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A Study of Some Changes in the Properties of Recycled PVC Plastic in Arbil Factories

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Abstract:

In Arbil recycling factories, the plastic materials are usually recycled for many times and this affect the physical, chemical and mechanical properties of the plastic materials. For the first time in the Iraq a research on dioctylphthalate (DOP) plasticizer extracted from recycled polyvinyl chloride (PVC) plastic industries in Arbil city was carried out after optimization conditions to obtain the maximum plasticizer percentage. Different physical and chemical tests were applied on the PVC samples, such as viscosity measurements, determination of Softening Points and bromine test. In addition, TLC chromatography and IR spectroscopy methods were used as identification methods. It was shown that the PVC plastic products lose many of its chemical, physical and mechanical properties after using for some months. The effect of the DOP plasticizer on the softening point of the PVC plastic samples was studied according to the seasons of the year. The outcomes of this study may be essential for future environmental studies.

Keywords: PVC, DOP plasticizer, recycled, extraction.

دراسة بعض التغييرات على صفات بوليمر بي في سي المدور في معامل مدينة اربيل

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الخلاصة

تتم عملية اعادة التدوير المواد البلاستيكية في معامل مدينة اربيل لعدة مرات وبالتالي تؤثر هذه العملية على الصفات الفيزيائية والكيميائية والميكانيكية للمواد البلاستيكية المنتجة. فى هذا البحث وللمرة الاولى فى العراق تتم دراسة مادة داي اوكتيل فثاليت المستخلصة من بوليمر فينايل كلورايد المعاد استخدامه او المدور فى مصانع مدينة اربيل عند الظروف المثلى للحصول على اعلى نسبة من الملدن . تم في الجزء التجريبي في هذه الدراسة استخدام العديد من الفحوصات الفيزيائية والكيميائية للمواد البلاستيكية منها قياس اللزوجة وتقدير نقاط الليونة وفحص البروم. كما تم استخدام طرق الكروماتو غرافيا وطرق الاشعة تحت الحمراء في التشخيص. اظهرت نتائج البحث بان بلاستك البولي فينايل كلورايد يفقد الكثير من صفاته الفيزيائية والكيميائية والميكانيكية بعد بعض الاشهر من الاستخدام. كما ان تاثير مادة داي اوكتيل فثاليت على ليونة نماذج بوليمرالبولي فينايل كلورايد تمت دراستها فى مختلف مواسم السنة. تعد نتائج هذه الدراسة ذات اهمية بالغة في الدراسات التجريبية المستقبلية في مجال البيئه.

كلمات مفتاحية: بوليمر البولي فينايل كلورايد؛ ملدن؛ البوليمر المدور؛ استخلاص

1. Introduction:

One of the first uses of PVC was the insulation on electric cables in 1930. Today, PVC is the second largest selling plastic in the world to polyethylene (PE) production. Bart [1] and Pritchard [2] reviewed that the additives for plastics are plasticizers, stabilizer, antistatic agent, coloring agents, UV absorption, fillers, organic brighteners, fire retardants and antioxidants.

Lee, Young-Ho et al. [3], studied the transferring of di-(2-ethylhexyl) adipate (DEHA) plasticizer from the PVC wrapping products to different food products using solvent extraction method and microwave technique in order to quantify the range of plasticizer transferring with period of contact at different exposure and heat conditions of the food product.

Literature is rich of different determination methods using different techniques for the determination of plasticizer content. For example, six phthalate types in child care items and toys by were determined using Gas Chromatography-Mass Spectrometry (GC-MS) [4]. Celso and Ademir studied the recycling of PVC to five times and the effect of the PVC reprocessing on mechanical properties like tensile strength, elongation at break and degradation of polymer through colour change and FTIR analysis after each recycling [5,6].

In another study, the leaching of (DEHP) Di(2-ethylhexyl)phthalate plasticizer from a wide range of commercial, food-liquid packaging, hospital and industrial equipment made from PVC was studied. The research explained the health risk and environmental fate of exposure to different levels of DEHP contamination food packaging and water bottle [7,8].

Recycling process is one of the essential methods to avoid the side effects of the PVC. Recycling of mixed PVC wastes and new recycling and separation technologies including the criteria of recycling process, waste management, problems, costs and energy requirements to calculate the benefits of recycling [9]. Jun and Bin studied the preparation of modified plasticizer di(2-ethylhexyl)phthalate and chlorinated paraffin-52 plasticizer that has excellent plasticizing efficiency as DOP with no leaking out and lower glass transition temperature of PVC polymer [10].

Yi-Bo Zhao et al., reviewed on an environmentally friendly and economical method for separation of plastics and recovery solvents extraction using dissolution/re-precipitation method and supercritical fluid extraction, to obtain high-quality recycled plastics for (PS, PC, Polyolefins, PET, ABS, and PVC) [11].

Michel studied the ability of replacement of conventional fossil plasticizers by renewable ones. The new plasticizers sources are: Vegetable oils, castor oil, epoxidized soybean oil, Esters and Isosorbide diesters (Polysorb ID), a nontoxic renewable alternative to the phthalates they soften rigid polymers, improve cold temperature properties, and having plasticizing properties for PVC [12].

Joanna et al., reviewed the conventional PVC plasticizers and the new plasticizers –polymer mixture to reduce the migration problem of plasticizer. The compression includes chemical and physical properties of PVC mixture for many synthesized and natural sources plasticizers with observation of the improvements in polymer performance, mechanical properties and high migration resistance in comparison to PVC plasticized with conventional plasticizer [13].

Carmen reviewed the microbial degradation of plastic additives (i.e. plasticizers, flame retardants, stabilizers and antioxidants) and discussed the technical approaches that depend on the biological activities of micro-organism to increase the enzymatic degradation of plastic additive to metabolize this organo pollutants (i.e. plastic additives) to avoid elution of harmful plastic additive to environment. [14]

Kazumitsu et al. [15] studied the analysis of 41 kinds of PVC samples with different derivative processing. E. Kampouris et al. [16] explained the recycling techniques for treatment of PVC bottles. D. papaspyrides and C. Diakoulaki [17] were studied recovery of reusable PVC by using water in washing stage of solvent recycling. Also, H. Juergen [18] discussed methods for recycling plastic from household waste by separating the types of plastics or by replasticizing unseparated plastics.

2. Experimental:

Instrumental & Chemicals:

Thermo Masttson IR-300 spectrophotometer, Thin layer chromatography apparatus and Ostwald viscometer were used.

Plastic waste (plasticized PVC) used as raw materials from Erbil factories, THF, MeOH, benzene, cyclohexane used as chemicals which supplied by Fluka, BDH and GC companies.

Plasticizer extraction from plastic wastes:

Plastic slippers (0.5gm) were dissolved in THF (different volumes) then methanol was added stepwise to complete precipitation of PVC which separated by filtration, dried in the oven at 80 ^{0}C the plasticizer will remain as an oily layer after the filtrate was evaporated. Optimization for plasticizer extraction from PVC before and after manufacturing as a function of time and volume of THF are listed in table 1&2.

Viscosity measurements:

In order to determine the Inherent viscosity of PVC samples in the two situations before and after extraction of plasticizer from Industrial PVC plastic (slippers). Seven samples of (0.5 gm/100 ml) were prepared by using cyclohexanone as a solvent in a thermostatic water bath at 60 °C. The η_{inh} were determined for each sample by using the equation: $\eta inh = \ln \eta red/C$. The results are listed in table 3.

Determination of Softening Points:

Softening points were determined by observing a very small sample on microscope slide which contacted with a hot plate. The sample was observed through magnifying lens which permits very detailed observation of the beginning and the end of the softening. The values are listed in table 4.

Bromine test:

The bromine test is a good identification test to know whether the precipitated PVC plastic was degraded or not. A solution of 0.1 gm of each sample of PVC in 6 ml THF was prepared then 2 drops of bromine in CCl_4 (10%) was added to the PVC solution. The color observations were listed in the table 5.

Plasticizer Identification method:

- TLC chromatography

The two samples of DOP, were putted on silica gel plate and benzene were used as an eluent the first is for standard DOP and the second is for extracted plasticizer, the yellow spots were developed by using the iodine and the Rf value for the extracted DOP and the standard DOP was the same Rf (0.872).

- IR- Spectrophotometry:

The solid materials (precipitated PVC) were pressed as discs with KBr. Liquid materials (extracted plasticizer) were measured by liquid NaCl cell. The spectra were taken in the range 600-4000 cm^{-1}, the spectra were explained in Table 6 and 7.

3. Results and Discussion:

In Arbil recycling factories, the plastic materials were undergoing recycling for many times and this cause to lose many plastic properties. Chain degradation can be identified by using viscosity measurements and bromine test. All the phthalate ester (plasticizer) which used in PVC applications are not chemical bound, they have a tendency of migration from PVC. Experimentally found that the extracting efficiency of THF is higher than cyclohexane. From Table (1) and Figure 1, it was seen that the optimum percentage for extracted DOP is 25.4% in 0.5 gm PVC plastic using 30 ml THF with extraction period 72 hours. This value is lower than the standard percentage (40%) by 14.6% which is migrated to the surrounding. In addition of 3% plasticizer to the PVC plastic (Table 2 and Figure 2) after manufacturing the percentage of recovered plasticizer increase and reach 28.9% in 0.5 gm PVC plastic using 30ml THF with extraction period 72 hours, from both tables we observe the effect of time and solvent volume of the extraction efficiency.

The addition of 3% DOP to the PVC plastic during the manufacturing process in the summer effect on PVC plastic properties by decreasing the softening point temperature of the PVC plastic products by 3.5 °C.

The bromine color observation explain that in standard PVC from Fluka and Zafaranya company the color not disappear while in the PVC waste samples before and after manufacturing the red color of bromine disappear because the PVC chain degradation to low molecular weight unsaturated products.

Thin layer chromatography shows two yellow spots with the same Rf value which is a good indication that the extracted plasticizer is the DOP. The disappearance of plasticizer band (1718-1728 cm^{-1}) after the extraction of DOP from PVC which refer to stretching vibration of C=O group in the DOP it shows that during extraction the plasticizer leaves the polymer. The IR spectra which achieved from NaCl liquid cell showed many bands due to stretching and bending vibrations of carbonyl group of plasticizer. The double bond (C=C) of phenyl ring appeared at 1550-1600 cm^{-1}. The band which observed at 1257-1297 cm^{-1} attributed to C-O stretching vibration of the ester and the other bands are listed in Table (5 and 6). The inherent viscosity of the samples before extracting DOP is higher than after extraction DOP, this result may explain the addition of plasticizer cause to increase the viscosity of the polymer because of the stability of the PVC chains, since the plasticizer is chemically and thermally stable at normal temperature.

Table 1: Optimization conditions for extraction and percentage of extracted DOP from PVC plastic products before manufacturing.

THF volume (ml)	Extracted DOP (%) at			
	24 hours	48 hours	72 hours	98 hours
20	21.2	21.9	24.1	22.7
25	21.6	22.0	24.2	23.2
27.5	21.7	22.1	24.7	23.4
30	22.3	22.6	25.4	24.1
32.5	22.0	22.1	24.2	23.7
35	21.7	22.0	23.9	23.5
40	21.3	21.6	23.1	22.9
50	21.3	21.3	22.6	22.1
60	20.5	20.9	21.5	21.1

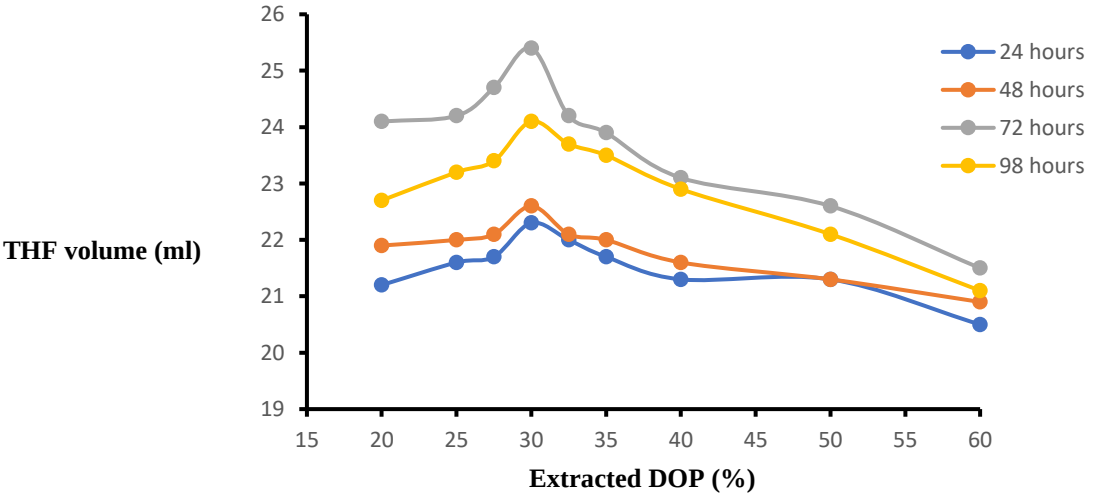

Figure 1. THF volume and extracted DOP at different temperatures for PVC plastic products before manufacturing.

Table 2: Optimization conditions for extraction and percentage of extracted DOP from PVC plastic products after manufacturing.

THF volume (ml)	Extracted DOP (%) at			
	24 hours	48 hours	72 hours	98 hours
20	23.2	24.2	24.3	23.7
25	23.3	25.1	25.5	25.2
27.5	23.6	25.9	26.7	26.0
30	26.9	27.4	28.9	27.7
32.5	26.3	26.7	27.4	27.1
35	26.6	26.1	27.2	26.5
40	25.2	25.8	26.7	26.3
50	24.9	25.3	26.1	25.9
60	23.0	24.4	25.6	25.3

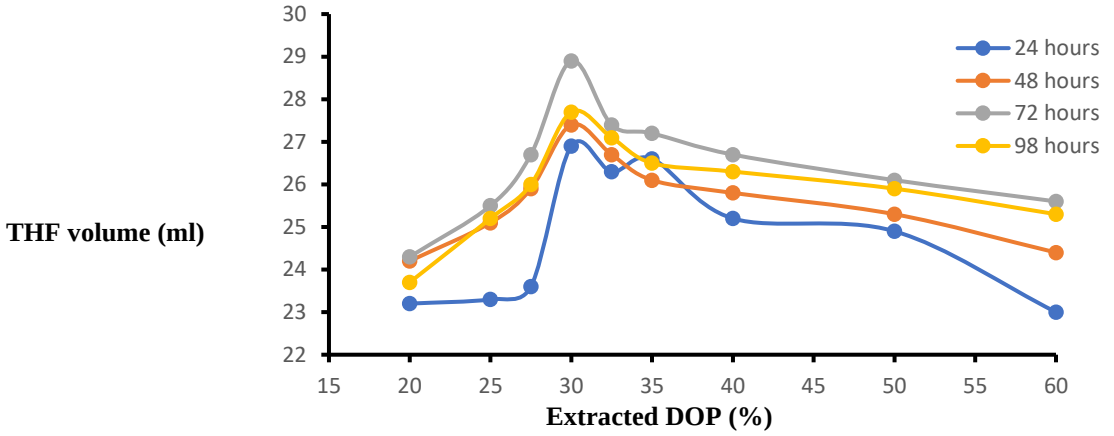

Figure 2. THF volume and extracted DOP at different temperatures for PVC plastic products after manufacturing.

Table 3: Viscosity results.

No.	The Sample		η_{inh}
1	Standard PVC without DOP (Fluka)		1.576
2	Before manufacturing PVC granular (Zafarania)	Before extracting DOP	1.631
		After extracting DOP	1.619
3	Before manufacturing PVC product (Arbil)	Before extracting DOP	1.558
		After extracting DOP	1.555
4	After manufacturing PVC plastic product with adding 3% plasticizer (Arbil)	Before extracting DOP	1.559
		After extracting DOP	1.557

Table 4: Softening points of PVC plastic samples

No.	The Sample	Plasticizer (%)	Softening point (°C)
1	Standered PVC (Fluka company)	-----	93
2	PVC granular (Zafarania company)	40	59
3	Standered PVC mixed with Standered DOP	39.9	59
4	Standered PVC mixed with extracted DOP	39.9	59
5	Before manufacturing PVC plastic product (without adding DOP)	25.4	66.5
6	After manufacturing PVC plastic product (with adding 3% DOP)	28.9	63

Table 5: Color observation in Bromine test.

No.	The Sample	Red color

1	Standard PVC without DOP (Fluka)		Not disappear
2	Before manufacturing PVC granular (Zafarania)	Before extracting DOP	Not disappear
		After extracting DOP	Not disappear
3	Before manufacturing PVC product (Arbil)	Before extracting DOP	disappear
		After extracting DOP	disappear
4	After manufacturing PVC plastic product with adding 3% plasticizer (Arbil)	Before extracting DOP	disappear
		After extracting DOP	disappear

Table 6: Characteristic IR frequencies of the PVC plastic in cm^{-1}.

No.	The compound	C-Cl Str.	C-C str.	C-H str. Aliph.	CH_2 def.
1	PVC plastic Before manufacturing (After extracting DOP).	610	1254	2916, 2851	1426
2	PVC plastic Before manufacturing (After extracting DOP)	612	1254	2916, 2850	1427

Table 7: Characteristic IR frequencies of the dioctylphalate plasticizer in cm^{-1}.

No.	The compound	C=C Str. Arom.	C=O str.	C-O str.	C-H Str. Aliph.	C-H def. o-dis, Benz.
1	Standard DOP	1585	1726	1250, 1075	2930, 2870	742
2	Extracted DOP from PVC plastic before manufacturing	1600	1726	1276, 1072	2928, 2860	742
3	Extracted DOP from PVC plastic after manufacturing	1600	1728	1278, 1072	2928, 2860	742

4. Conclusions

In this research, dioctylphthalate (DOP) plasticizer was extracted from recycled polyvinyl chloride (PVC) plastic from different industries in Arbil city. Different physical and chemical parameters were found for the PVC samples, such as viscosity measurements, determination of softening points and bromine test. It was found that the PVC plastic products lose many of its chemical, physical and mechanical properties after using for some months.

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