Effect of pure and modified gum Arabic on the mechanical properties of poly (vinyl chloride)

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ABSTRACT
Gum Arabic exudate was collected from Acacia Senegal trees around Zaria metropolis. The gum was hydrated in double strength chloroform water, purified in 95% ethanol and then washed with diethyl ether. Modification of the gum was performed with ethanol and Acetic anhydride. Densities of the samples were compared with that of the unmodified gum and it was found that both samples were less dense than the unmodified gum. From turbidity measurement, ethanol modified (EGL) gum appears more turbid than both acetic anhydride modification (AAN) and unmodified gum (PGM). In salinity, conductivity and TDS tests, AAN sample higher values than other samples. The melting point of EGL and PGM are only slightly different, 242°C and 245°C respectively while that of AAN was 229°C. The mechanical properties of the samples were measured using Honsfield Tensometer. 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. 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. 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.

Introduction
Virgin PVC is hard, difficult to process and extremely susceptible to rapid degradation at temperature necessary for its processing (Marvel et al, 1939). The degradation of PVC during processing is brought about by the effect of heat, pressure and shear which are exerted on the material. The mechanism of PVC degradation involves dehydrochlorination, liberation of hydrogen chloride gas (HCl) to form polyene structures, which serve as points at which undesired reactions are propagated, and as points at which undesired reactors are propagated, and finally leading to deterioration of physical properties of the PVC material (Thomas and Todd, 1971). In 1926, Waldo Semon and the B.F Goodrich Company developed a method to plasticize PVC by blending it with various additives. The resultants product was more flexible and more easily processed material that soon achieved widespread commercial use. The effective so called external plasticization of the PVC homopolymer by incorporating plasticizers caused a reduction in the softening of PVC (Tester, 1973). He noticed that when PVC was compounded with butylphthalate and other esters, which resulted in rubber-like properties at room temperature. It was also understood that alkaline earth metal soaps acted as heat stabilizers (Brydson, 2000). So it was realized that useful products could only be obtained if certain additives were incorporated into the polymer matrix by process known as compounding (Thomas and Todd, 1971). However, the addition of suitable additives such as plasticizers, stabilizers, lubricants, filters and other, can transform the polymer into a soft flexible material with rubbery characteristics or into a tough rigid material. Polymer additives are important areas of innovation for polymeric materials. An additive is a material that is added to a polymer melt to enhance the processability, performance, or appearance of the polymer. The ability to modify polymer has allowed the polymer industry to produce better and stronger materials.

Effect of additives, mainly plasticizers and fillers, on the mechanical properties of PVC were studied, 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 (Tg) and narrowed PVC melting range, while adipic acid and potassium hydrogen phthalate raised the Tg of PVC and widen its melting range. All additives did not affect PVC crystal system and all samples were in orthorhombic system.
Moreover, acetonilide and adipic acid shrunk 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 that the major chemical reactions were those involving hydrolysis of 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.

Azman and siranesswarm, studied the effects of rice husk ash (RHA) filler on processability of impact modified unplasticized polyvinyl chloride (PVC-U). They studied the processability to investigate the fusion behaviour of filled impact modified PVC-U, using Brabender plasticizer with fitted mixing head. The work was carried out on the pre-prepared RHA with different loading levels. Analysis of the result showed 10 phr RHA filled impact modified PVC-U samples had shorter fusion time and higher fusion torque compared with the other levels of filler loading. Zirconate treated samples showed longer fusion time and longer processability torque compared with the other types of coupling agents. The experimental results also related that the lower the loading of the filler, the faster the fusion during processing.

The mechanical properties of both unplasticized and plasticized PVC expose to 25% concentrated HCl/NH₃ 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 HC, 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 behaviour also indirectly measure other properties of the material for which corelaxation 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, Cellulose 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, CaCO₃, Cellulose or Luffa flour had lower pore volume but higher Young’s Modulus and stress values compared to unfilled samples.

Balakriahnan and Jayakrishnan, (2005) showed in their work the animation of PVC with a concentrated aqueous solution of ethylenediamine. The animated PVC was then reacted with hexamethylene disocyanate to incorporate the isocyanate group onto the polymer backbone. The Isocyanated PVC was further reacted with polyethylene glycol (PEG), where infrared spectra analysis showed the incorporation of PEG into PVC. The thermal stability of the modified polymer was found to be lowered by the incorporation of PEG. Contact angle measurement on the surface of polymer films cast from a tetrahydrofuran solution of the polymer demonstrated that the modified polymer gave rise to a significantly hydrophilic surface compared to unmodified PVC. They still showed static platelet adhesion studies using platelet rich plasma, which showed significantly reduced adhesion on the surface of the modified PVC compared to control PVC. The study showed that bulk modification of PVC with PEG using appropriate chemistry can give rise to a polymer that posses the anti-fouling property of PEG and such bulk modifications are less cumbersome compared to surface modifications on the finished product to impact anti-fouling properties to PVC surface. Jian and Zhen-Liang (2002), Prepared a symmetric PVC hollow fibric ultrafilteration members by phase inversion technique from 14 to 20 wt% solids including PVC and additives. They used polyvinyl pyrolidone (PVP 40, 000) Polyethylene glycol (PEG) with different molecular weights (PEG 600, PEG 800, PEG 1000) as additives and N,N-dimethylacetamide (DMAc) as a solvent. 95/5 DMAc/water and pure water were used as bore fluid to investigate the effect of gelation bath. The dope solutions, membrane structure, separation performance and mechanical properties of PVC hollow fibre membranes were studies. The membrane structure of PVC hollow fibre membranes including external surface, internal surface and cross-section were characterized by Scanning Electron Microscopy (SEM) and the mechanical properties of PVC hallow fibre membranes were discussed. It was found using PVC or PEG as additives can increase the membrane porosity and enhance the permeation flux by changing the membrane morphology. Three kinds of proteins having different molecular weights were applied for the measurement of rejection. Based on the experimental results, pure water permeation fluxes of PVC/additive/DMAc hollow fibre membranes might reach 100-200 L/(m² h bar) while the molecular weight cut-off at PVC hollow fibre membranes will be approximately 50,000.

Chao et al (2003) prepared polyvinyl chloride/Na+ - montmorillonite (PVC/MMT) nanocomposites with different MMT contents via melt blending. Wide-angle x-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM) were used to characterize the structures. Effects of MMT content on the machanicaal properties were also studied. It was found that PVC molecular chains can intercalate into the gallery of MMT layers during melt blending process, the stiffness and toughness of the composites were improved simultaneously within 0.5 - 7w% MMT content, and the transparency and mechanical properties decreased as MMT content further increased.

In another work, polyvinyl chloride/ethylene-vinyl acetate/montmorillonite (PVC/EVA/OMMT) composites were studied by melt blending method. Two kinds of montmorillonites were organically modified by trimethylolactadecyl ammonium and dimethyl bis(hydrogenated tallow) ammonium respectively. The morphology and tensile properties of the resultant composites were discussed in terms of
the modifier type and OMMT content. The PVC/EVA/OMMT composites had intercalated structure which was independent of the polarity of the modifiers, while the tensile properties showed strong dependence on the modifier type. The OMMT modified by polar modifier gave higher tensile ductile and strength of PVC/EVA/OMMT composites (Chao et al., 2003).

Mazatusziha, (2006) investigated the performance of rice husk (RH) as filler for unplasticised polyvinyl chloride (PVC-U) composites. In the sample preparation, composites with different RH loadings varied from 10 to 40 phr were prepared using two-roll mill at temperature 165°C before being hot pressed at temperature 185°C. Tensile, flexural and izod impact tests were conducted. Incorporation of RH fillers from 10 to 40 phr resulted in the increase of flexural modulus indicating an improvement in stiffness. The effects of acrylic impact modifier and LICA 12 coupling agent on the mechanical properties of PVC-U composite were investigated. The acrylic impact modifier was found to be effective in enhancing the impact strength at all levels of RH content. Effectiveness of the impact modifier in enhancing the impact strength decreases with increasing RH content. LICA 12 was found to be the most effective in increasing impact strength at 20phr PH loading. The processability of RH filled PVC-U composites was studied by using Brabender plastocorder. It was found that incorporation of RH resulted in decreasing the fusion time of the PVC compounds while the heat distortion temperature (HDT) increased at all RH loadings. The degradation temperature decreased with increased slightly with increasing RH content. The percentage of water absorption increased slightly with increasing RH content and treated samples exhibited lower percentage of water absorption compared to the untreated samples. The optimum composition which gave balance of properties based on stiffness and toughness of PVC-U composite were PVC-U at spher of acrylic impact modifier and 20 phr of RH treated with LICA 12.

Hassan et al (2002) studied the ion selective PVC membrane electrode for the determination of methycyclone hydrochloride in pharmaceutical formulation. They used methycyclone-tetraphenylborate as the electroactive substance and diocylphthalate as the plasticizing agent. They found that the potential responses of the electrode were influenced by pH of the tested solution when pH>3. Under the condition of pH 2.6, the linear response range, slope and detection limit obtained were 3.0x10^-7~6.0x10^-3 M, 52.9mv per decade and 3.4x10^-3 M respectively.

Mamza and Nwofo (2008) studied the swelling behaviour of polysyrene (PS)/polyvinyl acetate (PVA) blends in different solvents and the effects of α-cellulose used as filler on the electrical conductivity. They found out that the variation of the type of solvent was responsible for the differences in the swelling kinetics of the blends. Their result showed that the nature of solvent control affects the degree of swelling.

Research Methodology
Materials Used

The reagents used were Chloroform, ethanol, petroleum ether, concentrated sulphuric acid, acetic acid, acetic anhydride, glycerol and ethylene glycol were obtained from the British Drug House. The equipment used include: Brookfield’s Viscometer (Brookfield Engineering Lab, Inc. Middleboro, MA, USA), pH Meter (CRISON micropH 2000, Spain), FTIR-8400S Fourier Transform Infrared Spectrophotometer and GCMS-QP2010 plus Shimadzu Japan.

Different proportions of the gum arabic and PVC by weight were weighed to give different proportion 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 two solvents: tetrahydrofuran, (THF).

Film Casting

Each formulation was in 30cm³ 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 into 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 desiccator for 48 hours before taken for mechanical property testing.

Mechanical Property Testing

Hosfield Tensometer Testing Machine will be employed 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 can be calculated.

Stress at break will be evaluated using the following equation;

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

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

$$\Delta L_0 = \frac{(L' - L_0)}{L_0} \times 100$$

Where, L' is the length of the sample at break and L₀ is the initial length. The modulus of elasticity will be 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).

Percent Water Absorption

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

Percentage water absorption = \[
\left(\frac{\text{wt. weight} - \text{dry weight}}{\text{dry weight}}\right) \times 100
\]

Result and discussion

Water absorption

The water absorption test shows that ACT modified gum absorbs water the most. The next 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 concentrations, PGM Also 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 4.14: Graph of 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 for the three modified gums show different results from that of the pure gum Arabic. This is revealed in fig 4.15. 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 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 great 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 the 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.

Graph showing tensile strength of test samples at various compositions

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-alignment of molecules.

The result observed for the acetate derivative (AAN) of the gum Arabic also showed debranching of the chains. The effect is however also pronounced than the acetolysed samples, probably because of the acetate group. The re-alignment 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.

Graph showing modulus of elasticity of the test samples at varying weight percent of filler

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 4.16 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 180.15 at 10/90 gum/PVC and it becomes fairly constant at 30/70 and 40/60 gum/PVC composition.

ACT is the next with 177 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.

Percentage Elongation of the Samples

Fig. below shows comparism 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 comparism, the percent elongation of test sample depends on the composition, though chemically modified formulations show similarity in trend.

Conclusion

Water absorption results of the samples shows that the physically modified gum has greater water absorption capacity than the chemical modifications. 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 strength for 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 better structure changes due to reinforcement in the PVC matrix, and the AAN sample at 30%/70% Gum/PVC composition, was found to be the strongest with overall best adhesiveness property.

References


