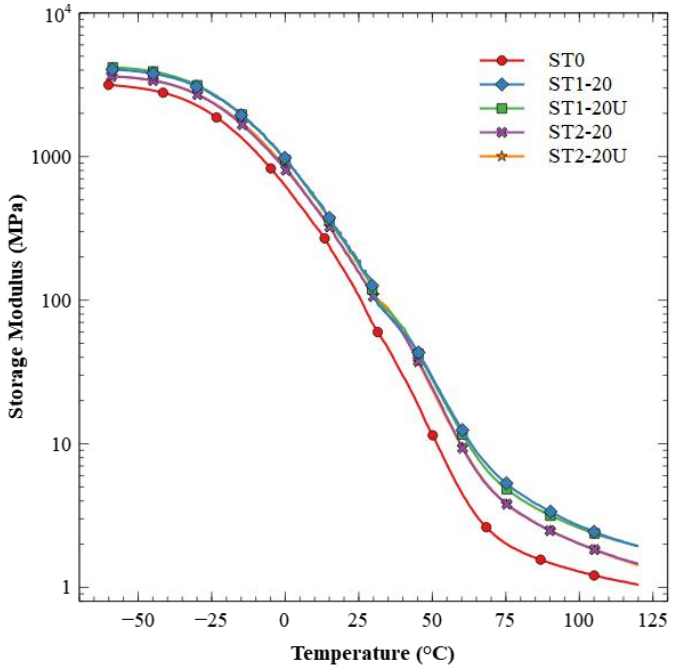

FIGURE 10. Dynamic storage modulus results for PVC samples

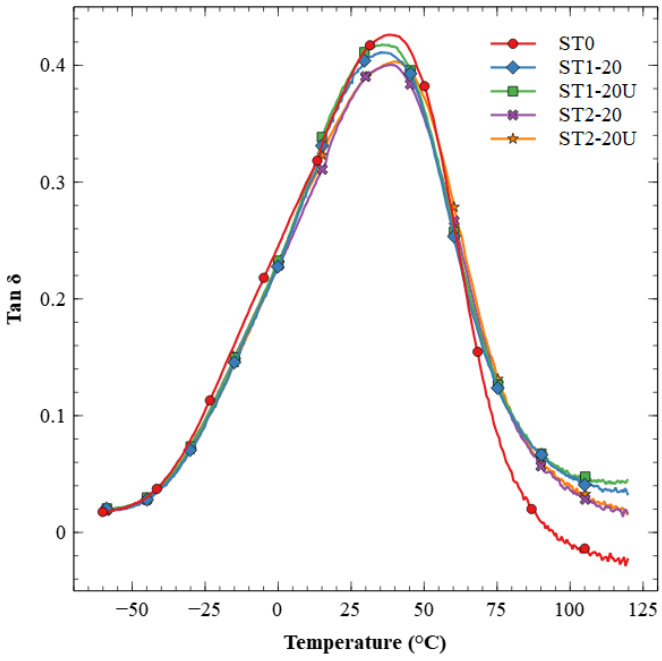

FIGURE 11. Loss factor (tan δ) results for PVC samples

The storage modulus of PVC decreased as a function of temperature that indicated that samples became in the rubber mood by increasing temperature [69]. The pure PVC (ST0) has storage modulus (3164.18 MPa) at temperature (-60 °C) which is lowest storage modulus comparing to other PVC samples at temperature (-60 °C). The highest storage modulus is in samples (ST1-20U) which it has (4180.93 MPa) at temperature (-60 °C) and (1.95 MPa) at temperature (120 °C). The storage modulus can be increased concurrently by the presence of $CaCO_3$ [78,91]. Loss factor (tan δ) of PVC samples is shown in Table 2. The glass transition of pure PVC is 37.9 °C and it is higher than comparing to the PVC micro- $CaCO_3$, but lower than nano-$CaCO_3$ samples.

TABLE 3
GLASS TRANSITION TEMPERATURE OF PVC SAMPLES

PVC samples	Glass transition temperature (T_g) (°C)
ST0	37.9
ST1-20	35.2
ST1-20U	35.5
ST2-20	38.7
ST2-20U	39.7

Comparing the glass transition temperature between micro-$CaCO_3$ and nano-$CaCO_3$ samples, it is obviously increased in nano-$CaCO_3$ [91,95,98,100], and the way of mixing affected the glass transition because the samples which mixed by ultrasonic has higher glass transition than those samples which mixed by normal mixing. It can be found that the stability properties of nano-$CaCO_3$ are better than that of the pure PVC resin. [97]. The DMA results are shown that loss factor (tan δ) of PVC/nano-$CaCO_3$ composites were higher than those of PVC, and all these indicate that the interfacial interaction between PVC and nano-$CaCO_3$ particles can be improved by modification of nano-$CaCO_3$ particles surfaces [98].

V. SUMMARY

PVC samples prepared for this research with micro and nano size of calcium carbonate particle with different phr (0 wt%, 10 wt% and 20 wt%), and different type of mixing. DIDP used as plasticizer added to PVC samples by 50 phr, which applied in the creation of plastic and covering to improve flexibility of plastic, and (Advastab TM181) added to PVC samples by 1.2 phr, which used for gives generally excellent long-haul tones and colors, and impact strength maintenance, and (wax E) added to PVC samples by 0.4 phr for softening to give low consistency of PVC. Roll-milling mixes were obtained utilizing a blender at 165°C for 5 minutes in a rotational speed. The obtained samples were shaped as 2-mm-thick sheets, and different ratio of each plasticizer and two type of mixing which is ultrasonic mixing and normal mixing. The ultrasonic electronic generator switches AC line power to a 20 kHz signal that powers a piezoelectric convertor/transducer.

The PVC samples were examined by FT-IR spectra considering appearance of the PVC resin carbon- chlorine bond and plasticizer groups of the plasticizers to study about the surface of the samples. The main absorption bands in the infrared were acquired. All samples observed the peaks of 2957 cm^{-1} which is related to CH_3 stretching and at the peaks of 2916-1918 cm^{-1} can be observe the CH_2 stretching which is a behavior of PVC polymer, and CH_2 Angular deformation mode at 1331-1333 cm^{-1}.Also C-Cl stretching mode at 834-610 cm^{-1} . The sample (ST2-20U) which contained 20 wt % nano particles of $CaCO_3$ with ultrasonic mixing acquired that it is extra homogenous and the plasticizer on the surface is not obvious, but its inside sample everywhere and well mixed, that is make it the best one among all of the samples.

The PVC samples were examined by tensile stress which measured the strength of a material, in this manner, it alludes to a power that endeavors to pull separated or stretch a material. The tensile strength measured highest in the sample (ST2-10U) which is 10 wt % of nano particle of $CaCO_3$ with ultrasonic mixing, and greater than any other compositions with value of (13.71 MPa). By increasing the amount of $CaCO_3$ above 10 % to 20 %, tensile stress decreased. The highest tensile strain is (428.33) which can be seen in two samples (ST2-10U and ST2-20U) which both of them contain nano particles of $CaCO_3$ ultra sonic mixed with 10 wt % and 20 wt %. The results showed that by increasing the amount of nano-$CaCO_3$ from 10 % to 20 %, does not affect the strain of the PVC and stay constant. Nano particle of calcium carbonate affected and increasing in tensile strain of the PVC more than the micro particles. The results of growth could be recognized to the huge boundary area between nano-sized particles and matrix.

The results showed that the tensile strain of nano particle of $CaCO_3$ is higher than micro sized particle of $CaCO_3$.

The maximum elongation was (6.97) which can be seen in sample (ST2-10U) which contain 10 wt % nano particles of $CaCO_3$, elongation at break initially increases until when the amount of $CaCO_3$ reach 10 wt %, and then decreases rapidly when the amount of $CaCO_3$ is greater than 10 wt %. Comparing the PVC samples contain micro size of $CaCO_3$ particles to pure PVC, the pure PVC has higher Elongation. The result showed that PVC samples filled nano particle of $CaCO_3$ have higher elongation than micro size of $CaCO_3$.

Young modulus examined and the results showed that young modulus increase by increasing the amount of $CaCO_3$ and it reached the highest value in 10 wt % of $CaCO_3$, but above 10 wt % Young modulus gradually decreasing. The results showed that using nano sized particles of $CaCO_3$ in PVC sample have more positive affect than micro sized $CaCO_3$ particles.

Hardness test examined and according to the results, the highest value in sample (ST2-10U) which is (93.52 °Sh) which contain 10 wt % nano particles of $CaCO_3$, and the lowest value is (91.43°Sh) for sample (ST0) which is pure PVC without $CaCO_3$ particles. The results showed that PVC samples have great resistance to indentation and they are hard materials. The raise in hardness is more considerable in nano $CaCO_3$ filled PVC compared to that of micro $CaCO_3$. The results showed that $CaCO_3$ affected the hardness of PVC and raise it respectively. The way of mixing also affected the raise of hardness, obviously the PVC samples with ultrasonic mixing results are much higher than the normal mixing of PVC sample.

The lowest value of standard deviation can be seen in sample (ST0) which is 0.11, and the highest value of standard deviation can be seen in sample (ST1-10) which is 0.45 as shown in figure 26. After that the standard deviation reduced in sample (ST1-10U) to 0.27. Then the value growth in sample (ST2-10) which is 0.31. The standard deviation decreases in sample (ST2-10U) to 0.23, then increase respectively in sample (ST1-20) to 0.24 and rise again sample (ST1-20U) to 0.29. After that it decreased in sample (ST2-20) to 0.19. Finally, in the last sample (ST2-20U) it increased to 0.28.

PVC samples examined with TSDC, electrical properties of them detected. In terms of their electrical properties, specific volume resistivity (ρ) with standard (IEC 93).The sample (ST1-10U) has the smallest electrical resistance which is (0.9 MΩ) and sample (ST2-20U) has the largest electrical resistance which is (6.1 MΩ). The PVC with nano $CaCO_3$ particles showed improvement in insulation resistance when compared to unmodified PVC. The maximum volume resistivity can be seen in sample (ST1-10U) with value (3.34×10^{12} Ωcm) which is a PVC refilled with micro particles of $CaCO_3$ Ultrasonic mixed. The specific volume resistivity in PVC micro sized $CaCO_3$ normal mixing is reducing by increasing the amount of $CaCO_3$ to 10 wt %, and slowly increase in 20 wt%. The specific volume resistivity in PVC micro sized $CaCO_3$ ultrasonic mixing is rapidly growth by increasing the amount of $CaCO_3$ to 10 wt %, and slowly decrease in 20 wt%. In contrast, the specific volume resistivity in PVC nano sized $CaCO_3$ normal mixing is growth by increasing the amount of $CaCO_3$ to 10 wt %, and rapidly decrease in 20 wt%. The specific volume resistivity in PVC nano sized $CaCO_3$ ultrasonic mixing is rapidly growth by increasing the amount of $CaCO_3$ to 10 wt %, and continue rising in 20 wt%.

Thermal characterization of PVC samples examined by DMA. Storage modulus and loss factor (tan δ) of PVC decreased as a function of temperature, that indicated that samples became in the rubber mood by increasing temperature. The storage modulus can be increased concurrently by the presence of $CaCO_3$. The glass transition of pure PVC is higher than PVC micro- $CaCO_3$, but lower than PVC nano-$CaCO_3$ samples. The way of mixing affected the glass transition because the samples which mixed by ultrasonic has higher glass transition than those samples which mixed by normal mixing. It can be found that the stability properties of nano-$CaCO_3$ are better than that of the pure PVC resin. Future work will be checking the thermal properties such as heat stability and flame retardancy, and colorization of the PVC samples.

In the PVC compounding industry the fillers are usually added in the high speed mixer. The general problem is the agglomeration of the filler particles. The lower is the particle size the higher is the danger of agglomeration. Therefore the advantages of the low particle size cannot be utilized. Nowadays the ultrasonic mixing is easily accessible even in industrial size therefore I tried to compare the mixing methods.

The mixing ratio is a question of application; it is decided at creating basic formulation. I have found that the ultrasonic mixing produces considerably better dispersion, by these way better properties. The limit of ultrasonic mixing is the filler/fluid ratio. The electrical industry, namely cable insulating materials, is the industrial sector where ultrasonic mixing is advantageous.

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