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A mini-review on different synthesis reactions of dioctyl terephthalate (DOTP) and properties of DOTP plasticized PVC

Farklı dioktil tereftalat (DOTP) sentez reaksiyonları ve DOTP ile plastikleştirilmiş PVC'nin özellikleri üzerine kısa derleme

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Abstract

PVC is one of the commonly preferred thermoplastics. Plasticizing additives or plasticizers are added to break interstrand-dipole interaction in PVC and soften PVC in general. Plasticizers have many applications such as electrical connectors, vinyl floorings, vinyl water stops, toys, bottle caps, and medical devices. Although a great majority of plasticizers are phthalates that harm to environment, Dioctyl terephthalate (DOTP) is known as a non-phthalate plasticizer. DOTP, one of the plasticizers preferred in the industry, is an aromatic terephthalate. There are two main production methods of DOTP; direct esterification and transesterification. In this review, different synthesis reactions of DOTP plasticizer were summarized. Studies have generally focused on different catalysts, solvents, reactant ratios, and reaction conditions such as temperature, pressure, and reaction time in literature. Synthesizing DOTP from scrap PET products is an environmentally friendly manufacturing method. Besides, properties of DOTP plasticized PVC, mainly migration, mechanical and thermal properties, have been reviewed. According to the results, DOTP has high compatibility with PVC, and DOTP plasticized PVC shows good migration, mechanical and thermal properties. DOTP is a promising plasticizer due to having good properties, low production cost, and low toxicity.

Keywords: DOTP, Esterification, Transesterification, PVC, Mechanical properties, Thermal properties.

Öz

PVC, yaygın olarak tercih edilen termoplastiklerden biridir. Plastikleştirici katkı maddeleri veya plastikleştiriciler, PVC'de dipol bağlar arası etkileşimi kırmak ve genel olarak PVC'yi yumuşatmak için kullanılmaktadır. Plastikleştiricilerin elektrik konektörleri, vinil zemin kaplamaları, vinil su tutucuları, oyuncaklar, şişe kapakları, medikal cihazlar gibi pek çok uygulaması bulunmaktadır. Plastikleştiricilerin büyük çoğunluğunu çevreye zararlı ftalatlar oluştursa da, Dioctyl tereftalat (DOTP), ftalat içermeyen bir plastikleştirici olarak bilinir. Endüstride tercih edilen plastikleştiricilerden biri olan DOTP, aromatik bir tereftalattır. DOTP'nin doğrudan esterleştirme ve transesterleşme olmak üzere iki ana üretim yöntemi bulunmaktadır. Bu derlemede, DOTP plastikleştiricinin farklı sentez reaksiyonları özetlenmiştir. Literatürde, çalışmalar genellikle farklı katalizör, çözücü, reaktan oranları ve sıcaklık, basınç, reaksiyon süresi gibi reaksiyon koşullarına odaklanmaktadır. Atık PET ürünlerinden DOTP sentezlemek çevre dostu bir üretim yöntemidir. Ayrıca, başlıca migrasyon, mekanik ve termal özellikleri olmak üzere DOTP ile plastikleştirilmiş PVC'nin özellikleri ele alınmıştır. Sonuçlara göre, DOTP, PVC ile yüksek uyumluluğa sahiptir ve DOTP ile Plastikleştirilmiş PVC iyi migrasyon, mekanik ve termal özellikler sergilemektedir. DOTP, iyi özelliklere, düşük üretim maliyetine ve düşük toksisiteye sahip olmasından dolayı gelecek vaat eden bir plastikleştiricidir.

Anahtar kelimeler: DOTP, Esterleşme, Transesterleşme, PVC, Mekanik özellikler, Termal özellikler.

1 Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer resin, which belongs to the family of polyester, and polyester is defined as a polymer that includes an ester group in its basic chain [1]. It is generally used as engineering plastics because of having good rigidity/weight ratio, chemical resistance, mechanical property, and low permeability to O_2 and H_2O [2],[3]. Due to the increase in the production of PET, the treatment of scrap PET has become a more and more important issue. Production of high-value molecule from scrap PET has both economic and environmental advantages [4]. On the other hand, PVC is widely used in various areas due to its high versatility, durability, contamination resistance, and inexpensiveness to produce [5]-[7]. It is utilized in packaging, plastisol, coatings, toys, household, automotive, construction, furniture, imitation leather, medical tubing, electrical and electronics areas, etc. [8]-[10]. However, having high glass transition temperatures (Tg) makes PVC brittle. Moreover, its phase at room temperature is rigid [11]. Therefore, plasticizers should be used to soften PVC and meet desired specifications [12]. Plasticizers generally have low molecular weight nonvolatile chemicals, especially in polymer processing [13], and they are applied to enhance some properties such as durability, stretch ability, flexibility, density, viscosity, elastic modulus, and elongation of products [14]-[18]. Plasticizers or plasticizing additives are used for interstrand-dipole interaction breaks in PVC, resulting in a material with not only mobility and flexibility properties but also with less interchain interaction [6]. Nearly 300 chemical materials may be utilized as a plasticizer for PVC, and 100 of those can be classified as commercially important materials [19]. Though phthalates are composed of the majority of the generated plasticizers, they are harmful to the environment. Alternative plasticizers, having low toxicity and leaching potential, to phthalates have been preferred. Di(2-ethylhexyl) terephthalate is known as a non-

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phthalate plasticizer. DEHT, DEHTP, DOTP, dioctyl terephthalate, bis-2-ethylhexyl terephthalate, bis (2-ethylhexyl) benzene-1,4-dicarboxylate and Eastman 168TM are the other used names of di(2-ethylhexyl) terephthalate [20]. In this paper, the names of the compounds have been used interchangeably. DOTP is preferred instead of dioctyl phthalate (DOP), which is a commonly used plasticizer in the industry for the reasons of being low in toxicity and having good performance [21]. DOTP is an aromatic terephthalate, and its molecular structure is shown in Figure 1. Di(2-ethylhexyl) terephthalate (DEHT), which is composed of 2- ethylhexanol and terephthalic acid with an ester linkage, and Di-(2-ethylhexyl) phthalate (DEHP) are isomers, but DEHT is less toxic than DEHP due to complete hydrolysis of ester bonds to non-toxic products [22],[23].

Figure 1. Structural geometry of DOTP.

DOTP has low volatility since it has a long hydrocarbon chain and its molecular weight is high [14]. Properties of DOTP are tabulated in Table 1. There are many applications of DOTP such as in coatings, coating for clothes, electric connectors, vinyl floorings, vinyl water stops, toys, bottle caps, membranes, drug absorption, and medical devices [24]-[28]. In this study, after the production methods of DOTP and different DOTP synthesis are reviewed, the properties of DOTP plasticized PVC are discussed.

Table 1. Properties of DOTP [29]-[31].

Properties	Values
Chemical Formula	$C_{24}H_{38}O_4$
CAS No	6422-86-2
Molecular Weight (g/mol)	390
Appearance	Colourless liquid
Colour (Hazen)	Max 30
Odour	Mild & characteristic
Density (g/cm^3 at 20 °C)	0.980-0.985 (ASTM D 1045)
Viscosity (cp)	86-94 (ASTM D 1045)
Flash Point (°C)	Min 210 (ASTM D 1045)
Water Concentration	Max %0.05 (ASTM D 1364)
Refractive Index (at 20 °C)	1.4830-1.4890 (ASTM D 1045)
Acid Index (mg KOH /g)	Max 0.1 (ASTM D 1045)

2 Synthesizing of DOTP

There are two main methods to produce DOTP. Esterification and/or transesterification reaction methods, which are utilized by 2-ethylhexanol and terephthalic anhydride/acid and/or terephthalate esters, respectively, is usually used to obtain DOTP. Hydrocarbon solvent is generally applied to the reaction with homogeneous catalysts.

Cook et al. synthesized DOTP by esterification of terephthalic acid (TPA) with 2-ethylhexanol (2-EH) at elevated pressure and temperature. Reaction has occurred with titanium or titanium compound catalyst, soluble in the reaction mixture. Reaction conditions were as follows: mole ratio of EH/TPA was at 2:1 to 2.5:1, total pressure was at 100 to 400 kPa, temperature range was kept at 180 °C-270 °C. Besides, an inert gas was used to remove the mixture of 2-EH and water from the reaction zone. Titanium tetraisopropoxide (TIPT) was utilized as a catalyst in examples. According to the analysis, obtained DOTP has approximately 99% in purity [32]. Similar work was done by Osborne et al. TPA and alcohol comprising one or more of C_6 to C_{10} alcohol were used to obtain DOTP. Temperature range was 150 °C-270 °C, and pressure was at atmospheric pressure. The alcohol/TPA mole ratio was at 2:1 to 2.5:1. Titanium catalyst was $Ti(OR)_4$, where R was an alkyl group having 1 to 8 C atoms. An inert gas such as nitrogen was provided to take water from the reaction mixture. A fractionation column is attached to the reactor to remove water [33]. Zeng synthesized DOTP by esterification reaction of TPA and 2-EH. The yield of DOTP was obtained to be higher than 99.5% when the mole ratio of 2-EH/TPA was 2.7-3:1 with tetrabutyl titanate catalyst weight amount of 0.5-0.7% [34]. In a study by Du et al., TPA was produced using a two-step reaction. After coal acid (CA) was synthesized at 260 °C, TPA was obtained by isomerization of CA with Cadmium carbonate ($CdCO_3$) as a catalyst and CO_2 pressure. Then, DOTP was obtained by reaction of isooctanol and refined TPA with the presence of tetrabutyl titanate catalyst. Ester proportions were observed by changing the mol ratio of TPA to isooctanol, amount of catalyst, and reaction time. The optimum mol ratio of TPA to isooctanol, catalyst and reaction time were evaluated to be 1:3, 1.0 g, and 1.5 h, respectively [35]. Purified terephthalate (PTA) from waste material and octyl alcohol were used to synthesize DOTP in a study by Hua et al. Optimum esterification conditions were determined as 1:2.30 mole ratio of PTA to octyl alcohol, 230 °C in temperature, and 5.5 h in reaction time [36]. Liao et al. investigated to produce DOTP by decreasing reaction time and enhancing reaction efficiency. PTA and straight-chain or branched-chain alcohol containing 6 to 10 carbon atoms (C_6-C_{10} alcohol) with the ratio of 1:0.8-1.5 were mixed and fined by a homogenizer up to particle size 80-110 µm. Excess C_6-C_{10} to final DOTP weight and one or more groups consisting of 2-EH, isononyl alcohol, and isodecyl alcohol were added to the obtained slurry. Then titanium-based catalyst of 0.1-2 wt% based on final DOTP weight was used. The reaction occurred between -30 and 1013 mbar in pressure and 200-250 °C in temperature. After the esterification reaction (2-3 hours), the alkaline metal hydroxide solution was used for neutralizing the mixture. Residual alcohol was removed, and DOTP was obtained by applying drying and filtration steps. Reaction time can reduce by 37.5-50%, and the purity of the synthesized DOTP is higher than 99.5% [37]. Li et al. analyzed the effects of pressure on the esterification reaction of DOTP from TPA and 2-EH. They concluded that keeping low pressure at the early reaction was beneficial. Negative pressure has advantages in promoting yield at later stage [38]. Xinpeng and Tianxiang examined the reaction kinetics of esterification of DOTP. Reactants were p-phthalic acid and isooctanol with $SnCl_2$

nonacid catalyst. Rate was defined as first order for nonacid catalytic esterification with the rate constant of $k=3.82\times10^4\exp(-4837/T)$. The activation energy was obtained as 40.22 kJ/mol [39]. Mechanism and kinetics of DOTP synthesis were investigated by Wei et al. TPA reacted with 2-EH with the presence of tetrabutyl titanate catalyst to obtain DOTP. They observed that change in the concentration of components with time fit consecutive reaction. While obtaining monoisooctyl terephthalate was a slow step (first step), synthesizing of DOTP from monoisooctyl terephthalate and 2-EH was a fast step (second step). The reaction rate constants ratio was found approximately 19. A second-order kinetic equation was suggested for DOTP synthesis, assuming that the controlling step was the first step [40].

Diester DOTP can be obtained by the transesterification method of dimethyl terephthalate (DMT) and 2-ethylhexanol (2-EH). Figure 2 shows the transesterification reaction of DMT and 2-EH to obtain Diester DOTP. R refers to 2-ethylhexyl in the figure.

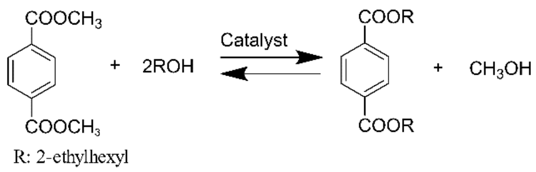

Figure 2. Transesterification reaction of dimethyl terephthalate (DMT) and 2-ethylhexanol (2-EH).

Firdovsi et al. [41] made a study to synthesize bis-(2-ethylhexyl) terephthalate by transesterification reaction using different heterogeneous catalysts in the absence of solvent. The molar ratio of DMT to 2-EH was selected as 1:2 with different temperature scales and reaction times. The type of catalyst, providing high conversion of DOTP in the experiment, reaction conditions, and conversion of DOTP is tabulated in Table 2. The conversion was calculated based on the amount of collected methanol. Methanol, a side product, was picked up in the Dean-Stark trap by distillation. According to the results, Cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$) and Sulfated zirconia with the conversion of 93% and 85.6% performed better activity than the other catalysts. Moreover, the extent of conversion increased under the inert gas stream because of the extraction of more methanol.

Table 2. Reaction conditions and conversions of DOTP with heterogeneous catalysts [41].

Catalyst	Temperature range of reaction (°C)	Reaction time (min)	Conversion (%)
$Cd(CH_3COO)_2{\cdot}2H_2O$	140-170	180	85.6
$Cd(CH_3COO)_2{\cdot}2H_2O$*	140-170	105	93.6
$Pb(CH_3COO)_2{\cdot}3H_2O$	140-170	160	77.2
Sulfated zirconia	140-180	260	85.6
$Zn(CH_3COO)_2{\cdot}2H_2O$	140-175	190	45.4
$Zn(CH_3COO)_2{\cdot}2H_2O$*	140-175	100	77.2

*: Under inert N_2 condition.

On the other hand, DOTP can be produced from terephthalate polyesters like PET by using degradative transesterification. This process is not only cost-effective but also environmentally friendly since scrap PET is utilized to obtain DOTP. Acids, bases, and some metal salts have been investigated as catalysts for PET degradation. Dupont and Gupta [42] studied on producing DOTP and executing cost accounting in 1994. Firstly, three different scrap PET products were cleaned and pelletized. Then, they were reacted with 2-ethylhexanol in a conventional esterification reactor. At nearly 220 °C, the reactants were heated with a catalyst between 4 and 6 hours. In the reaction, alcohol with a 20% excess amount was used. Reaction takes place as follows.

$$\text{PET} + 2 - \text{EH} \rightleftarrows \text{DOTP} + \text{EG} \qquad (1)$$

According to the authors, to obtain 1 kg DOTP, nearly 500 grams of scrap PET is sufficient [42]. Thavornsetawat et al. synthesized TPA with 92% purity from PET bottles using NaOH catalyst in non-aqueous ethylene glycol. Before using PET bottles, they were cleaned with water, exposed to 100 °C for 6 hours, and ground. The reaction took place at 180 °C for 1 hour in a nitrogen atmosphere. Then, DOTP was obtained by direct esterification reaction of TPA and 2-EH at 160 °C for 6 hours. The obtained DOTP has slightly yellowish color, refractive index of 1.472, a specific gravity of 0.936, and 0.0044 mg KOH/g acid value [43]. In a study by Zuoyun et al., DOTP was obtained from waste PET and 2-EH using a solvent which improved the separation rate of ethylene glycol (EG) from the system. $Zn(CH_3COO)_2$ with the amount of 2-5% was chosen as the appropriate catalyst. Optimum reaction conditions were observed with the weight ratio of PET/2-EH to be 1:2 and temperature range of 190 °C-230 °C. Besides, reaction time decreased as reducing sizes of PET [44]. Waste PET reacted with 2-EH to produce DOTP. Solid super-acid (SM), a new solid catalyst, was utilized. The optimum PET/2-EH molar ratio and catalyst/PET mass ratio were 1:3.8 and 1:8.4, respectively. The reaction time of 3h and reaction temperature range of 210 °C-220 °C were selected as optimum parameters, and the yield of the final product was calculated as 97.2% [45]. Zhang and Wu produced DOTP by degradative transesterification of 2-EH and waste sensitive film at 170 °C-220 °C. Mono-n-butyltin oxide was used as a catalyst. If the mol ratio of 2-EH/waste sensitive film and amount of catalyst was 3:1 and 0.25%, respectively, more than 99% of products included DOTP and yield of DOTP was calculated as higher than 90% [46]. Liang and Tao utilized a composite oxide (SnO_2-ZnO) for synthesizing DOTP from PET and 2-EH compounds. Optimum reaction conditions to obtain DOTP were evaluated as 1:3.8 for molar ratio of PET/2-EH and 13.10% for the quality ratio of catalyst/PET. Besides, when reaction temperature and time were 210 °C - 220 °C and 3 h, the productivity value of DOTP enhanced by 96.18% [47]. DOTP was synthesized from waste PET using tetrabutyl titanate catalyst in the aprotic solvent (N-methyl-2-pyrrolidinone) by Shi et al. Effects of molar ratio, reaction time, solvents type, and volume on the yield of products were investigated. According to the results, the initial phase was the nonhomogeneous reaction. The main impact on the reaction rate was the mass transfer coefficient between solid and liquid. The yield of DOTP was found as 78.1% using 2-EH/PET mole ratio of 4, N-methyl-2-pyrrolidinone/2-EH volume ratio of 4, catalyst/PET weight ratio of 0.5%, and reaction time of 2 h [48]. The isooctanol alcoholysis of the scrap PET with Brönsted-Lewis acidic ionic liquid (IL) was investigated for producing DOTP and EG.

Different catalysts for the alcoholysis were tested and evaluated with regards to the conversion of PET and yield of DOTP. Conversion and selectivity values are given in Table 3.

Table 3. Conversion of PET and yield of DOTP with different catalysts [49].

Catalyst	X_{PET}(%)	Y_D(%)
$ZnCl_2$	93.2	78.6
$Zn(CH_3COO)_2$	92.5	88.2
$(CH_3CH_2CH_2CH_2O)Ti$	93.2	89.0
H_2SO_4	70.1	67.5
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl$	40.1	35.4
$[C_4H_6N_2(CH_2)_3SO_3H]_3PW_{12}O_{40}$	97.5	94.7
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (x =0.50)	42.4	38.6
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (x =0.60)	86.0	84.2
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (x =0.64)	94.2	88.6
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (x =0.67)	100	97.6
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (x =0.75)	100	97.9
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ (x =0.67)	100	95.7
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_2$ (x =0.67)	87.7	78.9
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}CuCl_2$ (x =0.67)	40.3	37.3
$[C_4mim]Cl\text{-}FeCl_3$ (x =0.67)	92.1	91.4

According to results, by using IL (3-sulfonic acid) propyltriethylammonium chloroironinate $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$ (molar fraction of $FeCl_3$, x =0.67) catalyst performed better activity than the others. So, the reaction occurred by mixing 20 g PET, 4.0 g IL, and 33.9 g isooctanol with reflux for 8 h. Firstly, EG was separated by adding water into a separator. After the reaction, unreacted PET was taken by filtration, and IL was separated by decantation from DOTP and isooctanol. Finally, DOTP was obtained by applying distillation. In this study, PET was degraded 100%, and the yield of DOTP was found as 97.6 % [49].

To obtain DOTP, usage of [Bmim]Cl, which is an ionic liquid (IL) as cosolvent, tetrabutyl titanate ($Ti(OC_4H_9)_4$), and zinc acetate (ZA) as catalysts, isooctyl alcohol (2-EH) and PET is another technique. Firstly, PET was cleaned and heated at 318 K for 12 hours. After the alcoholysis process at atmospheric pressure, residual solid PET was separated, and distilled water was added to liquid products to take from the water-soluble substance like EG and IL. 2- EH was removed by distillation. Later, DOTP was obtained by using HPLC. Products of EG, solvent, and 2- EH were refluxed at nearly 200 °C. PET was degraded nearly 100%.

Yield of DOTP was determined as 93.1% at optimum conditions with 5 hours, and the weight ratio of catalyst to PET, IL, 2-EH, PET was 0,012:2:2:1, respectively [4]. Alcoholysis of PET was carried out by using sub, and supercritical isooctyl alcohol (2-EH) by Liu et al. Appropriate reaction conditions were selected 573 K as temperature, 4 as the weight ratio of 2-EH/PET, and 3 hours as reaction time. It was observed that by increasing the temperature and time of the reactions, DOTP converted into terephthalic acid (TPA). The reaction occurred in the autoclave batch reactor. PET was degraded by 100%, and the yield of DOTP was found as 97% without using catalysts. After 2-EH which is a water-soluble component was removed from liquid products, pure DOTP was obtained by using SiO_2 column chromatography [50]. DOTP was synthesized from PET by using 2-EH and choline chloride-based deep eutectic solvents (ChCl-based DESs) at a study executed in 2019 [51]. The DESs were generated by ChCl and $Zn(Ac)_2$ with different molar ratios. The reaction with various catalyst types was performed under atmospheric pressure and reaction time took nearly 1 hour. Conversion of PET and yield of DOTP are tabulated in Table 4.

Table 4. Reaction conditions and degradation of PET with different catalyst type [51].

Catalyst	Temperature (°C)	Time (h)	X_{PET} (%)	Y_D (%)
Without catalyst	185	1	1.5	-
ChCl	185	1	3.4	-
$ChCl/Zn(Ac)_2$ (1:1)	185	1	~100.0	84.2
$ChCl/Mn(Ac)_2$ (1:1)	185	1	96.5	80.6
$ChCl/Co(Ac)_2$ (1:1)	185	1	90.4	74.1
$ChCl/Cu(Ac)_2$ (1:1)	185	1	91.7	76.2
$ChCl/FeCl_3$ (1:1)	185	1	94.5	78.3
$Zn(Ac)_2$	185	1	46.4	40.6

After optimizing conditions, the molar ratio of $ChCl/Zn(Ac)_2$ and PET:2-EH were reported as 1:1 and 1:5, respectively, at 180 °C and 60 minutes of reaction time. Conversion of PET and yield of DOTP were obtained as 100% and 84.2%. Moreover, results indicated that the order of the PET alcoholysis reaction accompanied with DES was the first order, and the activation energy was found as 95.05 kJ/mol [51].

Zhao et al. aimed a novel approach for separation of PVC-PET mixtures by using surface micro-alcoholysis treatment (SMAT). Temperature, zinc acetate concentration, and operating time are variables in controlled in SMAT. Optimal design conditions were reported as 346.5 K in temperature, stirring rate of 100 rpm, 1:5 poly mixtures: 2-EH mass volume ratio, $Zn(Ac)_2$ with 0.3 wt%, and 84.13 minutes in operating time. However, DOTP was obtained at a retention time of 8.460 and 9.226 minutes according to the UPLC spectrum. The peaks at m/z of 602.113 and 805.324 show dimer of DOTP, while the other two peaks, 995.265 and 1197.496, should belong to trimeric DOTP composed of the majority [52]. In another study by Ding et al., the kinetics of the reaction were examined. When the sub-critical 2-EH was used at 533-593 K, obtaining DOTP from PET alcoholysis was slow with the activation energy of 82.14 kJ/mol. On the other hand, the decomposition of DOTP was fast in the super-critical 2-EH medium and the apparent activation energy was calculated as 30.29 kJ/mol. Moreover, it was observed that the batch-type reactor was suitable for sub-critical proses while for the super-critical process, a continuous flow reactor was a preferable reactor [53]. In the studies carried out so far, different synthesis conditions such as different catalyst, solvent, temperature, time, purification have been investigated rather than creating different methods.

3 Properties of PVC with DOTP

Many studies have been conducted on plasticizers and their properties. Plasticizers should meet the required specifications such as migration properties, stability, tensile strength, and volatility. These specifications can change according to the desired final products. One of these required specifications is the migration property of plasticizers from plasticized PVC films. Tüzüm Demir and Ulutan carried out a study about the migration property of certain plasticizers. According to their results, [6] although the molar mass of DEHP is the same as that of DOTP, the mass loss of the film with DOTP is less than that of DEHP, diisononyl-phthalate (DINP), and di-isodecyl phthalate (DIDP). Therefore, it was concluded that DOTP was more compatible with the PVC polymer chain than DEHP because of its planar spatial arrangement.

In a study by Chen et al., cardanol acetate (CA) and epoxidized cardanol acetate (ECA) plasticizers, made of cardanol, DINP, and DOTP were compared to each other. PVC and plasticizers were added with a ratio of 100:25. The study showed that the percentage of weight loss at 0-220 °C, 220-340 °C, and 420-600 °C were less than 1.5, 62.42, and 17.66 %, respectively. Besides, the weight loss of plasticizers with PVC was investigated after extraction, exudation process and volatility test (see Table 5). Tensile strength and elastic modulus of DOTP were high regard to the other plasticizers in the study. Moreover, dynamic stability for DOTP/PVC was observed as 12.8 minutes [8].

Table 5. Weight loss of PVC with different plasticizers after extraction and exudation process, and volatility test [8].

	Weight losses (%) of PVC films after		
	Extraction	Exudation (*10^3)	Volatility
CA/PVC	0.19783	1.84	0.27839
DOTP/PVC	0.21042	5.52	0.08151
DINP/PVC	0.23538	0.950222	0.09945
ECA/PVC	0.20953	0.0588474	0.14769

Migrations of five different plasticizers from child care articles and children's products were analyzed by Babich et al. Plasticizers were acetytributyl citrate (ATBC), DEHT, DINP, diisononyl 1,2-cyclohexanedicarboxylic acid (DINX), and 2,2,4-trimethyl-1,3 pentanediol diisobutyrate (TPIB). The minimum migration rate of plasticizers in saliva simulant was found as 1.41μg/10cm^2/min using DEHT. The lowest children's daily exposure was estimated as 0.74 μg/kg-d with DEHT. They concluded that DEHT, TPIB, ATBC, and DINX were still the main phthalate-free plasticizers used in children's products [54]. Liu et al. carried out a study on migration resistance, cold resistance, thermal stability, and mechanical properties of PVC with different plasticizers; a series of oleate plasticizers, di-octyl adipate (DOA), and DOTP. They synthesized 1,8-octanediol dioleate (ODD), 1,4-cyclohexanedimethanol dioleate (CDD), epoxy 1,8-octanediol dioleate (E-ODD), epoxy 1,4-cyclohexanedimethanol dioleate (E-CDD), acetyl 1,8-octanediol dioleate (A-ODD), and acetyl 1,4-cyclohexanedimethanol dioleate (A-CDD). 50 g DOTP was added per 100 g PVC resin. While maximum weight loss of DOTP occurred in petroleum ether, minimum DOTP migrated out of PVC in distilled water. DOA, E-CDD and A-CDD presented better plasticizing effects than DOTP under low temperature. Although the initial degradation temperature (T_i) of DOTP was higher than that of DOA, T_i of oleate plasticizers was about 20 °C higher than DOTP. Besides, weight loss at 150-330 °C, 330-425 °C, and 425-510 °C were observed as 63.0%, 14.4% and 15.8%, respectively. DOTP had the highest tensile strength and apparent modulus of DOTP at 200%, 400%, and 600% among them. Also, elongation at break, elastic modulus, and shore hardness were reported as 650.5 ± 17.6%, 7.2 ± 0.3 MPa, and 89.6 ± 1.4 HA, respectively. Transmittance values in the 400-800 nm wavelengths showed that DOTP had higher transparency than DOA, A-ODD and ODD plasticizers [55]. Altındağ and Akdoğan investigated migration of plasticizers in PVC based artificial leather with spectrophotometric characterization. For this purpose, five non-phthalate plasticizers; DOTP, DOA, tributyl trimelliate (TBTM), trioctyl trimelliate (TOTM), and dioctyl succinate (BIO) with three levels (40,60 and 80 phr) were used to obtain plasticized PVC film. According to their results, DOTP has high compatibility with PVC because of having stronger interaction with PVC. Migration of DOTP was found to be less than BIO and DOA at 40 phr. The leaching test demonstrated that DOTP migrated from PVC to water was less than BIO migration. However, DOTP had higher migration in isobutanol according to the weight loss of the PVC films [56]. In a study by Cheng et al., gel actuators with DOTP and PVC were synthesized and dynamical creeping deformation of them was studied by electrostimulation. Ratios of PVC mass to plasticizer mass were altered to 1:1, 1:2, 1:3, 1:4, and 1:9. The migration of DOTP indicates the deformation during electrostimulation. In this study, the migration of DOTP from the gel happened around the anode. Moreover, it was observed that deformation of the gel was related to concentrations of DOTP plasticizer. The memory effect of the deformation resulted from the DOTP residue after each shutdown [57]. Migration values of plasticized PVC in different fluids were tabulated in Table 6.

Migration rate of plasticizers can be reduced. Tüzüm Demir made researches on DOTP plasticizer to enhance migration rate properties by using clay filler (CF, kaolinite) and boron waste sludge (BWS). Diffusion of prepared plastisol film, including PVC resin, DOTP, CF, BWS, epoxidized soybean oil (ESBO) and hydrotalcite as heat stabilizer, into air was investigated at 100 °C, 130 °C and 150 °C. To conclude, the oxidation index of films generally increased with increasing temperature and treatment time. Besides, while the film without using filler has a maximum mass loss, films with BWS show lower mass loss than others. BWS addition to plasticizer improved the activation energy for the diffusion of DOTP [58].

Table 6. Migration of plasticized PVC in different fluids.

Plasticizer	Plasticizer composition in PVC sample	Migration in water (%)	Migration in isobutanol (%)	Migration in 15% (v/v) ethanol (%)	Migration in 3% (w/v) acetic acid (%)	Migration in n-hexane (%)	Ref.
DOTP	25/100	~0.21	-	-	-	-	[8]
DINP	25/100	~0.24	-	-	-	-	
ECA	25/100	~0.21	-	-	-	-	
CA	25/100	~0.20	-	-	-	-	
DOTP	50/100 g	~0.28	-	~0.55	~0.21	~18.1	[55]
CDD	50/100 g	~3.10	-	~3.50	~3.13	~23.5	
ODD	50/100 g	~5.45	-	~4.78	~5.22	~20.4	
TOTM	60/100 phr	-	~15.12	-	-	-	[56]
TBTM	60/100 phr	~0.18	~9.67	-	-	-	
DOTP	60/100 phr	~3.13	~21.10	-	-	-	
BIO	60/100 phr	~4.56	~22.60	-	-	-	
DOA	60/100 phr	~2.84	~27.12	-	-	-	

Zhang et al. prepared silicon dioxide@poly(acrylic acid) (SiO_2@PAA) microspheres at different concentrations. They added SiO_2@PAA microspheres and chlorinated polyethylene (CPE) with different amounts to PVC composites with DOTP. Volatility loss, exudation loss of DOTP, extraction loss of DOTP by distilled water, castor oil and absolute ethanol were analyzed, separately to understand the effects of SiO_2@PAA microspheres and CPE on the migration characteristics. Increases in CPE and PAA amount in SiO_2@PAA microspheres resulted in less volatility loss, and minimum weight loss was provided with PVC/7.5 g CPE/10 g SiO_2@PAA composites according to the volatility loss analysis. Compared to pure PVC, DOTP migration of PVC/SiO_2@PAA composites by used fluid reduced effectively. CPE prevents plasticizers from moving through the PVC matrix and migration to the PVC surface and, plasticizers cannot be extracted easily when CPE is present. SiO_2@PAA microspheres and CPE had synergistic effects on reduced DOTP migration, according to the extraction loss analyses.

Besides, tear strength, tensile strength and elongation at break of PVC composites were investigated. Results demonstrated that an increase in CPE amount caused a decrease in tear strength and tensile strength. On the other hand, elongation at break of the composite increased with CPE amount [59]. Mendizabal et al. used gamma radiation with different dose rate to enhance extraction resistance of DOTP plasticized PVC. Extraction resistances of DOTP plasticized PVC into hexane, soapy water and mineral oil were investigated. According to the study, extraction resistance was improved by irradiation compared to without irradiation, but a steady decline was not observed as the radiation increased [60].

In a study by Tüzüm Demir and Ulutan, PVC films with different plasticizers degraded to polyene under isothermal conditions. The activation energy of DOTP for obtaining polyene from PVC was found to be the largest among DIDP, di-isononyl 1,2-cyclohexanedicarboxylic acid (DINCH), and DEHP plasticizers. It showed that DOTP was resistant to decomposition at a temperature between 130 °C and 160 °C. Moreover, heat stabilities of the films were investigated by UV-vis spectroscopy, and according to the results, DINCH and DOTP were reported as having better properties than the others [61]. Degradation kinetics of PVC films containing various plasticizers examined by the same Authors in another study [62]. According to their results, the induction time of DOTP was higher than that of plasticizers including di-octyl maleate (DOM), DIDP, DOA, DEHP, and DINCH except for DINP at 140 °C. Also, the stability of DOTP is greater than that of the other plasticizers due to the compensation ratio. Wang et al. investigated thermal degradation kinetics of PVC with different plasticizers; DOTP, DOP, ATBC, acetyl trioctyl citrate (ATOC), TOTM, and isosorbide ester (ID-37). PVC/TOTM and PVC/DOTP have nearly 7 °C higher T_{onset} value than the others. $T_{20\%}$, $T_{50\%}$, and $T_{80\%}$ values were obtained as 264.9 °C, 290.0 °C, and 431.1 °C with a heating rate of 5 °C/min for PVC/DOTP. These values were also obtained for heating rates of 10, 20 and 30 °C/min. PVC/DOTP display better or comparative thermal stability compared to PVC/DOP. The first and second stages of decomposition were evaluated by Flynn Wall Ozawa (FWO) and Kissinger methods. While the maximum E_2 value was obtained with DOTP by Kissinger method, DOTP had the minimum E_2 value according to the FWO method. DOTP had a minimum E_1 value by both methods. Effects of conversion degree on average E values were also discussed in this study. It was observed that DOTP had high E_a values at a high conversion degree, such as 80% [63]. To reduce thermal degradation kinetics of PVC films, Xue et al. prepared DOTP plasticized PVC films by adding mercaptan methyltin (S) zinc stearate (Z) and dipentaerythritol (D). It was reported that the removal of carboxyl groups from DOTP was reduced substantially, and the release of CO_2 gas became less than 85.2% than that of PVC film without S, Z, and D [64].

Yang et al. synthesized four isosorbide diesters: isosorbide dibutyrate (SDB), isosorbide didecanoate (SDD), isosorbide dihexanoate (SDH), and isosorbide dioctanoate (SDO), as biobased plasticizers. Synthesized plasticizers and DOTP to comparison were blended with PVC, and then mechanical and thermal properties of prepared plasticized PVC were evaluated. Plasticized PVC includes 10 g of PVC, 4 g of plasticizer and 0.4 g of calcium zinc heat stabilizer. Tg value of PVC/DOTP was found as 32.8 °C, and according to the authors, PVC and DOTP are thermodynamically compatible with each other. Also, tensile strength, tensile modulus and elongation at break were evaluated as 18.4±0.2 MPa, 38.1±2.0 MPa, and 238.3±2.2%, respectively. Hardness tests indicate that plasticized PVCs have a lower hardness value than pure PVC. Moreover, temperatures at the mass loss of 5%, 10% and 50% and maximum weight loss were calculated. Accordingly, although the molecular weight of DOTP and SDO were similar, weight losses of DOTP for 24 h and 72 h were less than SDO. Besides, DOTP showed better stability with PVC due to the possibility of benzene ring providing excellent thermal stability [65]. Mechanical characteristics of plasticizers in PVC based artificial leather were also investigated by Altındağ and Akdoğan. The tensile strengths of the films, including DOTP and TOTM plasticizers, were higher than the others at all levels. Maximum elongation at break was acquired with DOTP plasticized PVC at 80 phr. Moreover, cold flexible features of plasticized PVC with 80 phr were studied. DOTP plasticized PVC was cracked after nearly 300.000 flex cycles [56]. Pereira et al. prepared PVC with biobased end-capped saturated polyesters (SPs) and evaluated the properties of plasticized PVC samples by comparing PVC with DOTP plasticizer. Obtained samples consist of PVC, plasticizer, stearic acid (StAc) and Baerostab NT/MZ-5 with the amount of 25.58, 12.79, 0.076, and 0.256 g, respectively. Results show that 10% of mass loss data by TGA and Tg value were obtained at 250.02 °C and 23.7 °C. Moreover, Young's modulus (E), elongation at break (ε) and tensile strength (σ) were measured 33.27±1.50, 20.30±0.44, and 295.17±8.96 respectively. According to the migration test, when cyclohexane and xylene nonpolar solvents were used, the amount of extracted DOTP was higher than that of SP. On the other hand, if ethanol, a polar solvent, was utilized, the weight percentages of extracted SP and DOTP plasticizers were low and almost similar [66]. In a study by Tan et al., dimer acid (DA) based esters plasticizers with the different structure were synthesized and compared with DOTP. According to the results, PVC-DOTP showed good properties in terms of transparency, glass transition temperature, and tensile properties. 5% weight loss occurred at 251.3 °C, and Tg value was detected as 34.7 °C. Also, transmittance of the PVC-DOTP was determined as 32.6%, which is the highest value in plasticized PVC samples, but close to PVC-DA-8 sample. Besides, PVC-DOTP did not lose a substantial amount of weight compared to the other plasticizers, after they were put in distilled water, sodium hydroxide and acetic acid [5].

Coman et al. analyzed the effects of plasticizer and manufacturing method on properties of PVC composites. They used $CaCO_3$ with a size of 2 μm as a reinforcement agent, Ca-Zn salt as heat stabilizer, stearic acid as lubricant and DOTP and DINP for plasticizers in composites. While one group of PVC mixtures were applied the extruding once, another group was passed through the extruder twice. Later structure, overall morphology, thermal behavior, mechanical features, and the limiting oxygen index (LOI) of obtained PVC composite samples were assessed. FTIR analysis showed that migration of DINP is more than DOTP according to reducing of intensity. A smoother surface on the surface of the sample with DOTP was obtained comparing to DINP. Also, DINP and DOTP have similar thermal stability according to TGA analysis. Tg values of the samples, including DINP, was observed nearly 3°C less than that of DOTP. When the extruding process was applied twice, remarkable enhancing in tensile strength and elongation at break properties were observed. LOI value of the sample with DOTP, which pass to extruder second times, was 24.5%. This value demonstrates the flammability of materials [67]. Bee et al. [14] studied the effect of plasticizers on physicomechanical, crystallinity, and thermogravimetry properties of PVC. They found that the highest tensile strength was obtained by adding DOTP to PVC comparing with DOA and DINP plasticizers. Due to having a symmetrical structure, DOTP could show a better balance between nonpolar and polar sections with higher consistency. Moreover, the formation of crystalline structures of DOTP with PVC is less than that of DOA.

Rheological characteristics of DOTP plasticized plastisol was investigated by Guo-min et al. Plastisols were prepared with 100 parts PVC resin and 60 parts plasticizer. Plastisol with DOTP demonstrated shear thinning behavior before and after aging processing. Non Newtonian index values (n) of Plastisol with DOTP were evaluated to be 0.22846, 0.25142, 0.23438 and 0.12576 for 15 °C, 25 °C, 35 °C and 45 °C, respectively. n values of plastisol with DOTP were higher than plastisols with DINCH and ATBC plasticizers. This indicated that DOTP was less dependent on shear rate than DINCH and ATBC plasticizers. In addition, n values of plastisol with DOTP before and after aging processing (1 week) at 25 °C were obtained as 0.20166 and 0.25725 [68]. A study about the viscosity and aging process of plastisols, PVC with using different plasticizers was conducted by Xu et al. In this study, diethylene glycol dibenzoate (DEDB), ATBC, and DOTP were mixed with PVC individually, and viscosities of plastisols were identified. It was found that the viscosity of ATBC/PVC was less than that of DOTP/PVC. Although the compatibility of DOTP/PVC is better than ATBC/PVC, DEDB/PVC has the highest compatibility but the most unstable [69].

He et al. prepared PVC-based tissue-mimicking material (TMMs) composing PVC powder and DOTP. X-ray attenuation coefficients, magnetic resonance imaging (MRI) relaxation times, and computed tomography (CT) numbers classified as medical imaging properties and mechanical properties, including elastic modulus and Poisson's ratios, were investigated. The ratio of PVC-DOTP was changed from approximately 0.079 to 0.23 g/ml and received materials were heated to 280 °C by mixing for 30 minutes. After the mixture became transparent, measurements were performed. According to the measurement, the CT number was reported −10 to 110 HU. The highest linear attenuation coefficient was obtained at the highest softener ratio in samples. While the elastic modulus of samples ranged from 7.000 to 12.376 MPa, Poisson's ratios were evaluated as 0.604-0.644 [70].

DOTP could create a synergistic effect when it is used together with some plasticizers. Wang et al. produced a polyurethane (PU) anchoring agent as a plasticizer for PVC substrate. It was noticed that when the anchoring agent and DOTP were used together, the migration rate at -10 °C was decreased by 95%, while the temperature sensitivity index decreased by 76% [71]. Coltro et al. analyzed the migration of plasticizers from PVC films to food simulants. While PVC with Di(2-ethylhexyl) adipate (DEHA) and ESBO plasticizers remained same, the third plasticizer was changed. ATBC, a mixture of glycerin acetates (MGA), DEHT, Acetylated glycerol monoester (AGM), and Polyadipate were used as third plasticizers separately. PVC film including only DEHA and ESBO referred to reference. Overall migration of DEHT into acidic food simulant exhibit a lower value than the limit set in the legislation. Besides, overall migration into olive oil fatty food simulant was reduced with using DEHT compared to the reference sample [72].

PVC films were prepared with different plasticizer combinations by Coltro et al. While DEHA and ESBO remained constant in PVC film; the third component was varied. When DEHT was the third component, tensile strength was reported to be significantly high [22]. A study about properties of GEHTMA-1, GEHTMA-2, GEHTMA-3, and GEHTMA-4 plasticizers obtained from tung-maleic anhydride and DOTP plasticizer at different ratios with PVC were conducted in 2018 by Wang et al. [73]. GEHTMA-1, GEHTMA-2, GEHTMA-3 and GEHTMA-4 plasticizers were synthesized with HHTT and TMA with the molar ratio of 1:1, 1:2, 1:3 and 1:4, respectively. According to Wang et al., the addition of GEHTMA-3 and DOTP plasticizer to PVC simultaneously improves plasticization properties, mechanical properties, migration resistance, and thermal stability of PVC compare to DOTP with PVC. DOTP and GEHTMA-3 plasticizers with different mass ratios were added to PVC, and strength and elongation properties of PVC film were investigated. (see Table 7) The highest tensile strength and elongation were attained as 31.19 MPa and 345.20%, respectively, using PVC/DOTP/GEHTMA-3 with the ratio of 100/28/12. Besides, optimal thermal stability was reported as PVC/DOTP/GEHTMA-3 with a ratio of 100/32/8, respectively.

Table 7. Strength and elongation values of PVC including different mass ratio of DOTP and GEHTMA-3 plasticizers [73].

Mass ratio of DOTP/GEHTMA-3	Strength (MPa)	Elongation (%)
40/0	22.39	254.62
36/4	27.89	343.09
32/8	29.19	343.5
28/12	31.19	345.2
20/20	33.13	307.75
10/3	29.52	243.16
0/40	31.13	247.67

Table 8 shows that some mechanical properties of plasticized PVC with DOTP and different plasticizers. Triacetin (TAG), which is a glycerol derivative plasticizer, was used as a secondary plasticizer for producing PVC film.

When TAG was added to DOTP based PVC, properties of films were enhanced. In addition to thermogravimetric analysis, density, tensile strength, hardness properties were determined. When DOTP, ESBO, TAG were added with the amount of 48, 2, 10 phr to PVC, density, maximum tension, elongation at break, tension at 100% and Tg values were obtained as 1.23 g/cm3, 15.79 MPa, 317.9%,6.183 MPa, and 13.8 °C, respectively. However, Tg values decreased to 1.3 °C and elongation at break value became 352.5% by increasing the amount of TAG to 20. Minimum Tg value was achieved by formulation including DOTP, ESBO, TAG with the amount of 53, 2, 15 phr [74]. Matos et al. [75] investigated structural, thermal and mechanical properties of PVC blends with DEHT and di(2-ethylhexyl) 2,5-furandicarboxylate (DEHF), which is a sugar based monomer. They prepared PVC blends using zinc stearate, stearic acid, and DEHT/DEHF mixture at five different amounts. Compatibility of PVC/DEHF-DEHT was enhanced compared to the only use of DEHF. Results showed that PVC blends presented reduced Tg (approximately from 97°C to 20°C) and an increased elongation at break (from 247% to 330%) with the addition of DEHF. However, stiffness of the blends decreased by nearly 8 MPa in Young's modulus. To evaluate migration resistance of the PVC blends, distillate water, cyclohexane and sodium phosphate buffer were used. Besides, volatile resistance was determined by burning PVC blends in active carbon. Weight loss percentages in water and sodium phosphate buffer were found to be lower than 0.3% and 0.2%, respectively, for all PVC blends. Weight loss in cyclohexane of PVC/DEHF-DEHT blends was observed to be less than PVC-DEHT. Moreover, PVC/DEHF-DEHT combination showed enhanced green content with cytotoxic results. Wang et al. [76] researched using DOTP with tung oil-based plasticizers as secondary plasticizers. After synthesizing N-(2-amino phenyl) tung maleamic acid (APTMA) and N-(2-amino ethyl) tung maleamic acid (AETMA), They obtained LABTMA-Ca, LAETMA-Ca, LAPTMA-Ca, LABTMA-Zn, LAETMA- Zn, and LAPTMA- Zn. PVC/DOTP composites were prepared by using different configurations. Long term thermal stability was acquired with LAPTMA-Ca and LAPTMA-Zn. Thermal aging test results were compatible with Congo Red test result. Thermal degradation behaviors of PVC composites were determined by TGA. First degradation temperature increased using PVC/DOTP/LAPTMA-Ca/LAPTMA-Zn (PVC1) and PVC/DOTP/LAETMA-Ca/LAETMA-Zn (PVC2) composites. Degradation kinetic parameters of PVC composites were determined by TGA and DTG within 185-375 °C (α = 30% and α = 60%). E_a of PVC1 composite was obtained to be higher compared to other control samples. Besides, PVC1 has a higher storage modulus than others, up to -40 °C. However, storage modulus significantly changed with temperatures. They concluded that partly replace DOTP with LAPTMA-Ca/LAPTMA-Zn in the PVC presented better plasticization performance [76]. According to Chen et al. [77], when DOTP with a ratio of 20% was mixed with a different plasticizer, epoxidized dimeric acid methyl ester (EDAMe), in PVC, the temperature of initial decomposition and first maximum weight increased to 267.2 °C and 298.9 °C, respectively. Thermal properties of plasticized PVC with DOTP and different plasticizers were summarized in Table 9. According to the studies, including DOTP and different plasticizers, substantial improvements in some properties of PVC has been observed.

Table 8. Mechanical properties of plasticized PVC with DOTP and different plasticizers.

Plasticizers in sample	Plasticizer compositions in sample	Shore A hardness (HA)	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Ref.
DEHA/ESBO	5.7/20.6%	83.2±0.1	-	24.5±2.9	227±38	[22]
DEHA/ESBO/DEHT	1.4/5.7/19.2%	91.2±0.4	-	34.5±2.2	190±26	
DEHT/DEHF	22/0 phr	-	8.96 ± 0.26	13.19 ± 0.55	246.64 ± 9.38	[75]
DEHT/DEHF	20/2 phr	-	8.20 ± 0.14	16.37 ± 0.51	316.26 ± 9.65	
DEHT/DEHF	18/4 phr	-	7.58 ± 0.29	17.46 ± 0.54	330.34 ± 11.66	
DEHT/DEHF	16/6 phr	-	7.72 ± 0.45	13.35 ± 0.24	238.63 ± 4.26	
DEHT/DEHF	14/8 phr	-	8.69 ± 0.31	14.57 ± 0.37	225.76 ± 7.49	
EDAMe/DOTP	0/40 g	89.1 ± 0.61	-	26.36 ± 2.84	362.72 ± 27.64	[77]
EDAMe/DOTP	4/36 g	89.5 ± 1.03	-	22.11 ± 0.44	396.24 ± 10.46	
EDAMe/DOTP	8/32 g	89.3 ± 0.45	-	25.83 ± 0.59	416.39 ± 15.01	
EDAMe/DOTP	12/28 g	90.0 ± 0.97	-	22.87 ± 0.90	345.89 ± 16.95	

Table 9. Thermal properties of plasticized PVC with DOTP and different plasticizers.

Plasticizers in sample	Plasticizer compositions in sample	T_{max1} (°C)	T_{max2} (°C)	T_g(°C)	Residue (%)	Ref.
DEHT/DEHF	22/0 phr	305.0	455.7	23.5	8.85	[75]
DEHT/DEHF	20/2 phr	298.7	460.3	22.1	9.93	
DEHT/DEHF	18/4 phr	297.5	459.4	20.4	13.22	
DEHT/DEHF	16/6 phr	295.1	459.2	21.1	10.44	
DEHT/DEHF	14/8 phr	292.3	458.3	21.5	12.75	
PVC/DOTP/LAPTMA-Ca/LAPTMA-Zn	100/50/4.8/1.2 g	305.50	461.40	22.50	12.69	[76]
PVC/DOTP/LAETMA-Ca/LAETMA-Zn	100/50/4.8/1.2 g	301.10	461.70	25.83	11.31	
PVC/DOTP/LABTMA-Ca/LABTMA-Zn	100/50/2.4/0.6 g	304.60	462.10	31.07	12.33	
PVC/DOTP/$CaSt_2$/$ZnSt_2$	100/50/2.4/0.6 g	302.70	462.50	29.47	10.74	
EDAMe/DOTP	0/40 g	292.50	460.30	47.16	8.77	[77]
EDAMe/DOTP	4/36 g	297.20	459.70	44.03	10.79	
EDAMe/DOTP	8/32 g	298.90	456.00	47.21	11.28	
EDAMe/DOTP	12/28 g	297.40	457.30	45.35	10.31	

Plasticized PVC has been used in different areas such as packaging, plastisol, coatings, toys, household, furniture, medical tubing, electrical and electronics areas. Recently, the use of plasticized PVC as a sensor has been investigated, and studies on this issue have been increasing rapidly. There are many studies examining the effect of plasticizers on selectivity in literature [78],[79]. Although many different plasticizers, such as dibutyl phthalate (DBP) [80],[81], DOP, di-2-ethylhexylsebacate (DOS) [78],[79], are used in these studies, there are not enough studies about the use of DOTP as sensor material [82]. Further studies are needed in this regard.

In summary, interest in alternative plasticizers has been increasing, as phthalates are among the harmful chemicals and forbidden in some countries. DOTP plasticizer has been commercialized around 1975 [83]. Due to the structural difference, DOTP is less toxic than DOP. DOTP has been used alternative to phthalate. Since DOTP is a petroleum-based plasticizer, some researchers are concerned about using it. However, it is a significant advantage that DOTP can be produced from waste PET in addition to direct esterification. Besides, the production cost is generally lower compared to bio-based plasticizers. Also, studies demonstrated that DOTP shows good compatibility with PVC, and DOTP plasticized PVC exhibits good properties. On the other hand, it has been observed that newly developed plasticizers have difficulty in providing the desired mechanical and thermal properties with PVC. Czogała et al. also asserted that compared to conventional plasticizers such as DOTP, DOP, novel developed plasticizers have poor properties in most cases [84]. Therefore, several studies have been carried out in which DOTP and different plasticizers are used together. This is a good solution for both improving the desired properties and reducing costs.

4 Concluding remarks

The plasticizers have been generally used for interstrand-dipole interaction breaks in materials and softening them. It is widespread to use polymers with plasticizers. Plasticized PVC is a polymer with a wide range of usage areas such as packaging, plastisol, coatings, electric and electronics. In this review paper, synthesis methods of DOTP and properties of DOTP plasticized PVC were evaluated and summarized. DOTP can be produced by direct esterification of aliphatic alcohols with terephthalic anhydride/acid or transesterification of terephthalate esters with aliphatic alcohols. It is also possible to synthesize DOTP from scrap PET. Since PET is commonly used as a material, there is a high amount of waste or scrap PET in the world. DOTP can be used to decrease scrap PET, and it can be qualified as an environmentally friendly production because it transforms scrap PET into a valuable chemical. In literature, studies have generally focused on different catalysts, solvent, reactant ratios and reaction conditions such as temperature, pressure, reaction time. They generally aimed to obtain DOTP with high yield and purity. Besides, properties of DOTP plasticized PVC, mainly migration, thermal and mechanical properties, have been reviewed. DOTP shows high compatibility with PVC. It also has good thermal and mechanical properties with PVC. Moreover, DOTP could create a synergistic effect with some plasticizers in terms of improvement in migration, thermal and mechanical properties. DOTP is a promising plasticizer as an alternative to phthalate plasticizers owing to having good properties, low production cost and low toxicity. In future, more studies about utilizing DOTP with other plasticizers and an increase in usage areas of DOTP plasticized PVC should be carried out.

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6 Author contribution statements

In the scope of this study, Aycan ALTUN, contributed to the conceptualization, supervision, literature review, writing-original draft. Mehmet Ferdi FELLAH, contributed to the supervision, writing-review & editing.

7 Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the article prepared.

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Appendix A

Nomenclature List.

Abbreviations	Meaning
$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$	IL (3-sulfonic acid) propyltriethylammonium chloroironinate
2-EH	2-ethylhexanol
ATBC	Acetytributyl citrate
ATOC	Acetyl trioctyl citrate
CA	Cardanol acetate
$Cd(OAc)_2 \bullet 2H_2O$	Hydrated cadmium acetate
ChCl	Choline chloride
DA	Dimer acid
DEDB	Diethylene glycol dibenzoate
DEHA	Di(2-ethylhexyl) adipate
DEHF	Di(2-ethylhexyl) 2,5-furandicarboxylate
DEHP	Di-ethyl hexylphthalate
DEHT	Di-2-ethylhexyl-terephtalate
DEHTP	Di-2-ethylhexyl terephthalate
DESs	Deep eutectic solvents
DIDP	Di-isodecyl phthalate

Appendix A: Continued.

Abbreviations	Meaning
DINCH	Di-isononyl 1,2-cyclohexanedicarboxylic acid
DINP	Diisononyl-phthalate
DINX	Diisononyl 1,2-cyclohexanedicarboxylic acid
DMT	Dimethyl terephthalate
DOA	Di-octyl adipate
DOM	Di-octyl maleate
DOP	Dioctyl phthalate
DOS	Di-2-ethylhexylsebacate
DOTP	Dioctyl terephthalate
ECA	Epoxidized cardanol acetate
EDAMe	Epoxidized dimeric acid methyl ester
EG	Ethylene glycol
ESBO	Epoxidized soybean oil
HHTT	N,N,N',N',N'',N''-hexakis-hydroxymethyl-[1,3,5] triazine-2,4,6-triamine
IL	Ionic liquid
PET	Poly(ethylene terephthalate)
PTA	Purified terephthalic acid
PU	Polyurethane
PVC	Polyvinyl chloride
SDB	Isosorbide dibutyrate
SDD	Isosorbide didecanoate
SDH	Isosorbide dihexanoate
SDO	Isosorbide dioctanoate
SiO_2@PAA	Silicon dioxide@poly(acrylic acid)
TIPT	Titanium tetraisopropoxide
$Ti(OC_4H_9)_4$	Tetrabutyl titanate
TMA	Tung-maleic anhydride
TMM	Tissue-mimicking material
TOTM	Trioctyl trimelliate
TPA	Terephthalic acid
TPIB	2,2,4-trimethyl-1,3 pentanediol diisobutyrate
ZA	Zinc acetate
$Zn(Ac)_2$	Anhydrous zinc acetate