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Effect of Dioctyl Phthalate Plasticizer Loading on Physico-Mechanical Properties of Several Polyvinyl Chloride Systems

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الخلاصة

بالنظر لعدم توفر معلومات دقيقة عن التغييرات الفيزيائية والميكانيكية التي تطرأ على مواصفات متعدد (كلورايد الفاينيل) من جراء إضافة مختلف النسب للمادة الملدنه ثنائي اوكتيل الفثالات فقد تم اجراء تجارب وفحوصات على ثلاث انواع مختلفة من متعدد (كلورايد الفاينيل) كبوليمر اساس مثبت بثلاث انظمة مختلفة من المثبتات الحرارية وباستعمال نسب مختلفة من المادة الملدنة.

تمت دراسة بعض الخواص الفيزيائية والميكانيكية، واظهرت النتائج انه بزيادة نسبة المادة الملدنة يحصل نقصان في قوة الشد وقوة الصدم والوزن النوعي لمركبات متعدد (كلورايد الفاينيل) بينما يحصل زيادة في استطالة القطع. تبين ان هناك تاثير بسيط خلال تغيير انظمة التثبيت الحراري، ولكن تأثير تغيير نوع متعدد (كلورايد الفاينيل) كان اكثر وضوحا وجاء متفقا مع الوزن الجزيئي للبوليمر المستخدم. اظهرت النتائج ان عملية إضافة وتحميل ١٠ جزء ملدن لكل مئة جزء من البوليمرلم يكن لها اي تأثير سلبي على خواص المنتج الفيزيائية والميكانيكية

Abstract

Blends were prepared of three grades of polyvinyl chloride (PVC) as a base polymer, with three different stabilizer systems; all were mixed with variable compositions dioctyl phthalate (DOP) as plasticizer. Physical and mechanical properties were measured for the blends. Results showed that as the plasticizers' concentration increased, the tensile strength, hardness and specific gravity of PVC compound decreased while elongation at break increased. There were slight noticeable effects while using different stabilizers systems. The grade of PVC has an influence that coincides with the polymer molecular weight. Furthermore, it was concluded that adding up to 10 phr of plasticizer didn't have any negative effect on final physical and mechanical properties of the products.

Keywords: *Polyvinylchloride; plasticizers; heat stabilizers; mechanical properties.*

1. Introduction

Polyvinyl Chloride (PVC) is considered to be the second largest commodity plastic after polyethylene with world production approximately over 18 million tons a year. From 2001 to 2004, European consumption of PVC rose from 6.4 million ton to around 6.8 million ton [1].

It is an important commercial thermoplastic which has vast unique properties including low cost, strength, moisture resistant, durability, and excellent fire resistance properties. These properties were the reason of its usage in different applications such as transportation, food packaging, pipes, windows profile, and wire insulations [2- 3].

Before shaping and forming, PVC resin must be blended with a wide variety of additives in different percentages. Unmodified PVC polymer is a brittle, inflexible material with rather restricted and limited commercial benefits. These additives involve plasticizers, stabilizers, processing aids, impact modifiers, lubricants and pigments. Plasticizers are almost the largest volume additive used in PVC, which lowers its glass transition temperature and serves to soften and increase its flexibility. Plasticizers are non-volatile solvents, usually high boiling organic liquids with solubility parameters close to that of the polymer [4]. The worldwide plasticizer demand in 2009 was about 5.7 million [5]. There are approximately one hundred types of commercially available plasticizers in the world. Currently, the most commonly used plasticizers are phthalates, especially dioctyl phthalate (DOP) as it combines high plasticizing efficiency, wide availability and low cost [6-7]. According to Ceresana Research report, plasticizer market in 2010, phthalate esters was the superior among other plasticizers, with DOP as the most widely used one where its consumption was 54 % [8].

Polyvinyl chloride (PVC) is known as a sensitive material towards both heat and light. It degrades by dehydrochlorination and oxidation reactions. This can be seen by the changing of color in PVC due the formation of conjugated double bonds. Even at low processing temperatures polyvinyl chloride decomposes that causes deterioration in most of its original physical and mechanical properties. From this point, thermal stabilizers are considered a vital additive to protect the product during processing. Stabilization mainly proceeds by the addition of compounds, which contain transition metals like lead, tin and zinc. Commonly used thermal stabilizers for PVC belong to one of four categories: lead salts, organic-tin compounds, metal soaps, and some auxiliary stabilizing materials. Stabilizers for PVC have low mobility but can change their function by consumption or degradation [9-11].

In any PVC formulation the largest component is the homopolymer. So, the selection of PVC grade, (represented by its molecular weight) must be studied well according to the desired final properties. This is usually expressed by means of K value that is considered as a molecular weight indication. Low K values indicate low viscosity that is an ideal case for filling all the cavities in the molds in case of injection molding.

There were some studies on the role of additives on PVC's final properties. Unar et al. [12] discussed the effect of various additives on the physical properties of two grades of PVC (K value ranging from 60 to 70) and concluded that increasing the plasticizer content results in lowering tensile strength and specific gravity, but there was an enhancement in elongation at break. While, Shah and Shertukde [13] compared mechanical, thermal and electrical properties of PVC plasticized with several phthalate plasticizers and their blends with DOP. Taghizadeh and Dasdar [14] showed

the influence of PVC molecular weight on its thermal stability. They concluded that the molecular weight slightly affects the thermal dehydrochlorination.

Davallo and Pasdar [15] studied the effect of using several types of plasticizers with PVC and concluded that mechanical properties of PVC were affected by the type of plasticizer used.

In another study by Elgozali and Hassan [16] the stress at break was found to decrease by 50 % with increasing plasticizer content from 21 to 32%. They also confirmed that the elongation at break and shore hardness were inversely proportional to plasticizer content. Brown et al [17] found that the addition of plasticizer has a small effect on the crystallinity of commercial PVC. On other hand, Nagi and Tamus [18] investigated the dielectric properties on PVC samples with different plasticizer content by using two measurement's methods. Each one of these studies covered a limited range of plasticizer loading. Also, none of these studies focused on the effect of PVC type or the stabilizer type.

Since physical and mechanical properties are considerably affected by the type of PVC resins and additives used mainly plasticizer and stabilizers, it was important to study the physical properties of PVC resins getting an idea about the proper amount of plasticizer used and to predict the properties of the product final product. The present study outlines the effect of a wide range of DOP loading as plasticizer to three different grades of PVC as a base resin compounded with different three types of stabilizers systems. The effect includes physical and mechanical properties i.e. tensile strength, elongation at break, hardness and specific gravity.

2. Experimental procedure

2.1. Materials

Three grades of PVC resin with the properties listed in **Table 1**, manufactured by Stauffer Company were used in this study.

Table 1: Specifications of PVC resins

Specification	**PVC -resins**		
	SCC/608	SCC/676	SCC/686
K value	53-55.5	65.5-67.5	70.5-72.5
Bulk density(gm./ml)	0.5 min	0.45	0.45
Ash content (%)	0	0	0
Volatiles(maximum)	0.75	0.5	0.5

- Several types of chemically different stabilizers from Ciba-Geigy, were used to study their effect on PVC. The stabilizers included:
  1. Irgastab BC 26 (Ciba-Geigy) Ba-Cd-soaps. This type provides good early color, light stability and heat stability.
  2. Irgastab 15 MS (Ciba-Geigy) Di-butyl-tin mercaptide. They give good heat, light and color stability, and promote fusion and reduce melt viscosity.
  3. Dibasic lead phosphite $(2PbO\text{-}pbHPO_3.\frac{1}{2}H_2O)$. They are inexpensive and provide good heat stability, excellent electrical properties and low water absorption.
  4. Dibasic lead stearate $(2PbO.Pb\ (C_{17}H_{35}COO)_2$.
- Dioctyl phthalate (DOP) was used as plasticizer. It has a specific gravity of 0.9826 at 25°C and its molecular weight is 390.56 g mol^{-1}.
- As a lubricant a system of (0.5 parts by weight stearic acid as an internal lubricant: 0.2 part hard wax as an external lubricant) was used.

2.2. Sample Preparation

Twelve PVC compound formulations were prepared, for each formulation, plasticizer loading level was varied from 0 to 100 part per hundred of resin, phr (i.e. The concentration of the base polymer is referred as 100 parts in the mixture; whereas the concentration of rest of the additives used is referred as parts per 100 resins), while concentration of other chemicals such as PVC resin, stabilizers and lubricant were fixed. Then the same series where prepared with a different stabilizers system from those listed below.

Three systems of stabilizers were used in preparation of the different formulation:

- Ba-Cd-soaps.
- Di-butyl-tin mercaptide.
- (Dibasic lead phosphide: Dibasic lead stearate) with a mixing ratio of (2:1 parts by weight, phr).

Three series of samples were prepared for each PVC type, at different plasticizer loading levels, and each one of the series were mixed with one of the above three stabilizers systems in order to understand the physical and mechanical changes on properties of the three grades of PVC.

Table 2: Formulations of PVC samples

Materials	Concentration (phr)
PVC resin	100 part
Stabilizer system	3 part
lubricants	0.7 part
plasticizers	0-100 part

The formulations of PVC compound summarized in **Tables 2** were first weighted. After that, PVC resin, stabilizer systems, and lubricants were dry blended using high speed mixer type Henschell FM_4, fitted with temperature indicator mounted inside the mixing chamber. Corresponding plasticizers' weight were then added into the PVC blend and mixed for 5 min again till 110 °C.

Next, the blended powders were plasticized using a laboratory two roll mill at 60 rpm, processing temperature was 170°C and processing time 5 (minutes). The samples were then compression molded at the same plastification temperature into sheets with 2 mm thickness by the aid of hydraulic press equipped with heated plates, and were subjected to further analysis. *2.3. Testing*

Five specimens were reproduced for each PVC compound formulation and the average of tensile strength, percent elongation at break, hardness and the specific gravity was determined.

Specimens for mechanical testing were cut out from the compressed sheet and then tested according ASTM D-638 [19]. Tensile strength is calculated by dividing the load at break by the original minimum cross sectional area. The result is expressed in megapascals (MPa). The tensile test was conducted with a Zwick testing machine at crosshead speed of 25 mm. min^{-1} a gauge length of 50 mm as indicated in ASTM D882-96 [20].

Percent elongation was also calculated by dividing the elongation at the moment of rupture by the initial gauge length and multiplying by 100.

The hardness test was accomplished according to (ASTM –D-2240-68) [21] by a device manufactured by ZWICK Co. Germany. The type used was Shore D that can be defined as resistance of a material against the penetration by a cone. The readings were taken after 1 sec of applying the load (5kg).

Since specific gravity is an important parameter that must be analyzed, specific gravity for samples was taken according to (ASTM-D792-2000) [22] by using a pyknometer. Five grams of the compounded material was measured in a pyconometer, and the specific gravity was calculated from the weight and volume difference.

3. Results and Discussions

3.1. Tensile Strength

The results of tensile strength of polyvinyl chloride (PVC) compounds were shown in **Figures 1, 2 and 3** where each figure represents a different type of stabilizer system. It was noted that the tensile strength started by a slight increase when a little amount of plasticizer was added and it reached a maximum at (5-10) phr plasticizer loading. After this point (at about 20 phr loading) the tensile strength of polyvinyl chloride (PVC) compounds started to decrease sharply with increasing plasticizer concentration for all stabilizer system types. And this decreasing reached about 50 % from its original value. After this point the decrease in tensile strength started to be less sharp till it reached 30 % from its original value at 60 phr plasticizer loading. Then the values dropped down to decrease down to reach 80 ,70 and 50 $kg.cm^{-2}$ at 100 DOP loading for PVC 608 when using Irgastab 15MS, BC 26 and (phosphate + lead stearate) stabilizers systems.

Our results are in accord with previous studies [12] [15]. When the plasticizer is incorporated to the resin it forms links between polymer molecules and that will increase the spaces between polymer molecules which takes an effect on the mechanical properties of the polymer. It was stated that a dipole interaction occurs between polar groups represented by chlorine atom in PVC and the ester polar groups in DOP. The bond forces of the polymer atoms became less in attraction each other due to the established new links and thus free volume increases with the addition of the plasticizer to the polymer, causing a lowering in the hardness, and tensile strength [23-24].

It was also noted that the tensile strength values of the three PVC grades were slightly different from each other by the order (SCC/ 608 < SCC/ 676 < SCC/ 686) and this coincides with their gradient in molecular weight. Also by examining the three figures it can be seen almost no large difference when the three types of stabilizer system were used.

3.2. Elongation at Break

The results of Elongation at Break were almost the same for all the three PVC grades and the three stabilizer systems, so the average values where represented in **Figure 4**. It was obvious that elongation at break for PVC compounds increased with increasing plasticizer concentration. The elongation at break of PVC systems at the (0 phr) till reaching (10 phr) was about 6 %, then it begins to rise suddenly from this point to 20 phr loading to be 200 %. After this point the increasing was almost linear, until reaching 455 % at 100 phr DOP loading.

This increase in elongation may be explained by the lubricating theory, which states that the plasticizer's molecules diffuses between the polymer and causes the secondary bonds to be weak, so when the polymer is stretched the polymer chains will elongate easily [23].

3.3. Durometer Hardness

The effect of plasticizer content on the shore hardness is given in **(Figures 5, 6 and 7)** which show obviously that the hardness started to decrease slightly during adding plasticizer until the loading was 10 phr. After this shore D Hardness of PVC compounds began to decrease sharply with plasticizer concentration. But an obvious change in slope can be noticed after reaching about 40 part per hundred plasticizer loading. This is in line with the study of Rehm [25] which stated that addition of plasticizer would soften the PVC compound and thus the hardness will reduce.

As explained previously the plasticizer softens PVC by resolving the intermolecular interaction, and the ductility decreased causing this decrease in hardness with increasing plasticizers content [23, 24].

There were no clear and large difference in behavior when the stabilizers systems were changed, but for the plasticizer type the effect was the same as for tensile strength (SCC/ 608< SCC/ 676< SCC/ 686)

3.4. Specific Gravity

The specific gravity of PVC compounds decreased with increasing plasticizer concentration for all plasticizer types as shown in **Tables 3 to 5**. This is because plasticizers have lower specific gravity than PVC resins. The specific gravity of a substance mainly depends on its density which considers the ratio of mass to volume.

Table 3: Specific Gravity of PVC 608 Systems with Various Loading of DOP

Parts of DOP	Systems of stabilizers		
	Pb-phosphate+ Pb-stearate	Irgastab BC 26	Irgastab 15 MS
0	1.2625	1.243	1.2549
5	1.2533	1.2374	1.2247
10	1.2303	1.2109	1.2156
15	1.2248	1.2065	1.1964
20	1.2059	--	1.1728
25	1.1999	1.1772	1.1664
30	1.1848	1.1619	1.616
35	1.1783	1.1542	1.1599
40	1.1371	1.1312	1.1474
60	1.1127	1.1153	1.0873
80	1.0712	1.0989	1.0745
100	1.0689	1.0639	1.0555

Table 4: Specific Gravity of PVC 676 Systems with Various Loading of DOP

Parts of DOP	Systems of stabilizers		
	Pb-phosphate+Pb-stearate	Irgastab BC 26	Irgastab 15 MS
0	1.2746	1.2461	1.2380
5	1.2595	--	1.2318
10	1.2349	1.2090	1.2230
15	1.2277	1.1997	1.1958
20	1.2125	1.1871	1.1855
25	1.1897	1.1838	1.1720

30	1.1850	1.1679	1.1552
35	1.1639	1.1607	1.1542
40	1.1499	1.1529	1.1464
60	1.1321	---	---
80	1.1061	1.0770	1.0829
100	1.0722	1.0584	1.0662

Table 5: Specific Gravity of PVC 686 Systems with Various Loading of DOP

Parts of DOP	Systems of stabilizers		
	Pb-phosphate+ Pbstearate	Irgastab BC 26	Irgastab 15 MS
0	1.2629	1.2410	1.2344
5	1.2494	1.2332	1.2341
10	1.2358	1.2189	---
15	1.2148	1.2014	1.1861
20	1.2068	1.1881	1.1897
25	1.1907	1.1826	1.1884
30	1.1744	1.1661	1.1791
35	1.1373	1.1631	1.1584
40	1.1298	1.1521	1.1536
60	1.1080	1.0953	1.0878
80	1.0844	1.0607	1.0769
100	1.0645	1.0561	1.0629

4. Conclusions

- Tensile strength decreases with adding plasticizer. Corresponding minimum value was 50 kg cm^{-2} at 100 % DOP loading for PVC 608, when using (phosphate + lead stearate) stabilizer systems.

- Elongation at break increases with increasing plasticizer content. The maximum obtained elongation at break was 455 % at 100 % DOP loading.

- There were slight noticeable effects in physical and mechanical properties while using the three different stabilizers systems.

- Adding plasticizer has no effect on the hardness of PVC until the loading reaches 10 phr, after this the hardness of PVC compounds began to decrease almost linearly with plasticizer concentration to reach minimum value (8 shore D) at 100 % DOP loading for PVC 608 with Irgastab 15MS stabilizer system.

- The grade of PVC represented by K value has an influence that coincides with the polymer molecular weight.

- It was concluded that adding up to 10 phr of DOP don’t have a negative effect on final physical and mechanical properties of the products and helps to improve flow properties during processing and shaping. It is possible for rigid PVC manufacturers to add up to 10 phr of plasticizer to the resin without any negative influences on the physical properties of the final product, and that little percentage can save energy consumption through improving the flow properties during processing.

- The established figures can enable and help the manufacturers to predict the correct percentage of plasticizers added to the formulation to give required properties.

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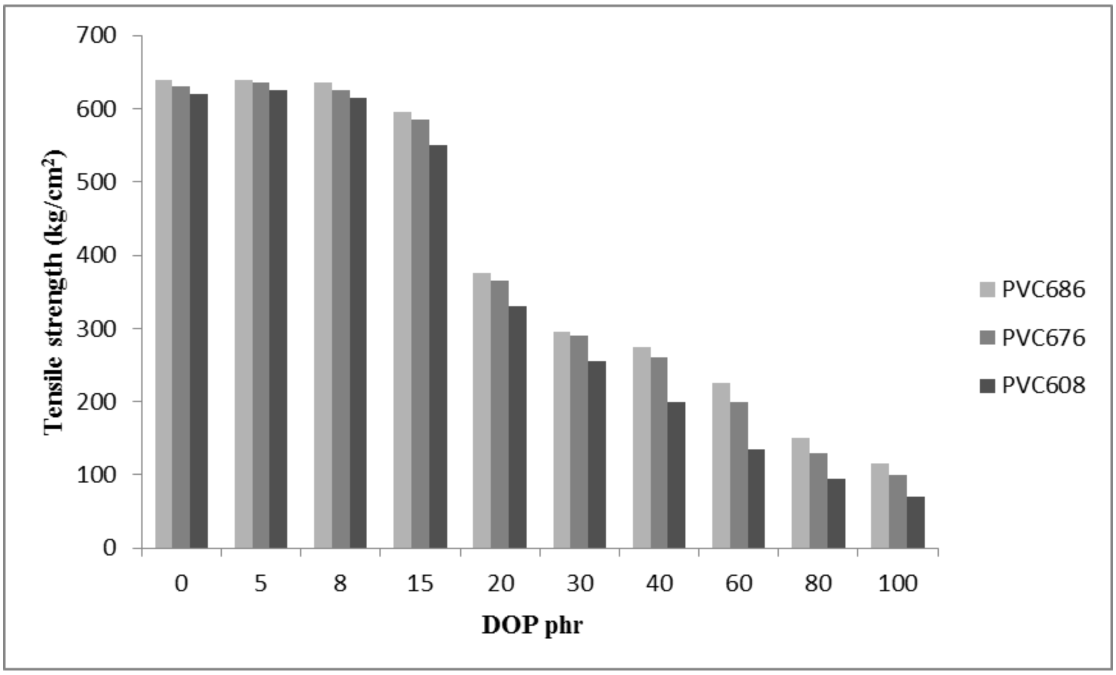

Figure 1: Tensile strength of PVC samples stabilized by Irgastab BC 26 systems with different DOP loading

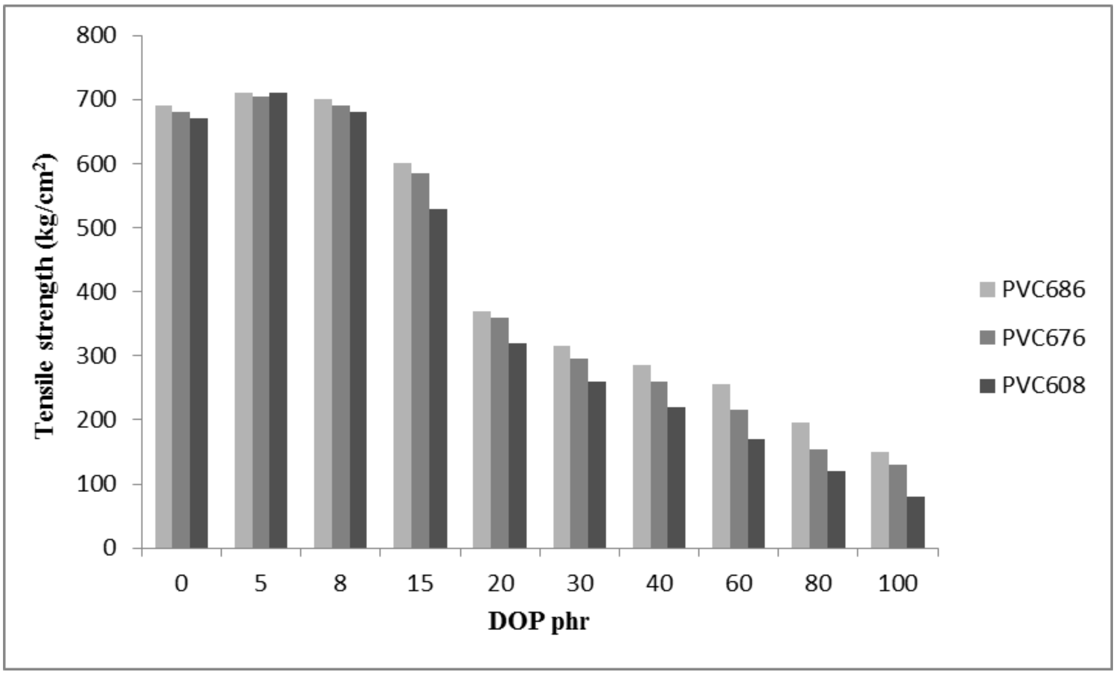

Figure 2: Tensile strength of PVC samples stabilized by Irgastab 15MS system with different DOP loading

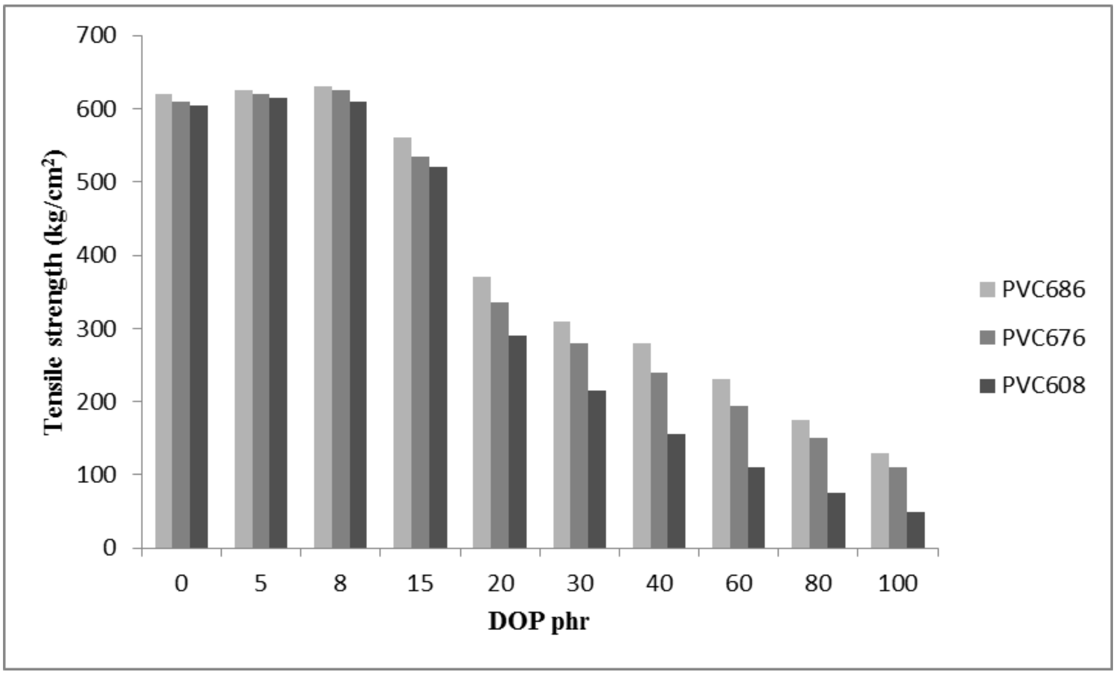

Figure 3: Tensile strength of PVC samples stabilized by (Dibasic lead phosphide + Dibasic lead stearate) system with different DOP loading

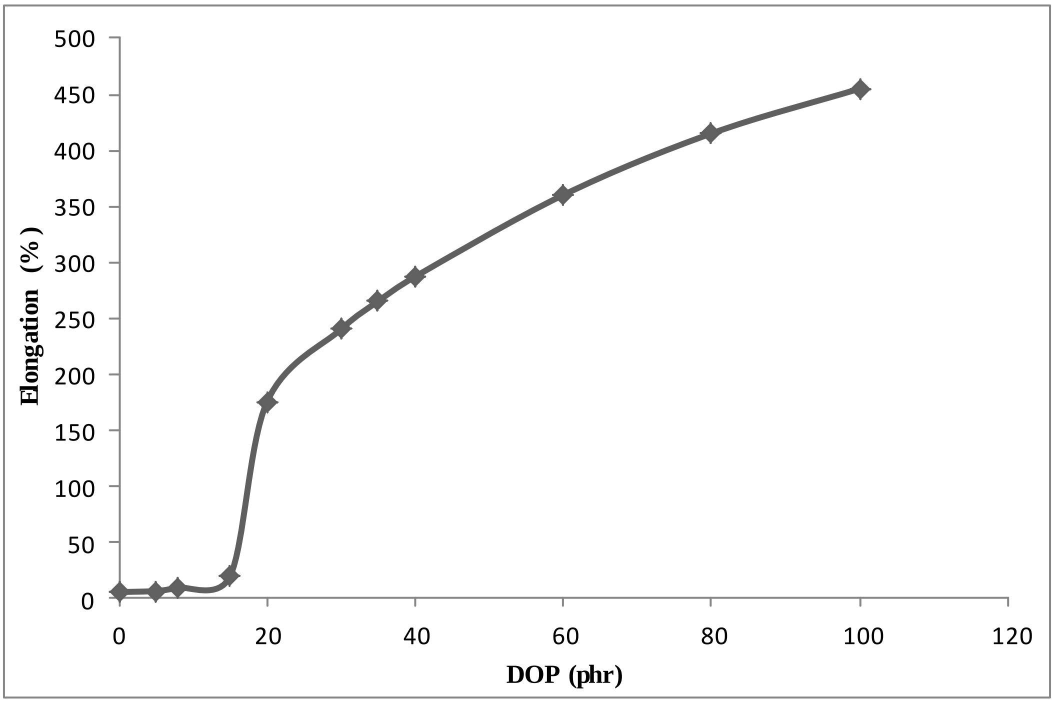

Figure 4: Effect of DOP loading on the Elongation-to-break of PVC samples

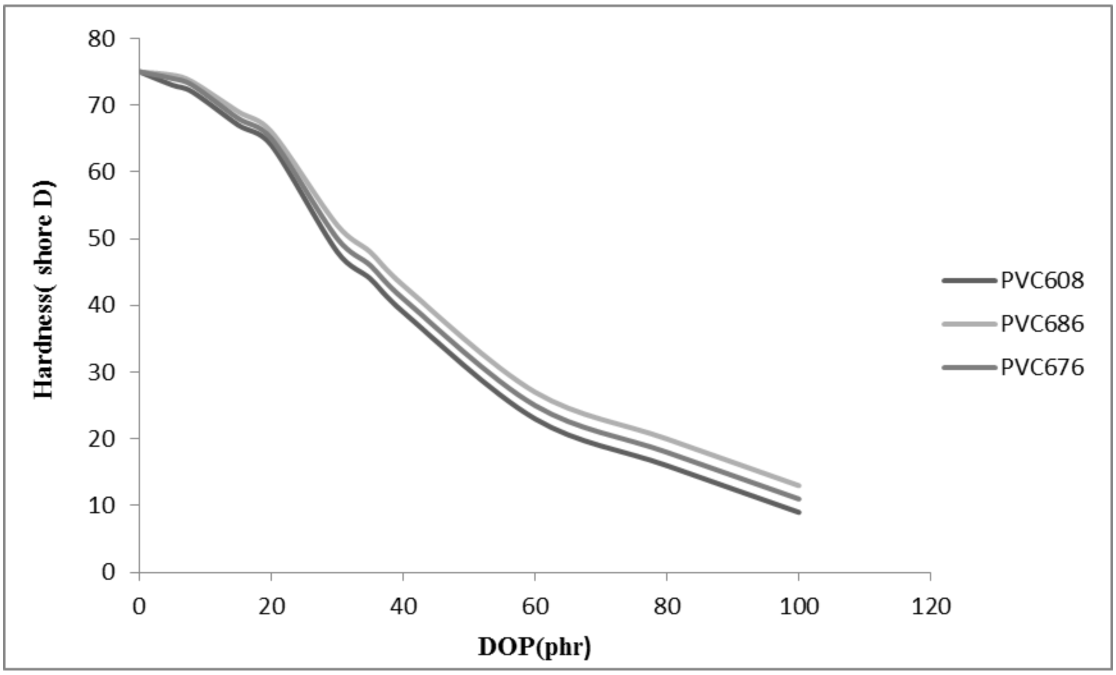

Figure 5: Effect of DOP loading on shore D hardness for PVC samples stabilized by Irgastab BC 26 system and different DOP loading

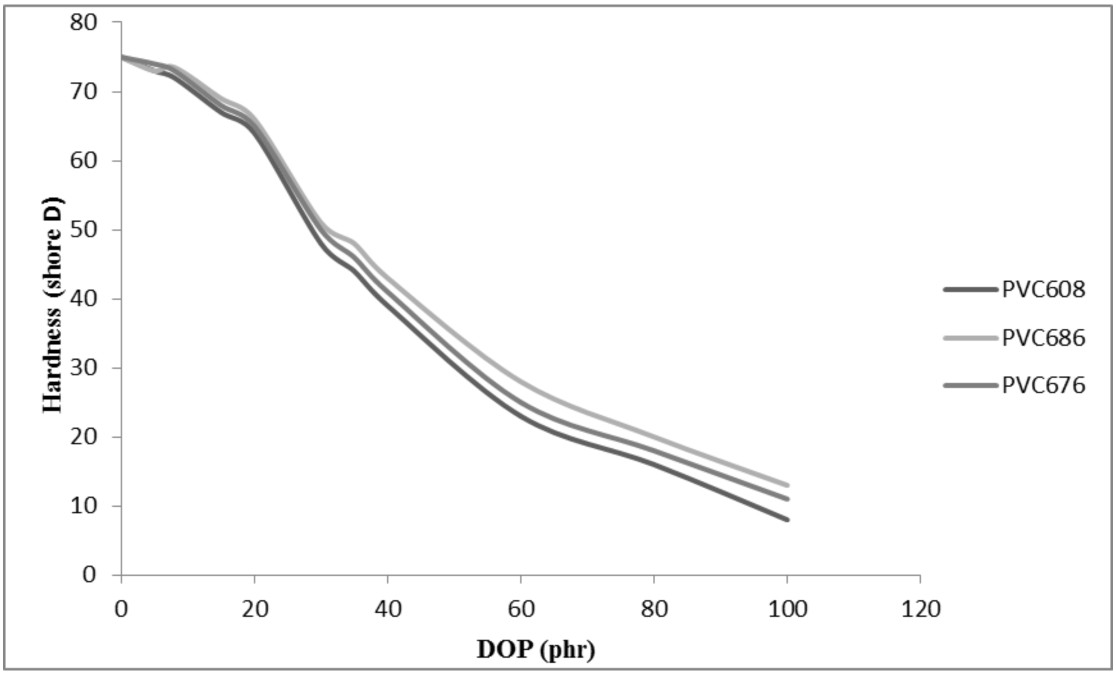

Figure 6: Effect of DOP loading on shore D hardness for PVC samples stabilized by Irgastab 15MS system and different DOP loading

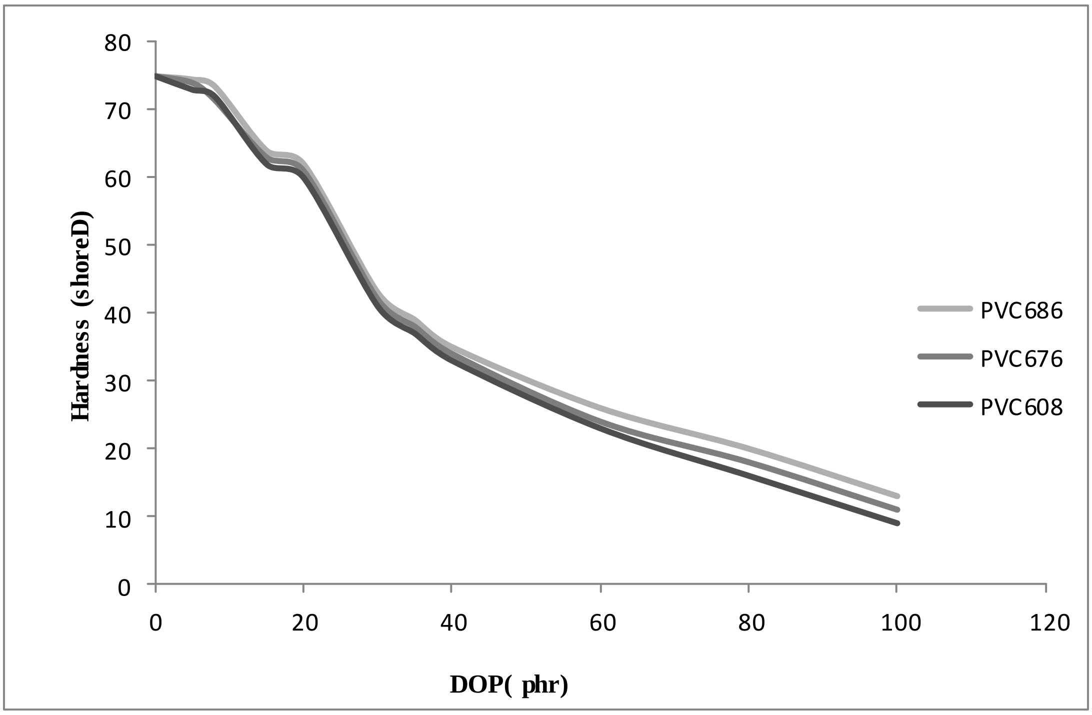

Figure 7: Effect of DOP loading on shore D hardness for PVC samples stabilized by (Dibasic lead phosphide + Dibasic lead stearate) system and different DOP loading