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The Effectiveness of Plasticizers in the Alteration of PVC

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Abstract:

This study looks into how well plasticizers work to modify polyvinyl chloride (PVC), specifically focusing on the effects they have on the material's mechanical properties, thermal stability, and durability. Finding non-toxic and biodegradable substitutes for phthalate plasticizers like DEHP is crucial because flexible PVC goods make up over 90% of plasticizer sales. This is as a result of the environmental and health concerns that have been voiced. This work examines the efficaciousness of several plasticizers in enhancing the properties of polyvinyl chloride (PVC), including bio-based substitutes such succinate esters and epoxidized soybean oil. It has been discovered that certain bio-based plasticizers function as well as or better than conventional phthalates. For the PVC sector, these plasticizers provide safer and more environmentally friendly substitutes.

Keywords*: PVC, polyvinyl chloride, flexible PVC, phthalate plasticizers, biodegradable substitutes*

Introduction

The polymer industry relies heavily on plasticizers as a vital ingredient since they considerably improve the workability and flexibility of polyvinyl chloride (PVC). Over ninety percent of the plasticizer that is used is flexible polyvinyl chloride (PVC), which is used in a wide variety of products such as cables, flooring, toys, medical equipment, and food packaging (Li, et. al, 2019). However, typical phthalate plasticizers such as DEHP pose dangers to both human health and the environment, which has led to legislative restrictions and a shift towards alternatives that are non-toxic and biodegradable. In order to ensure increased performance while complying to safety and environmental regulations, the purpose of this research is to investigate the efficacy of various plasticizers, including bio-based possibilities, in modifying the properties of PVC (Langer, et al., 2020).

Plasticizers, a broad category of compounds, are widely used as additives in the polymer industry to increase polymerization and polymer characteristics. There are several different types of polymers that require plasticizers; nevertheless, the flexible poly (vinyl chloride) (PVC) business is by far the most significant, accounting for more than 90% of plasticizer sales in volume (Li, et. al, 2019). Flexible PVC is widely used in a variety of products, including cables, floors, toys, medical equipment, and food packaging. A wide range of PVC applications may now make use of one of the approximately 500 commercial plasticizers on the market. Di(2-ethylhexyl) phthalate (DEHP) is one of several types of plasticizers. Unfortunately, phthalates are chemicals that easily leak out of polymers, have a severe impact on human health, and are environmentally harmful. Scientific research suggest that phthalate plasticizers may raise the risk of asthma, bronchitis, and cancer. As a result, the EU REACH Act prohibits the use of phthalic plasticizers in PVC items such as children's toys, food containers, and medical equipment, limiting the expansion of the plasticizer sector (Nosal, et. al, 2021). The use of biodegradable and non-toxic alternatives to phthalates is becoming commonplace and unavoidable.

Research Aim

The aim of the research is to analyse the effectiveness of plasticizers in the alteration of PVC.

Research Objectives

The objectives of the research include the following as:

1. To evaluate the impact of different plasticizers on the PVC.
2. To access the stability and durability of plasticized PVC.

Research Questions

The research will address the following questions as:

1. What is the impact of different plasticizers on the PVC?
2. What is the stability and durability of plasticized PVC?

Literature Review

An eco-friendly polymer additive known as a bio plasticizer has just appeared, propelling the plasticizers business. This is a direct result of the growing demand for environmentally sensitive products and the need to ensure the safety of both people and the earth. The worldwide bio plasticizer market is forecast to develop significantly, with a worth of $1 364 million in 2021 and a projected $1 709 million by 2027. Beginning in 2021 and continuing through 2027, the CARG is expected to reach 3.3% every year (Elsiwi, et. al, 2020). In recent years, the market has seen an influx of novel plasticizers derived from sustainable ingredients. Epoxidized soybean oil, or ESBO, is a bioplasticizer that is widely used in industry. All of the basic elements required for its creation are inexpensive, readily available, and biodegradable in nature. Esters, such as citric, succinic, lactic, fatty, glycerol, and isosorbide acids, are another major family of bioplasticizers.

Succinate esters might be a more ecologically friendly alternative to phthalate plasticizers in PVC. They are more resistant to plasticizer migration from the polymer matrix and safer than phthalate plasticizers. Kumar, (2019) synthesised di-n-heptyl succinate from renewable feedstock's, resulting in a biodegradable, efficient, and environmentally friendly PVC plasticizer. Stuart et al. obtained even more encouraging outcomes. Researchers designed an experiment to see how well several bio-based succinate esters—such as diethyl (DES), dibutyl (DBS), dihexyl (DHS), diethylhexyl (DEHS), didecyl (DDS), and didodecylsuccinate (DDoDS)—work as PVC plasticizers (Kumar, 2019). There was a saturation point for the succinate plasticizer's efficacy, which was shown to increase with alkoxy chain length. Furthermore, when compared to DEHP, this plasticizer was just as effective, if not more so, in plasticizing PVC. In addition, succinates with shorter alkoxy chains, such as DES and DBS, can behave as potent plasticizers when used in higher quantities. Researchers also investigated the influence of succinate molecule alkyl chain length on plasticizer and biodegradation properties. In this work, we altered the side chain length from n-ethyl to n-octyl (Zhang, et. al, 2019). The study discovered that DHS is the best PVC plasticizer because it contains the proper ratio of long molecules that facilitate plasticization and short molecules that facilitate biodegradation.

However, using 2-ethylhexyl diesters of fumaric acid (trans isomer), succinic acid (saturated counterpart), and maleic acid (cis isomer), researchers discovered DEHP replacement molecules (Ito, et. al, 2019). This study investigated the influence of molecular geometry on the plasticizing and degrading properties of PVC. Initially, it was considered that esters of maleic acid or succinic acid may be employed as PVC plasticizers since they were equally effective as DEHP. Nonetheless, further work has revealed that linear alcohol succinate esters are the most environmentally friendly plasticizers.

Most PVC compounds employ plasticizer combinations to increase physical characteristics and cost-effectiveness, hence succinic acid derivatives were used in plasticizer mixtures rather than as plasticizers on their own. Researchers studied the efficacy of succinate and maleate diester plasticizers in combination with PVC (Ito, et. al, 2019). Plasticizers having four to eight carbon atoms in their linear side chains, such as succinate and maleate diesters, have shown plasticizing performance in PVC comparable to commercially available DEHP and DINCH. In several testing, diester plasticizers were shown to improve the mechanical characteristics of PVC. Researchers investigated employing DEHS and ESBO together as a bio-based PVC plasticizer (Elsiwi, et. al, 2020). Combining these two plasticizers minimised the unfavourable effects of succinate alone, including increased migration, as demonstrated in the study. Furthermore, it outperformed ESBO in terms of plasticization efficiency. Stuart and colleagues investigated succinate diester blends as possible PVC plasticizers. The following were combined: DES, DHS, DEHS, DDoDS, and DDS. Instead of employing separate succinate plasticizers, it was discovered that mixing larger succinate diesters with smaller diesters increased PVC flexibility (Kumar, 2019).

Methodology

The research has used the data collection from the secondary sources which includes the data taken from the already published research papers, journals, and articles. The data is collected with the most reliable and relevant sources about the PVC effects and of the plasticisers effectiveness in the PVC. The data collected is analysed with the qualitative means, to deliver the research outcomes and attain the valuable insights from the research paper. The research has used a total of 10 secondary sources from which data is sourced to deliver the core analysis and findings of the study and attain the valuable study outcomes.

The entire paper is done within the ethical purview, indicating that the research is within the ethical code of conduct, and there is no data biasness in the data collection or analysis to deliver the authentic, reliable, and viable research outcomes.

Analysis and Findings

The first indication that propylene glycol was esterified with oleic acid was shown in Figure 1, where the C=O stretching vibration peak changed from 1709 cm^{-1} in oleic acid to 1739 cm^{-1} in the final product of the process. The C=O stretching vibration in esters is demonstrated by the high absorbance peak at 1739 cm^{-1}. The first step of synthesis revealed the formation of an ester bond due to the presence of an absorbance band at 1176 cm^{-1}, which corresponds to the stretching of a C-O bond in the ester group. The FT-IR spectra of the product from the initial phase of synthesis revealed an absorbance band at 3405 cm^{-1}. This band matches the OH group's stretching vibration. Because propylene glycol monooleate is the primary product of the synthesis, this outcome was expected. Although this band was observed in the FT-IR spectra of propylene glycol, its amplitude was significantly lower than the absorbance band associated with the stretching vibration of the OH group at 3324 cm^{-1}. In FT-IR spectra, oleic acid and the first step product showed absorption bands at 3005 cm^{-1} and 3004 cm^{-1}, respectively (Figure 1) (Ledniowska, et. al, 2022).

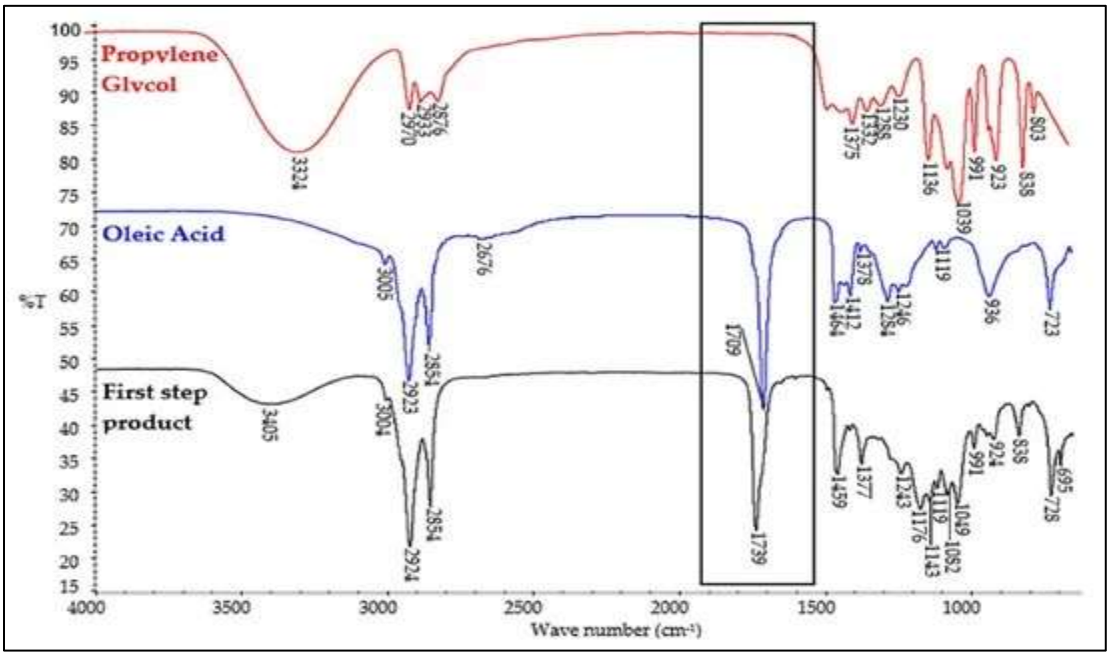

Figure 1: FT-IR spectra of raw materials (propylene glycol and oleic acid)

Source: Ledniowska, et. al, (2022)

Unsaturated -HC=CH-bonds have vibrations that correspond to these bands, which are caused by stretching and bending C-H bonds. Because monounsaturated fatty acids were used in the manufacturing process, the outcome was predictable. Afterward, the chemical composition of the obtained goods was examined. After the first step of synthesis was completed, the esterification products' chemical compositions were determined, as shown in Figure 2. Figure 2 shows the components arranged in descending order of retention duration. When the study was first planned, it was assumed that the esterification products would contain varying amounts of propylene glycol diesters in addition to the expected monoesters. The original reaction mixture consisted of 58.4% propylene glycol monooleate, 25.0% propylene glycol dioleate, and 10.4% unreacted propylene glycol by weight (Ito, et. al, 2020). Additionally, a small amount of dipropylene glycol (0.4 weight percent) was produced during the procedure. Propylene glycol monoesters are most likely classified as volatile medium-molecular-weight components. Except for oleic acid, the volatile high-molecular-weight components are most likely diesters of fatty acids. Their existence is due to the use of oleic acid technology at a concentration of 90.0%.

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Composition (wt.%)	First Step Product
Propylene glycol	10.4
Dipropylene glycol	0.4
Volatile low-molecular-weight components	0.5
Oleic Acid	0.7
Propylene glycol monooleate	58.4
Volatile medium-molecular-weight components	2.4
Propylene glycol dioleate	25.0
Volatile high-molecular-weight components	2.2

Figure 2: Compositions after the plasticizer synthesis by GC/MS and GC/FID

Source: Ledniowska, et. al, (2022)

The given graph in Figure 3 represents the variation of logarithmic decrement (Δ) and the glass transition temperature (T_g) of PVC plasticized with different concentrations of EHP. According to the weight ratios of EHP to PVC which are prepared in a 40/60 to 100/0 ratio, the plasticizer affects the thermal properties of PVC. It is observed that with the increase in the ratio of EHP there is a continuous shift of the T_g value to a lower temperature which implies the improvement in flexibility of the polymer (Halloran, et. al, 2021).

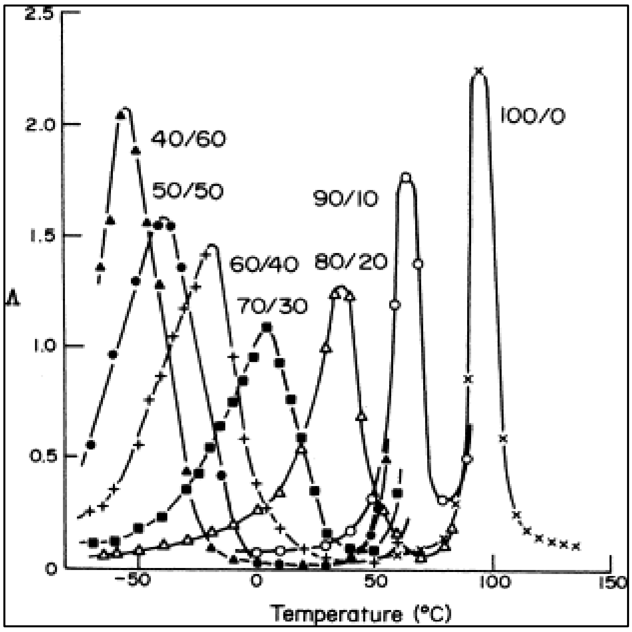

Figure 3: Logarithmic decrement of poly (vinyl chloride) plasticised with various amounts of ethyl hexyl phthalate

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Source: Nosal, et. al, (2021)

At a 100/0 ratio (pure EHP), there is only one TGA peak at a temperature of approximately 100oC, which refers to the intrinsic glass transition temperature of EHP. As the EHP 'content' decreases from 90/10 to 40/60, the T_g of the plasticized PVC also moves gradually downward from 100°C to below room temperature for the 40/60 mixture. This trend also shows how EHP weakens the intermolecular forces in the PVC matrix which leads to higher mobility of the polymer chains and lower T_g (Liu, et. al, 2020). The height and shape of the peaks also differ, which imply that there are changes in the viscoelastic properties of the mixtures, and the broadening of peak implies that the transition is more gradual in less plasticized samples.

This graph exemplifies the fundamental principle behind plasticization: plasticizers like EHP help in the lowering of the T_g of PVC making it more flexible and easier to process at low temperatures (Figure 3). The extent of plasticization increases with the incorporation of EHP, as revealed from a reduction in T_g values. This information is rather important for the purpose of fine-tuning the mechanical and thermal characteristics of PVC to meet the needs of particular uses, giving the manufacturers a possibility to create materials with needed flexibility and practicability. The fact that T_g of PVC can be altered by adjusting the concentration of a plasticizer means that plasticizers are useful tools in polymer science as they can convert a rigid product such as a pipe into a flexible film (Li, et. al, 2019).

Figure 4 represents the variation of the hardness of PVC (Shore A) with different plasticizer levels (phr, parts per hundred resin); as depicted by curves 1, 2, 3 as well as 4 all the formulations have shown that the increasing concentration of a plasticizer has the effect of decreasing the particular hardness of the material (Elsiwi, et. al, 2020). For example, curve 1 that represents Shore A hardness, shows a dramatic reduction in values from a bit over 95 at phr 0 to about 55 at phr 100. This trend shows that, by increasing the concentration of plasticizers the hardness of PVC is reduced hence makes it rigid – suitable for use in applications which require softer material.

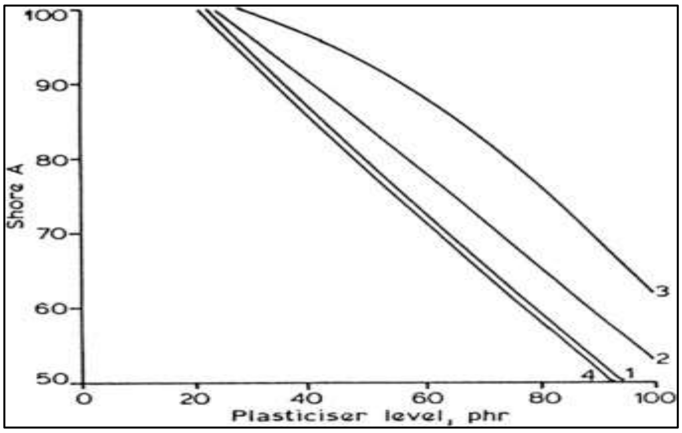

Figure 4: Effect of plasticizer level on Shore A hardness 1. Dioctyl phthalate; 2. Di-iso-decyl phthalate; 3. Di-isotridecyl phthalate; 4. Dioctyl adipate

Source: Liu, et. al, (2020)

These behaviours all result from the reactions between the base resins of the different PVC formulations and possibly, other additives. However, all the curves of different recipes share the same general trend of declining, thus acting in support of the plasticizer role in changing the mechanical properties of PVC. Still, the decrease in the hardness value with the increment of marked time differs a little for the identified curves, which indicates that the specific type and proportion of plasticizers and other additives also affect the ultimate hardness reduction (Langer, et. al, 2020). For instance, curve 3 of the causal t-process deploys a less steep descent than curve 1, suggesting a formulation that could be less plasticized. These points, in addition to indicating the kind and concentration of the plasticizer to offer the desired PVC characteristics in a certain application, also depict how other characteristics like burning direction and lucidity play out.

Conclusion

The research conclusions indicate that plasticizers can successfully alter polyvinyl chloride's (PVC) characteristics, enhancing its flexibility, toughness, and thermal stability. Because classic phthalate plasticizers, such DEHP, are effective, laws have been put in place to restrict their use. However, these plasticizers also pose serious risks to the environment and human health. Bio-based plasticizers such as succinate esters and epoxidized soybean oil (ESBO) have become competitive substitutes, providing performance on par with or better than that of traditional plasticizers. Numerous studies have found that these bio-plasticizers reduce the harmful effects associated with phthalates while also improving the mechanical properties and biodegradability of polyvinyl chloride (PVC). Compared to other options, succinate esters in particular have a lower migration rate and a stronger plasticizing efficiency. The study emphasises how important it is to keep working towards the creation and application of environmentally friendly plasticizers in order to meet industrial standards and prioritise environmental and human health at the same time. The PVC industry's future depends critically on this shift to environmentally benign alternatives in order to guarantee customer safety and regulatory compliance.

References

Elsiwi, B.M., Garcia-Valdez, O., Erythropel, H.C., Leask, R.L., Nicell, J.A. and Maric, M., 2020. Fully renewable, effective, and highly biodegradable plasticizer: di-n-heptyl succinate. *ACS sustainable chemistry & engineering*, *8*(33), pp.12409-12418. https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.0c02859

Halloran, M.W., Nicell, J.A., Leask, R.L. and Marić, M., 2021. Small molecule plasticizers for improved migration resistance: Investigation of branching and leaching behaviour in PVC blends. *Materials Today Communications*, *29*, p.102874. https://www.sciencedirect.com/science/article/pii/S235249282100862X

Ito, Y., Kamijima, M. and Nakajima, T., 2019. Di (2-ethylhexyl) phthalate-induced toxicity and peroxisome proliferator-activated receptor alpha: a review. *Environmental health and preventive medicine*, *24*, pp.1-9. https://link.springer.com/article/10.1186/s12199-019-0802-z

Kumar, S., 2019. Recent developments of biobased plasticizers and their effect on mechanical and thermal properties of poly (vinyl chloride): a review. *Industrial & Engineering Chemistry Research*, *58*(27), pp.11659-11672. https://pubs.acs.org/doi/abs/10.1021/acs.iecr.9b02080

Langer, E., Bortel, K., Waskiewicz, S., Lenartowicz-Klik, M. and Lenartowicz-Klik, M., 2020. Research trends in plasticizer production. *Plast. Deriv. Post-Consumer PET*, pp.101-126.

Ledniowska, K., Nosal-Kovalenko, H., Janik, W., Krasuska, A., Stańczyk, D., Sabura, E., Bartoszewicz, M. and Rybak, A., 2022. Effective, environmentally friendly PVC plasticizers based on succinic acid. *Polymers*, *14*(7), p.1295. https://www.mdpi.com/2073-4360/14/7/1295

Li, Q., Ma, S., Xu, X. and Zhu, J., 2019. Bio-based unsaturated polyesters. In *Unsaturated polyester resins* (pp. 515-555). Elsevier. https://www.sciencedirect.com/science/article/pii/B978012816129600020X

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Liu, D., Jiang, P., Nie, Z., Wang, H., Dai, Z., Deng, J. and Cao, Z., 2020. Synthesis of an efficient bio-based plasticizer derived from waste cooking oil and its performance testing in PVC. *Polymer Testing*, *90*, p.106625. https://www.sciencedirect.com/science/article/pii/S0142941819324055

Nosal, H., Moser, K., Warzała, M., Holzer, A., Stańczyk, D. and Sabura, E., 2021. Selected fatty acids esters as potential PHB-V bioplasticizers: Effect on mechanical properties of the polymer. *Journal of Polymers and the Environment*, *29*, pp.38-53. https://link.springer.com/article/10.1007/s10924-020-01841-5

Zhang, H., Zhu, F., Fu, Q., Zhang, X. and Zhu, X., 2019. Mechanical properties of renewable plasticizer based on ricinoleic acid for PVC. *Polymer Testing*, *76*, pp.199-206. https://www.sciencedirect.com/science/article/pii/S0142941819300200