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The Impact of Plasticizer Levels in Hardening PVC Plastic

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Abstrak

Penelitian ini menginvestigasi efek kadar plastisizer Trioctyl trimellitate (TOTM) pada kekerasan material Polyvinyl Chloride (PVC). Penelitian ini dilakukan dengan memvariasikan jumlah plasticizer TOTM pada proses pembuatan sampel PVC dan kemudian mengukur kekerasannya menggunakan alat durometer dengan merujuk pada standar DIN EN ISO 868. Uji kekerasan tersebut dilakukan dengan beban 1 kg selama 15 detik dan kekerasan diukur dalam satuan kekerasan ShA (Shore A). Studi ini menyimpulkan korelasi terbalik antara jumlah plastisizer TOTM dan kekerasan PVC, dengan hasil peningkatan level TOTM mengarah pada penurunan nilai kekerasan. Hasil ini konsisten di semua sampel PVC, meskipun perbedaannya minor. Peran plastisizer dalam menentukan sifat fisik dan mekanik PVC dapat dieksplorasi lebih lanjut, dengan menekankan fungsinya dalam mengurangi kristalinitas PVC, sehingga menghasilkan material yang lebih fleksibel. Penelitian ini berkontribusi pada pemahaman tentang bagaimana plastisizer dapat digunakan untuk menyesuaikan sifat PVC, yang mengarah pada pengembangan dua jenis PVC yang berbeda: PVC fleksibel, yang mengandung plastisizer, dan PVC kaku, yang tidak mengandung plastisizer. Temuan ini menekankan pentingnya plastisizer dalam desain dan teknik material, untuk memodifikasi sifat mekanik dan fisis dari plastik PVC.

Kata kunci: Trioctyl Trimellitate (TOTM), Kekerasan Polyvinyl Chloride (PVC), Plasticizer

Abstract

This paper provides a detailed investigation into the effects of Trioctyl Trimellitate (TOTM) plasticizer levels on the hardness of Polyvinyl Chloride (PVC) materials. This study included varying the quantity of TOTM plasticizer during the manufacture of PVC samples and subsequently assessing their hardness with a durometer, following the DIN EN ISO 868 standard. The test was conducted under a load of 1 kg for a duration of 15 seconds, with hardness measured in ShA (Shore A) units. The study reveals an inverse correlation between the level of TOTM plasticizer and the hardness of PVC, with an increase in TOTM levels leading to a decrease in hardness. This trend is consistent across various PVC samples, despite minor variations. The role of plasticizers in determining the physical and mechanical properties of PVC is further explored, emphasizing their function in reducing PVC's crystallinity, thereby producing a clearer and more flexible material. This research contributes to the understanding of how plasticizers can be used to tailor the properties of PVC, leading to the development of two distinct types of PVC: Flexible PVC, which contains a plasticizer, and Rigid PVC, which does not. The findings underscore the importance of plasticizers in material design and engineering, offering valuable insights for future applications.

Keywords: Trioctyl Trimellitate (TOTM); Polyvinyl Chloride (PVC) Hardness; Plasticizer

1. Introduction

The field of polymer science has seen significant advancements in recent years, particularly in the study of polyvinyl chloride (PVC), a widely used synthetic polymer with applications in numerous industries [1], [2], [3]. Since its widespread use in the 1930s, Polyvinyl Chloride (PVC) has become a crucial material in various industries, from building materials to children's toys [4]. However, its hard and brittle nature requires additives, particularly plasticizers, to enhance its flexibility [5].

The hardness of PVC can be altered through the incorporation of additives such as plasticizers, co-polymers, or fillers like calcium carbonate

($CaCO_3$). Co-polymerization entails altering the polymer chain by including additional monomers that can lower the stiffness or hardness of PVC. Calcium carbonate ($CaCO_3$) is frequently utilised as a filler in PVC to enhance specific qualities and decrease costs. However, the addition of fillers enhances the rigidity of PVC, lowers flexibility, reduces impact strength, and presents processing difficulties that necessitate elevated temperatures and advanced techniques for adequate dispersion within the polymer matrix. in other hand, co-polymerization, although providing decreased hardness relative to plasticisers, frequently entails more intricate methods, elevated cost of production, and augmented formulation complexity, along with restricted flexibility compared to plasticised PVC [6], [7], [8].

Defined by the IUPAC as substances that increase a material's flexibility, workability, or distensibility, plasticizers reduce a polymer's deformation tension, hardness, density, and viscosity while increasing its flexibility and resistance to fracture [9], [10], [11].

Furthermore, Polyvinyl Chloride (PVC) is a polymer that, compared to Polyethylene (PE) and Polystyrene (PS), possesses lower thermal properties, yet it can be processed relatively easily. However, its low thermal stability makes it prone to degradation. When PVC is mixed with a plasticizer, it undergoes changes in its physical properties: while its tensile strength and density decrease, its ductility increases. On the other hand, incorporating filler into PVC has a contrasting effect. It enhances the tensile strength of PVC but at the expense of reducing its ductility [12].

Historically, PVC has predominantly been modified using phthalate-based plasticizers [4], [13]. Plasticizers are classified into two groups depending on how well they dissolve and match the polymer. Primary plasticizers are either the only plasticizer or the main plasticizer part of the bendable polymer system. These substances can dissolve the polymer well and keep good compatibility over time. Secondary plasticizers are products usually mixed with a primary plasticizer to boost some performance features such as fire resistance, better flexibility at low temperatures, or to lower production costs [13]. However, environmental and human health concerns have prompted an increase in bio-based plasticizers. PVC blends created with these green plasticizers exhibit desirable properties such as thermal stability, migration resistance, and mechanical robustness, making them suitable for medical and industrial applications [14].

Previous research has explored various bio-based PVC plasticizers, such as vegetable oil-based plasticizers, cardanol-based plasticizers, lactic acid-based plasticizers, and others [1], [5], [14], [15]. These studies have provided valuable insights into the relationship between the chemical structure of plasticizers and their plasticizing performance. In another paper, S Kumar investigated the use of natural resource-based plasticizers instead of phthalates in PVC production, leading to the development of novel biobased plasticizers that are environment-friendly and have lower toxicity and low migration levels. The results showed that these biobased plasticizers result in less leachability, volatility, toxicity, and good compatibility with PVC and increase the mechanical and thermal properties of the PVC materials. His research also covers the extensive global utilization of plasticized poly (vinyl chloride) (PVC) and the toxic effects of phthalate plasticizers on the environment and human beings [1]. In another context of plasticizer, A Bodhagi reviews the reactive plasticizers, which are additives that make polymers flexible and durable. Based on his research, reactive plasticizers lower the temperature and the resistance of the polymer to flow and enhance its strength and elasticity. They hardly move out of the polymer matrix [3]. Unar et al focused on enhancing the properties of Polyvinylchloride (PVC) by using different additives. Two PVC mixtures were created for this purpose: one without a plasticizer and the other with a plasticizer. The PVC used in both mixtures had a K value, indicating its molecular weight and degree of polymerization, between 60 and 70. The goal was to understand how a plasticizer could alter PVC's properties and potentially improve its performance in various applications [12]. The other research related to mechanical strength of PVC conducted by Syamsul Hadi. His paper aimed to analyze the impact of DOP plasticizer on PVC resin used in symmetrical sandal base products through tensile testing. PVC resin, a material widely used in sandal production, was the focus of this study. The research concluded that an increase in DOP composition in PVC resin from 300ml to 500ml per 2000g of PVC resin resulted in a 46% decrease in the tensile strength of the PVC resin, dropping from 16.20MPa to 8.74MPa [16].

Despite the extensive research on plasticizers, including bio-based plasticizers, the chemical structure and performance of plasticizers, green plasticizers, petroleum-based plasticizers, and the use of environmentally friendly plasticizers to overcome the impact of phthalates, there remains a significant gap in the literature. Specifically, while studies have explored the application of plasticizers in PVC, focusing on the softness of PVC with plasticizer materials such as Dioctyl phthalates (DOP) and some bio-based plasticizers, these studies have overlooked mechanical testing. Furthermore, the application of varying levels of plasticizers in PVC has been underexplored, particularly in relation to hardness testing. Therefore, this research aims to fill this gap by investigating the impact of various levels of plasticizers on the hardness of PVC, thereby contributing to an understanding of the role and effects of plasticizers in PVC.

2. Methodology

The process starts with a literature review to gather data from various sources, forming a theoretical basis for product creation. This is followed by the production of PVC plastic pellets, which involves mixing raw materials and forming plastic pellets using an extrusion machine. The quality of the plastic pellets depends on the composition of the raw materials and the final mixture. The extrusion process uses a twin-screw extruder type machine to press, mix, and push the plastic inside the heating tube. The extrusion tube has a controlled heater in eight areas. The process concludes with obtaining the extrusion process parameters for producing PVC plastic pellets, ensuring high-quality output. The research flow chart, which provides a visual representation of these steps, illustrated in Figure 1.

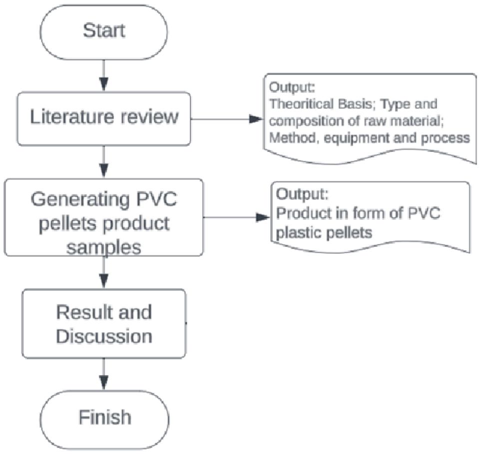

Figure 1: Research Flow Chart

The process of PVC plastic pellet production is initiated with the use of a twin-screw extruder, as discussed in this section. The first step involves the mixing of all types of raw materials. The mixer, equipped with propellers, accelerates the mixing process, resulting in evenly mixed powder (see Fig.2).

Figure 2: (a) The Mixer used for Mixing Raw Material, (b) Mixed Powder Processed in The Hopper

In this study, Polyvinyl Chloride (PVC) was used as the base material, enhanced with a Calcium Zinc stabilizer for heat stability and weather resistance. Trioctyl Trimellitate (TOTM) was incorporated as a plasticizer, and Calcium Carbonate ($CaCO_3$) was added as a filler to improve mechanical properties and surface gloss. A standard lubricant was also included as the additive. The PVC resin (100 phr - per hundred resin) and plasticizer (45 phr) are first mixed evenly in the mixer. Subsequently, a stabilizer (5 phr), and finally filler (25 phr) are added. The mixture is stirred until it is even and forms a powder. As part of this process, there are five types of product samples to be made with varying levels of plasticizer according to Table 1.

TABLE 1 VARIETY OF PLASTICIZER AMOUNTS IN PRODUCT SAMPLES

Material	Sample A	Sample B	Sample C	Sample D	Sample E
	PHR (Gram)	PHR (Gram)	PHR (Gram)	PHR (Gram)	PHR (Gram)
Resin VMC	100	100	100	100	100
Plasticizer	45	48	51	54	57
Filler	25	25	25	25	25
Stabilizer	5	5	5	5	5

The next stage involves the use of a hopper feeder, which serves to hold the powder produced from the mixing process. The hopper, shaped like an inverted cone, facilitates the transfer of the mixed powder into the barrel. The screw barrel plays a crucial role in pushing the mixed powder that is channeled from the upstream barrel towards the end of the barrel (dies). During this pushing process, mixing and heating occur within the barrel (see Fig.3). The mixed powder undergoes a transformation from a powdery form to a solid hard unit.

Figure 3: Twin-Screw Extruder

The pelletizer and die set function as key components in the production of plastic pellets, shaping them to the desired dimensions. The extrusion process generates a melt in the barrel, which is then pressed through the die set's apertures. This results in plastic pellets that conform to the shape and size of the die set's holes. The melt, once passed through the die set holes, is segmented by a pelletizer knife to yield plastic pellets of the desired length.

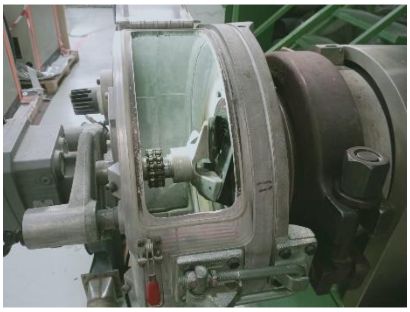

Figure 4: The Pelletizer and Die Set

The vibrating bed, as shown in figure 5, operates as a size-based separator for the plastic pellets. Pellets exiting the die set are channeled to the vibrating bed, propelled by the blower's air pressure. As the pellets traverse the vibrating bed, those of smaller size enter through the bed's holes, emerging as the primary product. Concurrently, products that deviate from the shape and size of the vibrating bed's holes are segregated from the production process.

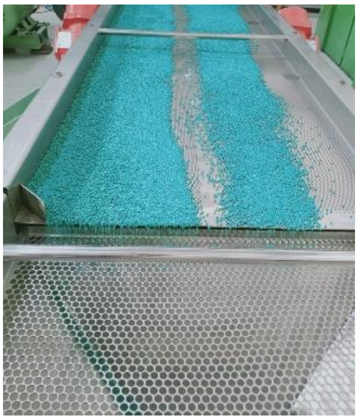

Figure 5: The Vibrating Bed Equipped with Uniformly Sized Holes Aperture

Post-filtering on the vibrating bed, the plastic pellets are accumulated in a hopper. Weighing is then carried out using a scale prior to packaging in sacks, with each package possessing a net weight of 25 kg. The packaging process aims to achieve several objectives, including the preservation of the plastic pellets' quality, prevention of contamination, and reduction of friction with the equipment utilized during the distribution phase.

Figure 6: Packaging Process

Compacted PVC plastic composite specimen is produced post the pellet creation process. The plastic pellets undergo a compaction process to transform into a workpiece specimen with dimensions of length, width, and thickness as 100 x 100 x 6 respectively, intended for hardness testing. In this research, the aging process of the specimens does not necessitate an aging oven. The specimens are merely left at ambient conditions for a duration of six hours. Post the aging procedure, specimens were subjected to a hardness test employing a durometer, in accordance with the ASTM D2240 and DIN EN ISO 868 standards. The test was conducted under a load of 1 kg for a duration of 15 seconds, with hardness measured in ShA (Shore A) units [17], [18]. The durometer, an instrument that gauge hardness by quantifying the resistance strength of needle penetration into the test material under a known spring load, was utilized. There are a variety of durometers available, each designed for specific materials such as rubber, plastic, pipe, wood, and others [19].

3. Result and Discussion

PVC plastic composite specimen is produced by a specific process. The first crucial step involves the combination of resin and stabilizer. This blend is subjected to a temperature of 70°C for a duration of 10 minutes.

Observations from this stage indicate that the powder remains non-adherent within the mixer, signifying a successful mixing process. Subsequently, the TOTM plasticizer is incorporated into the blend. This component is mixed at an escalated temperature of 105°C for a period of 15 minutes.

Following this, the $CaCO_3$ filler is introduced and subjected to a mixing process for 5 minutes at a temperature of 120°C.

TABLE 2 TEMPERATURE AND TIME PARAMETERS IN PVC MATERIAL MIXING PROCESS

Sequence	Temperature (ºC)	Time (min)	Observation
Resin + Stabilizer	70	10	Powder is not sticky in the mixer
Plasticizer	105	15	NA
Filler	120	5	NA

The compacted plastic pellet specimens are subsequently subjected to hardness testing after the aging process. Five PVC specimen samples, each with varying levels of plasticizer, are included in this testing process. The outcomes of the hardness test are tabulated and can be observed in Table 3.

TABLE 3 HARDNESS VALUE TEST IN VARIOUS LEVEL OF PLASTICIZER

Sample PVC Material	Hardness (Shore A)	Plasticizer (Trioctyl Trimellitate) Level PHR (Gram)
Sample A	89.0	45
Sample B	86.0	48
Sample C	83.5	51
Sample D	82.0	54
Sample E	78.0	57

The table provides data on the hardness of various PVC material samples and their corresponding levels of Trioctyl trimellitate (TOTM) plasticizer. It is observed that Sample A, which has 45 units of TOTM, exhibits a hardness of 89.0. As the level of TOTM increases to 48 units in Sample B, the hardness decreases to 86.0. This trend continues with Sample C and Sample D, where the hardness values are 83.5 and 82.0, respectively, for 51 and 54 units of TOTM. Finally, Sample E, which contains the highest level of TOTM at 57 units, also has the lowest hardness value at 78.0. This data suggests an inverse correlation between the level of TOTM plasticizer and the hardness of the PVC material.

Mechanical testing of Polyvinyl Chloride (PVC) samples, with varying amounts of a specific plasticizer called TOTM, revealed no significant differences in hardness, a crucial property that determines its applications. The hardness, defined as the material's resistance to deformation, varied significantly depending on the type of PVC and the amount of plasticizer used in its formulation. The PVC sample with 57 grams of TOTM exhibited the lowest hardness, measured as 78 on the Shore A scale, while the PVC sample with 45 grams of TOTM demonstrated the highest hardness, with a value of 89 on the Shore A scale. The differences in hardness between the PVC samples with different amounts of TOTM were too small to have a detectable effect on the mechanical properties of the samples. Plasticizers' level, such as TOTM, play a pivotal role in determining the physical and mechanical properties of PVC. They function by reducing the crystallinity of PVC, thereby producing a plastic that is clearer and more flexible. This leads to the creation of two distinct types of PVC: Flexible PVC, which contains a plasticizer, and Rigid PVC, which does not contain a plasticizer. In essence, the more plasticizer added to a PVC formulation, the softer the resulting material becomes. This is due to the decrease in hardness value associated with increased plasticizer content. Conversely, a reduction in the amount of plasticizer leads to a harder material. These findings underscore the importance of plasticizers in tailoring the properties of PVC to suit specific applications.

4. Conclusions

The compatibility assessment of Trioctyl Trimellitate (TOTM) plasticizer with Polyvinyl Chloride (PVC) for use in various applications revealed a significant influence on the hardness of the material, though not as a swelling agent. Results from mechanical testing have noted a lower hardness value for PVC samples with higher levels of TOTM. PVC samples with lower levels of TOTM exhibited a higher hardness value, indicating an inverse correlation between the level of TOTM plasticizer and the hardness of the PVC material.

The immersion of the same samples in different levels of TOTM showed a slightly different hardness behavior and lower hardness values in comparison to PVC samples with lower levels of TOTM. The effect of TOTM sorption on the mechanical properties of PVC showed significantly higher softening efficiencies for higher levels of TOTM in comparison to lower levels.

In essence, the more TOTM added to a PVC formulation, the softer material becomes. This is due to decrease in hardness value associated with increased TOTM content. Conversely, a reduction in the amount of TOTM leads to a harder material. These findings underscore the importance of plasticizers in tailoring properties of PVC to suit specific applications.

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