Effect of Pure and Modified Gum Arabic on the Mechanical Properties of Poly (Vinyl Chloride)

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Abstract- Physical modification of pure gum arabic was carried out by plasticization of gum arabic with ethylene glycol. The chemical method was performed by acid hydrolysis, acetolysis and acetate formation. Both the pure and modified gums were mixed with PVC at different compositions and cast into films using tetrahydrofuran as solvent. Water absorption study revealed that the acetolysis sample (ACT) absorbs water the most at 14% water absorbtion , followed by ethylene glycol formulation (EGL) at 3.9%. However, pure gum (PGM) has the lowest water absorption at 2.1%. From the mechanical test, it shows that the acetic anhydride sample (AAN) has the highest modulus with 180.14N/mm^2 at 10, 140.1N/mm^2 at 20%, and 147.67N/mm^2 at 30% gum composition. For pure gum (PGM), the modulus drops from 139.66 to 97.18N/mm^2 at 10 to 30% gum composition then finally increases. The ACT formulation shows decrease in modulus as the percent of filler increases. Modulus of ethylene glycol (EGL) drops at 20, 40 and 70% filler composition. It was found that the tensile strength of the chemical modification formulations reinforced the PVC matrix at 10%/90%, 20%/80% and 30%/70% gum/PVC compositions for AAN and at 10%/90% and 20%/80% gum/PVC compositions for ACT. Though EGL showed increase at 30%/70% composition, its tensile strength is similar to that of the unmodified gum (PGM), decreasing with increasing gum concentration.

Index Terms- elastic modulus, percent elongation, gum arabic, poly (vinyl chloride), tensile strength

I. Introduction

Polysaccharides have been described as high molecular weight polymers formed by condensation of many monosaccharide units or their derivatives. They have also been defined as polymeric substances, the building blocks of which are monosaccharide. From the foregoing, polysaccharides could be said to be long chain carbohydrate molecules built from some monosaccharides such as glucose, rhamnose, galactose, etc. or their derivatives. Polysaccharides could be classified based on their chemical compositions. In this regard a polysaccharide which yields only one type of monosaccharide on hydrolysis is called homoglycan e.g starch, while those which yield two or more types of monosaccarides are called heteroglycan e.g. gum Arabic.

PVC can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, electrical cable insulation, inflatable products and many other applications in which it would originally have replaced rubber (Titow, 1984). As an amorphous polymer, PVC resin is extensively formulated to produce an extremely large variety of compounds (Blanco, 2000). Also due to its inexpensive nature and flexibility it is used in plastic pressure pipes systems for pipelines in the water industries. The capability of PVC to perform such diverse functions is due to its ability to incorporate various additives to suit the numerous applications (Titow, 1984).

Fillers are particulate material, such as minerals, diatomaceous earths, and tale, which are added to polymers to reduce cost. Fibrous reinforcements, such as glass and carbon fibers, are added to polymer to increase stiffness and to some degree strength. Both types of materials tend to increase the viscosity of the polymer, especially at low shear rates, resulting in the formation of yield stress. At high shear rates, the effect is less pronounced as the viscosity approaches that of the neat resin. In addition to increase in pressure drops associated with processing these composite materials, they tend to lead to wear of the screws, eventually reducing the performance of the extruder (Mascia, 1974). Fillers have been used in plastics industrially worldwide for many decades. The primary purpose for using in thermoplastic matrix is its ability to modify properties (e.g to improve strength and stiffness, scuff resistance, enhance thermal conductivity and electrical properties, dimensional stability etc. (Charles et al, 2005).

Effect of additives mainly plasticizers and fillers, on the mechanical properties of PVC were studied and the experimental results have shown that tensile strength decreased with increasing plasticizer content for the group of samples free of filler (Elgozali and Hassan, 2008). The trend was completely reversed in the group where the sample contained filler. They also confirmed that the elongation at break is inversely proportional to plasticizer content for the group free of filler, while it is directly proportional to plasticizer content for that containing filler. In another study by Liu and Zhang (2007), the effects of acetanilide, adipic acid and potassium hydrogen phthalate as nucleating agents on PVC crystallization were investigated by differential scanning calorimetry (DSC), wide angle x-ray diffraction (WAXD) and fourier transform infrared spectroscopy (FTIR). The experimental results indicated that all the three additives were compatible with PVC to some extent, but adipic acids compatibility with PVC was less satisfactory. They confirmed that the three additives improved PVC crystallinity and acetanilide decreased PVC glass transition temperature (T_g) and narrowed PVC melting range, while adipic acid and potassium hydrogen phthalate raised the T_g of PVC and widen its melting range. All additives did not affect PVC crystal system and all samples were in orthorhombic system. Moreover, acetanilide and adipic acid shrinked PVC spacing and improved the crystal perfection of PVC, but potassium hydrogen phthalate swelled spacing and reduced the perfection of PVC crystal.

Labib and Williams, (1984) studied the surface properties of polyvinyl chloride containing organotin stabilizers and calcium stearate, and the surface properties of the additives themselves. They used Zeta-potential measurements to determine the charge on the surface of additive-containing polyvinyl chloride and related this to chemical reactions of the additive materials. They discovered the major chemical reactions were those involving hydrolysis of tin-ester linkages in the organotin compounds and dissociation of carboxylic acid groups. They also discovered that as a result of these reactions, the surface charge of the polymer depends strongly on the pH of the aqueous medium in contact with the surface.

The mechanical properties of both unplasticized and plasticized PVC expose to 25% concentrated HCl/NH_3 solutions were another set of studies investigated by Mamza and Solomon, (2008). In their study, the stress/strain relationship before and after exposure of the samples compressed molded film, to acidic and basic media for 72 hours was investigated. The tensile testing suggested that depolymerization of PVC is enhanced in basic medium due to neutralization of liberated HCl, hence resulting to decrease in its mechanical properties, while the mechanical properties of those exposed to acidic medium are appreciably reinforced due to minimal depolymerization. According to Harris (1969), the tensile properties of polymers, apart from defining the quality of production as well as their design and engineering behavior also indirectly measure other properties of the material for which correlation exist. For example, a plastic film of high tensile strength and elongation, in all directions, will likely have high impact strength. Tensile properties may also be used to monitor chemical or physical changes taking place in a polymer. The study of the effects of Ca/Zn stearate and organotin heat stabilizers and Zeolite, CaCO3, Celluose and Luffa flours filler, and their concentrations (2.5, 2, 10 and 20% by weight) on production of flexible PVC foams by chemical blending agent, azodicarbonamide was done by Demir et al., (2008). They determined foam morphology density, compressive mechanical properties and water uptake capacities of the samples. Morphology of the sample without any filler showed that employment of Ca stearate and Zn stearate stabilizers instead of organotin stabilizer increased foam formation and decreased pore sizes and regularity in pore size distribution. Foams having organotin stabilizer were more resistant to heat than the ones with Ca/Zn stearate for long heating period. Foams, including organotin-based heat stabilizer, have compact structure. It was observed that, samples containing Zeolite, $CaCO_3$, Cellulose or Luffa flour had lower pore volume but higher Young's modulus and stress values compared to unfilled samples.

II. RESEARCH METHODOLOGY

Materials Used

The reagents used include: chloroform, ethanol, petroleum ether, concentrated sulphuric acid, acetic acid, acetic anhydride, glycerol and ethylene glycol were obtained from the British Drug House. Honsfield Tensometer was used for mechanical property testing.

Gum Arabic Extraction

Gum Arabic exudates was hydrated in double strength chloroform water, precipitated in 95% ethanol and then washed with diethyl ether (oluyemisi et al, 2010). Physical and chemical modification of the gum was carried out according to the method described by Sawumi, (1990).

PVC Formulation

Different proportions of test samples and PVC by weight were weighed to give different compositions by percentage: (PVC: GA), 100%:0%, 90%:10%, 80%:20%, 70%:30%, 60%:40%, 50%:50%, 40%:60%, 30%:70%, 20%:80%, and 10%:90%. Each of these formulations was used for film casting using tetrahydrofuran, (THF) as solvent.

Film Casting

Each formulation was prepared in $30cm^3$ of tetrahydrofuran. The resulting solution was stirred vigorously and allowed to stand on a water bath for 30 minutes while stirring before it was poured in to a clean dry 8.50cm Petri dishes. The dishes were kept on a flat surface in a fume cup board and allowed to stand for the solvent to evaporate. The film were removed by pouring distilled water sufficiently enough to cover the film surface and allowed to stand for few minutes after which it was removed using spatula. Thereafter, the films were dried by blotting then between filter papers and allowed to dry in a dessicator for 48 hours before taken for mechanical property testing.

Percent Water Absorption

This was carried out according to ASTM D570. The specimens were dried in an oven for 24hours at 50^oC and then placed in a dessicator to cool. Immediately upon cooling the specimens were weighed. The materials were then immersed in water at 25^0C for 24hours. Specimens were then removed, patted dry with lint free cloth and weighed.

Percentage water absorption =

$$\left[{(wet\ weight - dry\ weight)}/{dry\ weight}\right] \times 100$$

Mechanical Property Testing

Hounsfield tensometer testing machine was used for this determination by the method of ASTM D-882. From the plot of stress-strain curves, the ultimate tensile strength, modulus of elasticity and elongation at break for each film was calculated.

Stress at break was evaluated using the following equation;

$$\tau_b = \frac{F}{A}$$

Where A is the cross-sectional area of the sample and F is the applied tensile force. The elongation at break was calculated using the following equation.

$$\Delta L_b = \left(\frac{L' - L_0}{L_0}\right) \text{X } 100$$

Where, L' is the length of the sample at break and L_0 is the initial length. The modulus of elasticity was evaluated using the equation below.

$$\varepsilon = \frac{\tau_y}{(L-L_0)/L_0}$$

Where L is the length of sample at yield and τ_y is the stress at yield (Elgozali and Hassan, 2008).

III. RESULT AND DISCUSSION

Water Absorption

The water absorption test shows that ACT modified gum absorbs water the most as shown in Fig 1. The next to it is EGL, followed by AAN. At 10/90, 20/80% and 30/70% (PVC/GUM) ratio, AAN samples have the lowest water absorption. However at higher compositions of gum, PGM samples showed lower absorption values than AAN. At 50/50%, ACT and PGM showed a drop in absorption. Generally, the result shows that the water absorption of the formulations increases with increasing concentration of gum sample. This behavior was expected since the water absorption of these formulations is mainly due to the presence of the gum; because the PVC matrix absorbs little water while the gum Arabic contains numerous hydroxyl groups (-OH), which are available for interaction with water molecules by hydrogen bonding. The fact that water absorption was observed, this suggests that the gum Arabic satisfactorily encapsulated the water in the PVC matrix, suggesting that no significant changes occur in the microstructure of the composite.

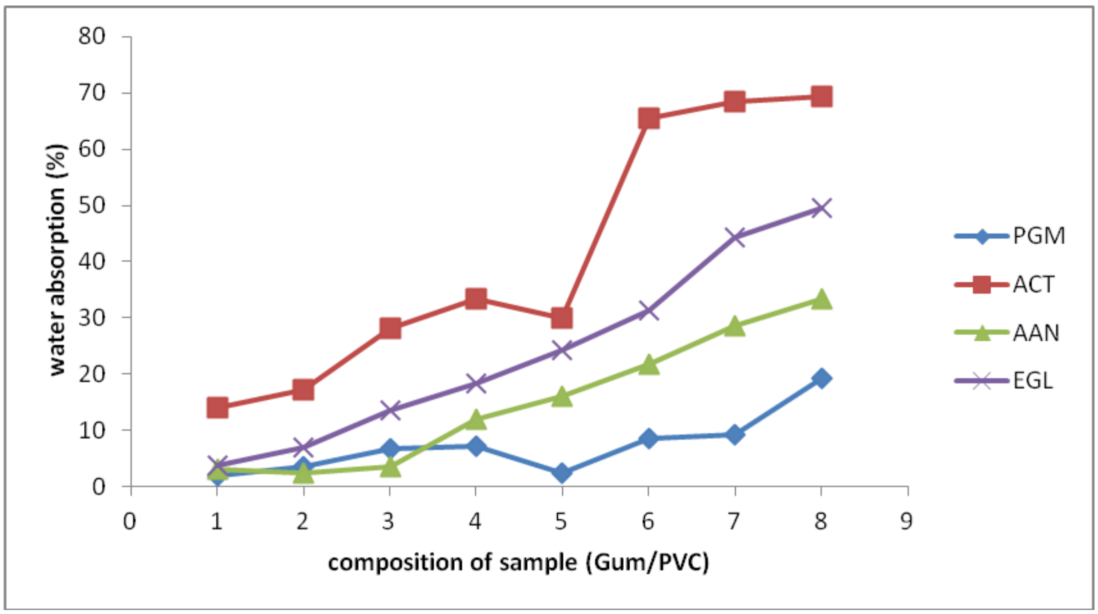

Fig 1: percent water absorption of test samples at various composition.

Mechanical Properties

Mechanical properties were carried out to study the tensile properties of polymer blend films and they become important as polymer technology moves from laboratory into process development. It is well known that mechanical properties might be used to assess the miscibility in polymer blends through a comparison of experimental results and predictions based on various models. Indeed, the mechanical properties of polymer blends depend on the intermolecular forces, chain stiffness, and molecular symmetry of the individual polymers used to prepare the blend (Mudigoudra et al, 2012).

Tensile strength

The tensile strength of the three modified gums show different results from that of the pure gum arabic. This is revealed in fig 2. The tensile strength of the pure gum (PGM) records 18.8 at 90%/10% PVC/gum, it drops to 14 at 80%/20% PVC/gum and rises again to 16 at 70%/20% PVC/gum. It then continues to drop as the percentage of the gum increases tending towards zero. In EGL sample, 20.5 was recorded as the highest strength at 90%/10% PVC/gum. The value drops to 14. 2 at 80%/20% PVC/gum and increases again to 16.9 at 70%/30%. The tensile strength decreased afterwards as the percent composition of the gum increases. ACT and AAN modified materials increases with the addition of gum to the PVC matrix and increases as the amount of gum increases to a point in which the PVC can no longer support the gum. This is where the tensile properties of the formulations begin the drop, approaching zero. The results shows that there is an increase in the polymer chain length, and also cross linking of the polymer chains as the amount of modified gum increases, forming a system of interpenetrating network (IPN). This was responsible for the increase in the tensile strength as observed, whereas, PGM and EGL shows a decrease in tensile strength as the amount of the filler is increased. The plasticizer forms links with the PVC molecules and acts as a spacer between molecules of the PVC. Due to this linkage, gum Arabic has a positive effect on the mechanical properties of the polymer. It was stated that dipole interaction which occurs between polar groups of chlorine atom in PVC resin and free hydroxyl, ester, amino, etc groups in gum Arabic stand for polar group in the plasticizer. The bond forces of the polymer atoms strengthened due to the linkage established and thus free volume decreases with the addition of gum Arabic to the polymer which leads to increasing tensile strength. In the above cases, it shows that the tensile strength of the materials increases with increase in the amount of gum Arabic; this is attributed to its polarity which increased the cohesive energy density, such that the materials tend to be held together more tightly resulting in induced mobility and flexibility.

The expected results from the chemical modifications are based on the fragmentation pattern from the gum Arabic after chemical treatment. The stress-strain curve exhibited by the gum Arabic could be linked to its relatively high molecular weight in addition to the rigid backbone. Possession of branch linkages would also add to the rigid nature of the gum. The result of this is that when cast into a film, it is very brittle and thus its main drawback in adhesion formulations. Therefore it is believed that scission of these linkages might result in low molecular weight structures which will reduce the rigidity inherent in the structure. There are two main structural linkages that are susceptible to bond scission. These are the main backbone chain of (1-3) linked D-galactopyranose units and the branching or substitution of these units at the C-6 position with various side chains.

The branch (1-6) linkages are, however, easily broken by acetolysis. The acetolysed gum Arabic was observed to exhibit lower values of tensile strength than pure gum arabic. This may be because scissions in the acetolysed system occurred at branch points. The effect is debranching which results in reduction of chain rigidity and proper re-allignment of molecules.

The result observed for the acetate derivative (AAN) of the gum Arabic also showed debranching of the chains. The effect is, however, more pronounced than the acetolysed samples, probably because of the acetate group. The re-allignment of the molecules with the polar nature of acetate group might have increased the intermolecular force of attraction, the result of which is tougher material than the untreated gum Arabic also. It is therefore suggested that the acetate group is capable of increasing the modulus of rigidity and increase the strain at break of the gum Arabic.

From the result also, EGL being a physically modified gum has a similarity in trend with the pure gum sample. While the chemically modified gums i.e ACT and AAN are also similar in trend. The presence of PVC is believed to increase the strength of the blend due to interlocking of the polymeric chains as well as the dipole-dipole interaction between O-H groups in the gum samples and C-Cl groups in PVC (Kim et al, 1997)

The results have shown that the structure-property typical of the unplasticized gum Arabic can be modified by the addition of plasticizing agents. The effect of the chemically modified additives was significant in the increase in values for ultimate tensile strength to a maximum value before decreasing. While the physically modified sample (EGL) does not show this property.

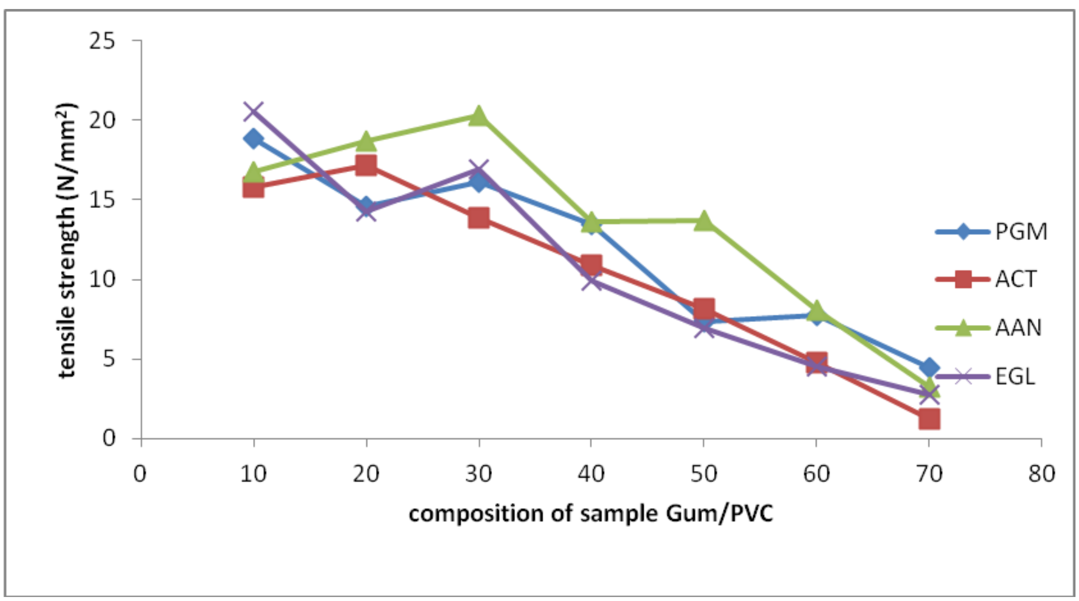

Fig 2: tensile strength of test samples at various compositions.

Elastic Modulus

The tensile stress data show the maximum stress supported by the plastics. The tensile stress decreased as the gum Arabic content increased. Fig 3 gives the elastic Young`s modulus of all the test samples. This implies that the modified gums have improved upon the pure gum Arabic. The AAN modification has the highest elastic modulus of 180.15N/m^2 at 10/90 gum/PVC and it becomes fairly constant at 30/70 and 40/60 gum/PVC composition. ACT is the next with 177N/m^2 at 10/90 gum/PVC ratio but it begins to drop as the gum concentration increases except at 30/70 gum/PVC composition where it shows a slight increase. The value for EGL records 164, still a higher value than the pure gum samples. It can be observed that the sample with the best modulus is AAN and the composition that showed good elastic behavior is 30/70 gum/PVC.

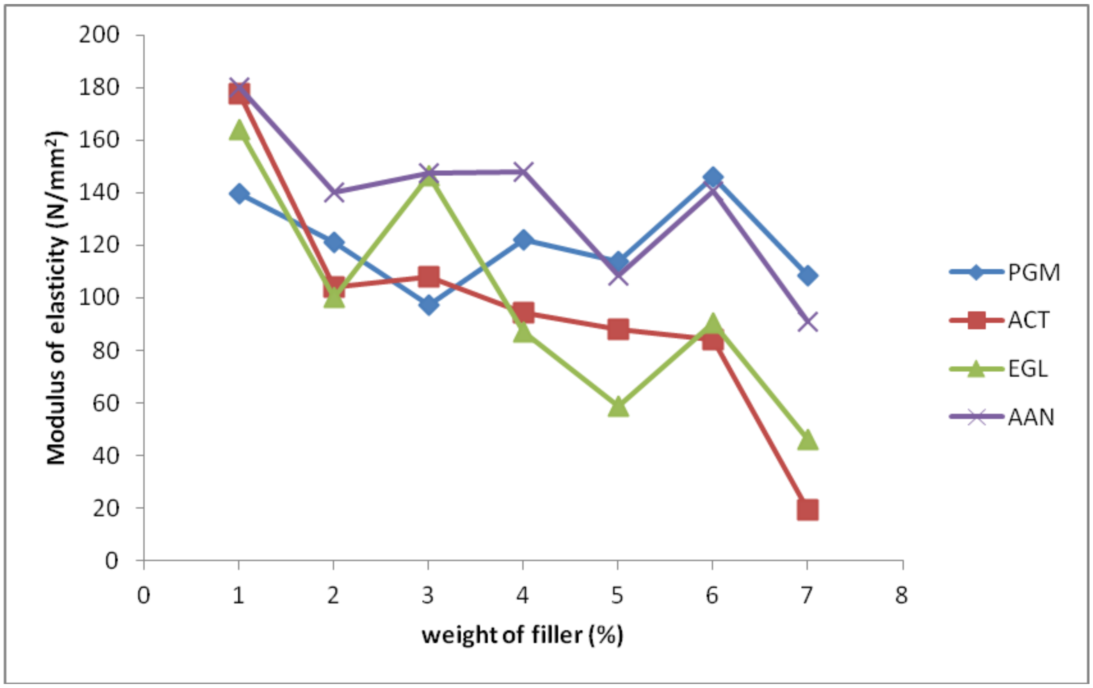

Fig 3: modulus of elasticity of the test samples at varying weight percent of filler

Percentage Elongation of the Samples

Fig 4 shows comparison between pure gum sample and gum modification formulations at different compositions. At 10/90 and 20/80 gum/PVC all modified gums have higher values than the pure gum Arabic. At 30/70 however the pure gum Arabic records 17.8% while all other samples record values below that. At 50/50%, similar values of 12 and 12.3% were recorded for PGM and AAN, respectively. On comparison, the percent elongation of test sample depends on the composition, though chemically modified formulations show similarity in trend.

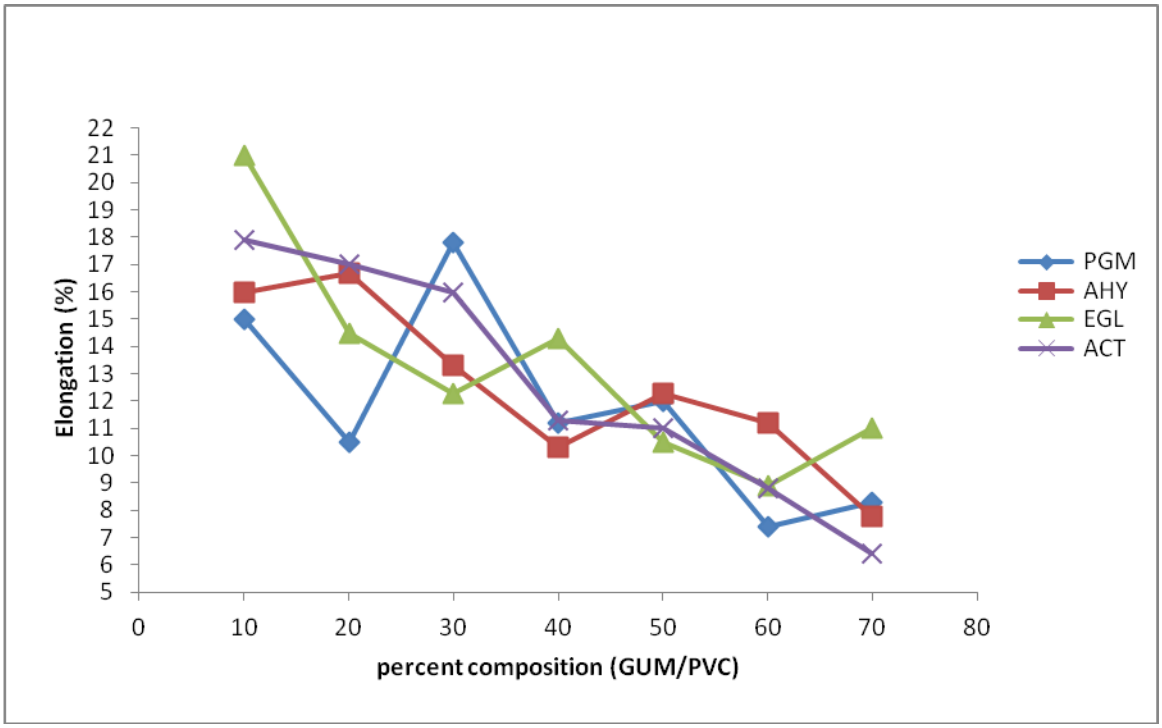

Fig 4: percent elongation of the test samples at varying composition

IV. CONCLUSION

Water absorption results of the samples show ACT has the highest wa*ter absorption capacity*. There are fluctuations in absorption depending on the composition of the sample, but the general trend is that absorption increases with increasing gum concentration. The AAN sample has the highest modulus at 10, 20, 30 and 40% gum composition. For PGM the modulus drops from 10-30% gum composition then finally increases. The ACT modification shows decrease in modulus as the percent of gum increases. Modulus of PGM drops at 20, 40, 60 and 80% gum composition. This study revealed that the tensile strength of the chemically modified formulations shows similarity in trend, while the physically modified formulation also shows similarity in trend with the pure gum formulation. ACT and AAN formulations show high strength at 10%/90%, 20%/80% and 30%/70% for AAN and 10%/90% and 20%/80% for ACT before generally decreasing. This was not the case for EGL and PGM formulation which show decrease in tensile strength as the composition of gum increases.On comparative effectiveness, the chemical modifications showed reinforcement in the PVC matrix, while the physical modification showed plasticizing property due to decrease in tensile strength as the percentage of gum increases. The AAN sample at 30%/70% Gum/PVC composition was found to be the strongest with overall best adhesive property.

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