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# Effect of epoxidised soybean oil loading as plasticiser on physical, mechanical and thermal properties of polyvinylchloride

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**Abstract**. The aim of this paper is to study the effect of epoxidised soybean oil (ESO) as an alternative plasticizer on physical, mechanical and thermal properties of plasticised polyvinyl chloride (PPVC). Samples were prepared using 10, 20, 30 and 40% by weight percent of ESO. The samples were characterized for density, water absorption, tensile, hardness and thermal properties. The addition of ESO as plasticizer in PVC had caused significant effect on the physical and mechanical properties of PPVC. Increasing of ESO loading had resulted in decreased density, tensile strength, tensile modulus but increased in elongation at break and shore hardness. From water absorption study, it was observed that the all the samples reached the plateau absorption at days 8 to 10 with absorption percentages of between 1.8 to 2%. In general the crystallinity of PPVC maintained between 10 to 13% with increase in ESO loading while the melting point ( $T_m$) is slightly decreased about 3 to 6°C. In this study, ESO which acts as plasticiser were found to result in lower glass transition temperature ($T_g$). The enhancements of super cooling with higher ESO loading were found to increase the crystallization temperature, promoting crystallisation and act as nucleating agent.

## 1. Introduction

Polyvinyl chloride, (IUPAC Poly(chloroethanediyl)) commonly known as PVC had been played an important roles in thermoplastic industries over the many years. However, due to its inherent limitations such as low thermal stability, high melt viscosity and brittleness, it cannot be processed on its own but blended with other additives to achieve desired material quality and application. PVC uses the highest proportion of additives compared to other plastics where it may comprise up to 60% of a PVC products weight [1, 2]. PVC which is compounded without plasticizer is known as unplasticised polyvinyl chloride (UPVC) which is naturally strong and rigid while PVC which is compounded with plasticizer is known as plasticized polyvinyl chloride (PPVC) which flexible and soft.

Currently, the most widely used plasticizer are phthalates due to its high plasticising efficiency, wide availability and low cost [3]. However, the toxicity issue of the phthalates plasticisers had mimic human hormones and also affect various life forms including animals. Medical devices, children toys and items, bottles etc employed plasticisers to increase flexibility of PVC inherent brittleness. Use of phtalates, phosphates sebacates had been established in PPVC compound but they face ban by various countries due to its toxicity. In 2005, the European Commission banned Bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and butyl benzyl phthalate (BBP) Di-isononyl phthalate (DINP),

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diisodecyl phthalate (DIDP), and di-n-octyl phthalate (DNOP) from use in toys and childcare articles [3]. PPVC are also manufactured for medical devices,vinyl flooring and food packaging, which involve sizeable market applications.

Hence, it is necessary to find a new solution for immediate and future requirements. Conventional plasticizers are a rich family opening the door to many innovative opportunities for safe and sustainable plasticisers such as such as adipates, citrates, epoxies, terephthalates, trimellitates, diisononylcyclohexane-1,2-dicarboxylate (DINCH) and phosphate esters polymerics.

There are various possible alternatives for phthalates in plasticized PVC. Citrate-based plasticizers, like ATBC, and have been available for years as plasticizers in medical devices. DINCH is an alternative for applications such as medical devices. Another chemical, trioctyltrimellitate (TOTM) performs as a plasticizer in PVC and it has potential to be use commercially. Promising non-phthalate substitutes for DEHP in vinyl flooring material include DGD (dipropylene glycol dibenzoate) and DEHA (di(2-ethylhexyl) adipate). Other possible phthalate substitutes include: phosphate esters (e.g., tris(2ethylhexyl)phosphate); sebacate and azelate esters (e.g., diisodecylsebacate (DIDS), di-butyl sebacate, and di(2-ethylhexyl) azelate (DOZ)); isosorbide esters (made from renewable resources), and other organic esters such as isobutyratetrimethylpentanediol and diethyl succinate [4].

Polymeric esters or sustainable additives such as isosorbide esters, soya derivatives or hydrogenated phthalate of low molecular weight polymers and reactive plasticizers had been used. Isosorbide diesters, obtained from vegetable oils which are renewable resources, have excellent plasticizing properties for PVC and represent a non-toxic alternative to the phthalates [4]. Table 1 shows the list of vegetables oil and their chemical composition for example palm oil, soybean oil and other ester based oils.

**Table 1**. The major composition of fatty acids from some of the plant sources [5-12].

| Fatty acid | Palmitic (C16/0) | Palmitoleic (C16/1) | Stearic (C18/0) | Oleic (C18/1) | Linoleic (18/2) | Linolenic (18/3) | Iodine value |
|---|---|---|---|---|---|---|---|
| Palm oil | 40.13 | - | 3.1 | 43.4 | 13.2 | - | 50.4-53.7 |
| Canola oil | 4.1 | 0.3 | 1.8 | 60.9 | 21.0 | 8.8 | 110-126 |
| Jatropha oil | 14.2 | 1.4 | 6.9 | 43.1 | 34.4 | - | 10.362 |
| Soybean oil | 11.0 | 0.1 | 4.0 | 23.4 | 53.2 | 7.8 | 125-140 |
| Linseed oil | 5.5 | - | 3.5 | 19.1 | 15.3 | 56.6 | 175-204 |
| Sunflower oil | 4.8 | 0.8 | 5.7 | 20.6 | 66.2 | 0.8 | 123 |
| Flax seed oil | 5.0 | - | 4.0 | 19.0 | 14.0 | 58.0 | 153-189 |

Polymeric plasticizers derived from polymeric multifunctional alcohols give long chain molecules whose properties can be determined by the choice of the used alcohols. Molecular weights can be, for example, in ranges from 800 up to more than 8000 versus 390 for the dioctyl phthalate

(DOP). The precise solution that leads to balance between processing properties, functional characteristics, durability, cost and impact to environment is important. ESO is chosen as it has functional group epoxidised ring triglyceride chain, modified through epoxidation of soybean oil. Studies using ESO for various application in polymers include use of ESO in rubbers in coatings and as plasticisers etc [10, 13].

Hence, in this paper, the studies on physical, mechanical and thermal properties were performed to determine the final properties of PVC, which is applicable as plasticised PVC. Its aim is to replace phthalates and other toxic long ester aromatic chain groups which has high toxicity to human and animals [4]. Using sustainable epoxidised oils for PPVC, it can impart more environmentally safe and sustainable products.

## 2. Experimental

### *2.1 Materials*

The polyvinyl chloride (PVC), (grade HP65, a product of Malaysian Electrochemicals Industry) Malaysia is used. Epoxidized soybean oil (ESO) EO-132, stearic acid as lubricant, tin as stabilizer and china clay as filler was supplied by Na Ya Plastics Corporation, China. The ESO has chemical composition of acid value below 0.7, Oxirane content 6.4 to 6.8% and iodine value of 5.0 or below. Compound formulation with different loadings is as tabulated in Table 2.

**Table 2.** Compound formulation used with different loadings of ESO (parts by weight).

| PVC (%) | ESO (%) | Stearic acid (%) | Tin stabilizer (%) | China clay (%) |
|---|---|---|---|---|
| 100 | 0 | 1 | 7 | 20 |
| 100 | 10 | 1 | 7 | 20 |
| 100 | 20 | 1 | 7 | 20 |
| 100 | 30 | 1 | 7 | 20 |
| 100 | 40 | 1 | 7 | 20 |

### *2.2 Fabrication of Plasticised PVC*

Twin-screw machine model TSE 16TC with machine number 2093-8/R was used for mixing the compound formulation. Counter rotating screw used to suit with heat sensitive of PVC because they allow greater temperature control. A neat PVC compound (0% ESO plasticiser loading) was also made as control sample. The extruded compound was palletized using PRISM cutter machine. All compounded PPVC were microinjection moulding machine (HAAKE MiniJet) for moulding process. The pressure (bar) of the microinjection was maintained at 800 bar. For microinjection process, cylindrical temperature were set to temperature ranges between 195°C and 190°C and mould temperature set at 110°C and 100°C respectively.

*2.3 Physical Characterization*

The densities of neat PVC and plasticized PVC were determined using electronic densitometer according to ASTM D1895. Water absorption test were carried out according to ASTM D570. All the specimens were immersed in distilled water at room temperature and were weighed until constant weight was obtained. Water absorption percentage were calculated using equation 1 [14, 15].

Water absorption, WA (%) = $(W_2 - W_1)/ W_2 \times 100$ (1)

Where $W_2$ represents the weight of the composite after immersion and $W_1$ is the weight of the composite before immersion. Five replicates were tested for each formulation and test.

*2.4 Mechanical Characterization*

Tensile test were performed using Universal Tensile machine (Testometric MICR0500) according to ASTM D638. Ten replicates were tested for each formulation. Test was conducted with crosshead speed 2mm/min. Hardness test were performed using shore A hardness tester (HW Wallace) with serial number C30022/19 in accordance with ASTM D2287. Ten replicates were test tested for each formulation.

*2.5 Thermal Characterization*

The glass transition temperatures (Tg), melting point (Tm), ESO vaporisation temperature, percentage of crystallinity, crystallization temperature (Tc) and supercooling temperature were measured using Perkin Elmer Thermal Analysis Controller (TAC7/DX) DSC-model. The procedure involved rapidly heating the sample from 30 to 220°C at heating rate of 20ºC/min and the flow rate of the nitrogen purge was 40 mL/min then holding under isothermal condition for 1 min at 220°C. The system was then cooled from 220 to 30°C at a heating rate of 20°C/min using liquid nitrogen as a cooling medium.

## 3. Results and Discussion

*3.1 Effect of ESO Loading on Density Properties of PVC*

The density of the ESO plasticised PVC with varying ESO loading is given in Table 3. The density of the plasticised PVC decreased with increasing of ESO loading from 1.45 to 1.34g/cm$^3$. This perhaps because of the formation of links with polymer molecules and ESO act as spacer between molecules of the polymer. Free volume are increase with the addition of ESO to the PVC, increasing of free volume had reduced the density of the PVC compound as ESO loading are increased [16]. Thus, ESO chain can move freely between the interspacing of PVC compounds.

**Table 3.** Variation of density of plasticised PVC with ESO loading.

| Sample | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Density (g/cm3) | 1.453 | 1.414 | 1.406 | 1.367 | 1.336 |

*3.2 Effect of ESO Loading on Water Absorption Properties of PVC*

Figure 1 shows the effect of ESO on water absorption of PVC. It can be noted that, the water uptake or absorption of the plasticised PVC increases with the increasing of ESO loading. Initially highest rate of water absorption within 4 days are exhibited by 10% ESO and the lowest rate of water absorption were found for 40% ESO. Upon water absorption after 10 days immersion in water, all reached its maximum water absorption value which range from 1.5 to 2.5%.

PVC itself absorbs water and achieves about 1.8% absorption. Polarity of the PVC and water cause hydrogen bonding linkages to exist form and PVC experienced some water absorption ability. The increases of water absorption for the plasticised PVC could be attributed to ESO that form links with polymer molecules and act as spacer between molecules of the polymer. The bond forces of the polymer weaken due to other linkage of ether to water molecules being established. Thus free volume increases with the addition of ESO to the polymer, increasing of free volume hence increase the ability of compound to absorb water, thus lead to decreasing of water absorption. The water absorption of PVC and plasticised PVC reached a plateau of water absorption at days 8 to 10.

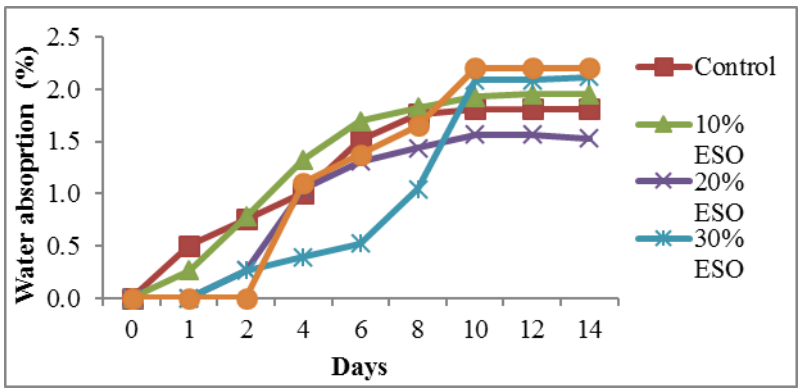



**Figure 1.** Effect of ESO on water absorption of PVC.

Higher water absorption compared to PVC control were exhibited for sample with 40, 30 and 10%. These ESO with 40% and 30% has slow rate of water absorption initially but upon saturation with water, the higher ESO tend to increase the water absorption after prolong time as ESO may have reduced the interaction and bonding of ESO and PVC itself. The weakening bonding of more hydrophobic ESO with the PVC exceed the interaction of hydrogen bonding capability of water molecules and PVC. Bonding of plasticised PVC with higher amount of ESO surpassed the interaction

with PVC water system; hence, a threshold amount of oil content could have acting as spacer between the PVC chains.

*3.3 Effect of ESO Loading on Tensile Properties of Plasticised PVC*

Figure 2 demonstrates the effect of ESO on the tensile properties of PVC. The total ESO loading of PVC is varied from 10 to 40%. The tensile strength and modulus of the plasticised PVC exhibited similar decreasing trends with increasing ESO loading from 0 to 40%. The tensile strength and tensile modulus of the plasticised PVC ranged from 48 to 17.42 MPa and 2603 to 153MPa, while the addition of ESO caused an increase in elongation from 3 to 63%.

A considerable decrease of tensile strength indicates that the ESO has interdiffuse into the chain system, reduce the interaction and bonding between PVC chain. This was due to action of the plasticizer itself on the molecules of the polymers, which is believed to act as spacer between molecules of the polymers by forming links with polymer molecules. It was mentioned that dipole interaction occurs between polar groups in the polymer and the polar groups in the plasticizer. In such case, the chlorine atom in the PVC resin plays the role of the polar group, while ester group in the epoxidised oil stands for polar group in the plasticizer. More random and long chain ESO oil affects the interaction and bonding. Hence, the bonding forces between polymers weaken due to less interaction within themselves.

The formation of these links weaken the bond forces of the polymer atoms and in addition, incorporating plasticizer to the polymer increases the free volume, which leads to lowering of tensile strength [16, 17].

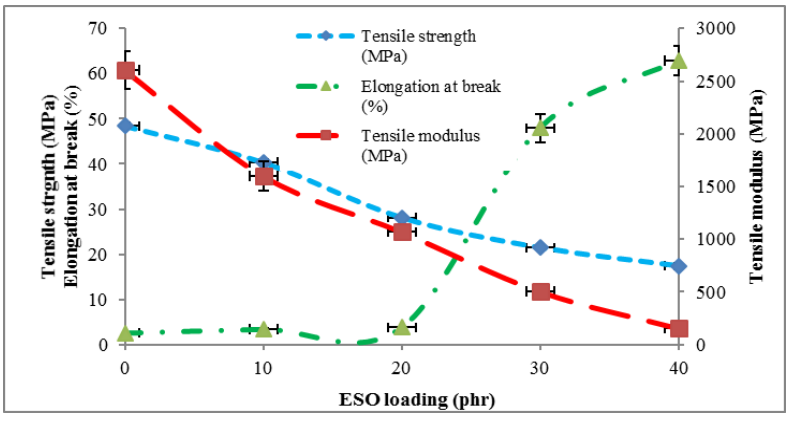



**Figure 2.** Effect of ESO loading on tensile properties of PVC.

Increasing the ESO loading resulted in decrease of tensile modulus. Unplasticised PVC is rather brittle. Thus by the increasing the weight percentage of ESO has improved flexibility of PVC

significantly. It is noticed that the modulus of elasticity decreases with increasing plasticizer. In this work, with variation of ESO from 10 to 40%, the corresponding elasticity varies significantly from 153 to 1599MPa, while for 20 to 30% ESO, the modulus ranges between 502 to 1069MPa. This value showed better modulus as compared to work by Elgozali and Hassan [18], which used di-octyl phthalate (DOP) as plasticiser, where the researcher found that, 21 to 32wt.% of addition of di-octyl phthalate (DOP) as plasticiser has corresponding modulus of elasticity ranged between 8 to 15MPa. On a molecular level, plasticization is the weakening or selective breaking of bonds between molecules, while leaving others intact, to increase intermolecular space, known as free volume. Thus increased space allows for changes in shape, flexing or molding of the final material. The PVC polymer is amorphous rigid material and may be thought of as comprising small areas of order and crystallites among amorphous areas of molecules [19,20]. According to Saeki K *et al.*, (2003), analysis under infrared spectroscopy showed that, the incorporation of plasticizer is into the PVCresin had solvated the amorphous chain segments, but not the crystalline ones and type of plasticiser content in PVC can be identified [21].

Meanwhile, elongation showed increasing trend upon increasing ESO loading. This is also a normal consequence of the increase of ESO loading wt.% which is having a high strain compared to PVC compound without ESO. This is due to presence of ESO acting on PVC as spacer and increase the free volume, which make PVC become softer and weaker and allows it to be elongated longer at low loads [16, 22].

### *3.4 Effect of ESO Loading on Hardness Properties of Plasticised PVC*

Figure 3 demonstrates the effect of ESO loading on the shore hardness of PVC. The hardness showed decreasing trend with increasing of ESO loading with the shore hardness ranged between 99 to 93. ESO is a flexible chain unit which act as spacer between molecules of the polymer and assimilate between the rigid PVC particles.

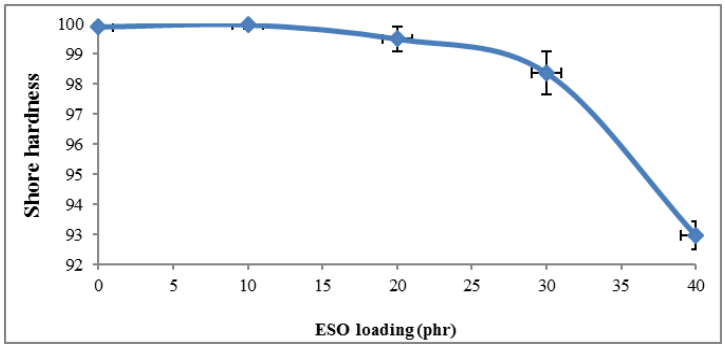



**Figure 3.** Effect of ESO loading on hardness properties of PVC.

The bonds forces of the polymer weaken due to the link establish and flexibility imparted by ESO thus reduced the brittleness and hardness of the compound. According to the Free Volume Theory, plasticiser molecules will separate the polymer chains and increase the free volume in the polymer matrix [23].

*3.5 Effect of ESO Loading on Thermal Properties of Plasticised PVC*

The DSC analysis of plasticised PVC with different percentage of ESO loading is showed in Table 4. ESO act as plasticiser had decreased the glass transition temperature and the melting temperature, however it had increased the crystallization temperature. For pure PVC, Tg was 81°C, which is in the temperature range found in literature [24, 25]. The presence of ESO as plasticisers decreased the Tg value of PVC from 81 to 65°C respectively.

**Table 4.** Effect of ESO loading on DSC analysis of PVC.

| ESO (%) | Glass transition temperature, Tg (°C) | ESO Vaporisation (°C) | Melting temperature, Tm (°C) | Crystallization temperature, Tc (°C) | Percentage of crystallinity (%) | Supercooling Tm – Tc (°C) |
|---|---|---|---|---|---|---|
| 0 | 81 | - | 163 | 60.93 | 10 | 129 |
| 10 | 76 | 122 | 166 | 64.60 | 12 | 122 |
| 20 | 71 | 123 | 165 | 64.93 | 13 | 121 |
| 30 | 71 | 123 | 161 | 65.27 | 10 | 115 |
| 40 | 65 | 124 | 160 | 65.60 | 10 | 114 |

Melting temperature varies to only few degrees, between 3 to 6°C. The melt temperature is the point upon which all crystallite melt. The crystallinity is low for PVC which is only 10% and it varies with amount of plasticiser ESO added from 10 to 13%. Higher amount of ESO had maintained the crystallinity value to 10%. The difference in crystallization temperature between melting temperature can determine how the PVC reacts to cooling phenomenon and this behaviour can determine the supercooling effect brought about by plasticiser.

As proven by many researchers, the function of plasticiser is to make the polymer more pliable and soft and thereby enhancing the flexibility and plasticity to the materials by enhancing the mobility of the polymeric chain and it intensely related to its chemical structure and rate of interaction with the polymeric material present in the formulation [26]. In the PVC formulation, ESO which acts as plasticiser caused Tg to decrease, this is because ESO has high number of non-polar groups caused by reduction in polar forces between polymer chains, thus lowering Tg, and improving low temperature of flexibility.

The crystallization temperature (Tc) increased as ESO loading increased. In the plasticized PVC, the plasticiser molecules were found in the amorphous area. Formation of crystalline structures

were found to be faster with high plasticiser content as crystal growth are enhanced , however crystallinity or amount of enthalpy is lower as orientation of the aligned PVC chain is impeded.

Cooling causes the transition of polymers from flow-viscosity or high-elasticity states into glassy states. The transition temperature of an elastic polymer to a glassy state is a parameter of its freezing resistance which meant lower temperature limit of retention of elastic proper [27]. Super cooling exists due to presence of foreign material namely nucleating agents or small crystalline particle dispersed in the crystallizing melt and remain solid at crystallization temperature which can grow and form large number of small crystals formed around matrix. In this work, increase of ESO loading will promote supercooling as lower difference of (Tm – Tc) exhibited, hence the ESO can be the site for nucleation centre. Finally, the presence of ESO can increase supercooling and the rate of crystallization.

## 4. Conclusions

For plasticised PPVC compounded, the density of plasticised PVC decreased from 1.45 to 1.34 g/cm$^3$ as compared to neat PVC. Constant water absorption was reached at days 8 to 10 and maximum water absorption value obtained were in ranges from 1.5 to 2.5%. As the ESO loading increased, the tensile strength and tensile modulus decreased, while elongation at break increased. The tensile strength and tensile modulus of the plasticised PVC ranged from 48 to 17MPa and 2603 to 153 MPa, while the elongation at break increased from 3 to 63%. High elongation of PPVC with increase in ESO caused an increase in flexibility, presence of ESO act as spacer which increase the free volume allowing PVC chain to be elongated longer and cause softer and weakening of strength. Shore hardness decreases with increasing ESO loading and lowest reduction of hardness is about 7 for 40% ESO loading. The plasticised PVC decreased the glass transition temperature and the melting temperature, however it had increased the crystallization temperature. Faster formation of crystalline structures with higher plasticizers due to enhancement of crystalline growth and orientation of the aligned PVC chain. Supercooling or difference between melting and crystallization temperature were reduced and this assist in faster crystallization that can be advantages as ESO can function as nucleating agent.

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