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Recent Developments of Biobased Plasticizers and Their Effect on Mechanical and Thermal Properties of Poly(vinyl chloride): A Review

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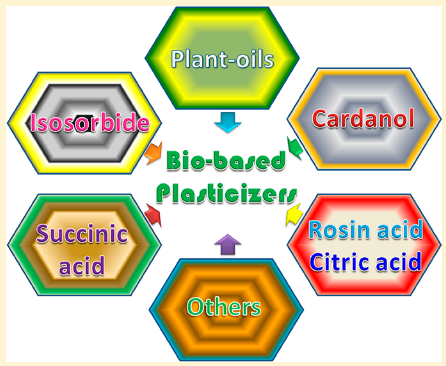
ABSTRACT: Plasticized poly(vinyl chloride) (PVC) has been extensively utilized globally, with various applications in construction, piping, wiring and cable, installation, flooring, nonfood packing, windows, doors, and more. Phthalates have been the most commonly employed plasticizers for PVC, but some of these plasticizers demonstrate many toxic effects on the environment and human beings, which consequently limits the use of phthalate plasticizers. Growing awareness of the effects of plasticizers on the environment and the depletion of petroleum-based resources has made the development of an alternative biobased plasticizer for PVC formulation necessary. Recently, there has been an increased consciousness of the use of natural resource-based plasticizers instead of phthalates in PVC production, because they are eco-friendly in nature. This review paper covers the utilization of traditional and biobased plasticizers for PVC plasticization, and their effect on environmental, mechanical, and thermal properties has been reported.



1. INTRODUCTION

Poly(vinyl chloride) (PVC) is used worldwide as a thermoplastic polymer for various applications such as electrical cables and wire insulation, medical supplies, packaging materials, pipes fitting, and children's toys, etc.[1−8] However, PVC demonstrates a hard and brittle nature due to the existence of a dipole on every C−Cl bond and the interaction between PVC chains, which in turn hinders chain mobility.[9] To enhance the mechanical and thermal properties of PVC, plasticizers are required.[10,11] Furthermore, the plasticizers also provide sufficient flexibility, elasticity, and malleability to the final products. The generally used plasticizers are diesters of the phthalic acid, and also known as phthalates, which are produced in several million tons per year.[12] Figure 1, demonstrated the global utilization of plasticizers in the market.[13]

Currently, 500 types of plasticizers have been industrialized and phthalate is most extensively employed plasticizers (e.g., dioctyl phthalate; DOP) for PVC and covers more than 80% of the overall plasticizer utilization.[14−17] This is attributed to the excellent plasticizing effect and comparatively low cost.[18,19] On the other hand, the used of phthalate plasticizers are problematic owing to their toxic effect on humans and the environment.[20−24] Hence their applications are limited in particular fields such as medical devices, toys, and children's products. Furthermore, many courtiers such as the US and European have restricted the utilization of phthalate in flexible PVC products.[25]

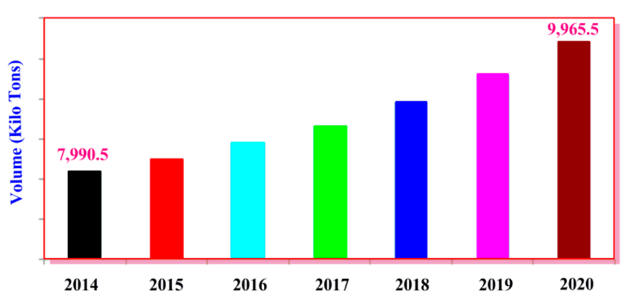


Figure 1. Worldwide plasticizers market, 2014−2020 (kilo-tons).[13]

Conversely, phthalates depend on low molecular weight compounds and easily migrate from the polymer matrix, which is critical for degradation under natural conditions. As a result, the leached out plasticizers have a toxic effect on human health, and are dangerous to the environment.[26−32] Therefore, environmental concerns and deficiency of petroleum resources have generated extensive research on a substitute for the plasticized PVC formulation.[33−35] Thus, many researchers focus their attention on employing biobased plasticizers that are suitable for the environment and are observed as a substitute to phthalates in the plasticization of PVC.[36−42]

Several researchers have described the production and application of biobased plasticizers from renewable resources, for example, plant oils,[43−45] lactic acid,[46] glycerol esters,[47] succinate esters,[48] isosorbide,[49] fatty acids,[50] castor oil derivative,[51,52] and citrate esters.[53,54] In addition, the use of renewable resources-based plasticizers in the PVC matrix prevents their leaching, minimizes deterioration, and offers an

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eco-friendly product for the environment.[55,56] Figure 2 exhibits the application of plasticizers in various fields.

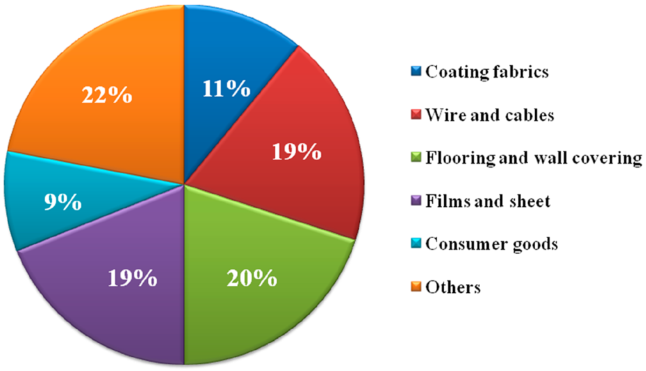

Figure 2. Plasticizer use in various applications.

The present article addresses the contribution of biobased plasticizers to the enhanced mechanical and thermal properties of PVC materials. This Review also provides information about the plasticization mechanism and environmental effect of the traditional and biobased plasticizers. It also widely covers the use of biobased plasticizers in the PVC matrix, working toward the preparation of flexible PVC materials and their future applications.

2. NEED OF PLASTICIZERS

The plasticizer is found in liquid form and added into the resin or elastomer materials to provide softness and more flexibility via the reduced glass transition temperature (T_g) of the polymer, and to ease processing.[57] PVC is the most plasticized polymer in the world because it has exhibited excellent compatibility with plasticizers.[58] The development of the plasticizers is closely related to the synthesis of the commodity polymer, and also plasticizers are employed with other polymer types.

The quantity of plasticizer incorporated into the polymers alters the performance of the polymer. The addition of small amounts of plasticizers enhances the workability of the polymer melts.[59,60] Conversely, the addition of a large amount of plasticizers with a particular objective absolutely changes the properties of the product.[61] Unplasticized PVC (U-PVC) is used in different applications such as siding, window profiles, and pipes while the plasticized PVC is utilized in products such as cable insulations, automotive interior trim, PVC floorings, and jacketing.[62]

2.1. Types of Plasticizers. The types of plasticizers are based on availability, and the toxic effects of the plasticizers can be classified into two categories as shown in Figure 3.

2.2. Traditional Plasticizers. Plasticizers are one of the most significant plastic additives and employed to enhance the durability, plasticity, and flexibility of the polymeric materials. Phthalate esters are the most commonly used plasticizers and account for 80% of the total consumption of plasticizers.[37] The generally employed traditional plasticizers are depicted in Table 1.

2.2.1. Chemistry of Traditional and Biobased Plasticization. In the case of traditional plasticizers such as DOP, DIOP, etc., tthere are fewer polar functionalities, and as a result, there are increasing PVC−PVC chain interactions as shown in Figure 4. Moreover, this phenomenon decreases the free

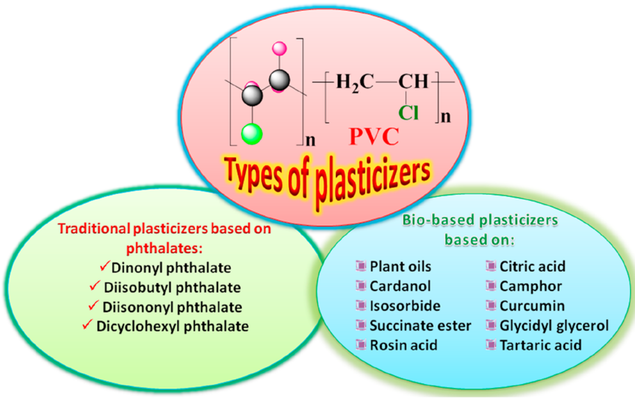

Figure 3. Types of plasticizers used in PVC materials.

volume generated between polymer chains and increases the crystallinity compared to that of the biobased plasticizers. On the other hand, the motion of the polar groups also restricts and decreases the free volume in the polymer chain and provides the rigidity of the polymer.[64]

The biobased plasticizers exhibit more polar groups such as epoxy groups (e.g., diglycidyl ester groups, aromatic ring), and long alkyl chains interact with the polar parts of the PVC molecules, reducing the polymer−polymer (PVC−PVC) interactions and enhancing greater free space among polymer molecules as represented in Figure 5. Further, the movement of the alkyl chains of the biobased plasticizers also creates free space in the polymer. As compared with virgin traditional plasticizers, the addition of biobased plasticizers enhances the indiscriminate movement of the PVC chains in the non-connected areas of the polymer and the volume of the amorphous fraction of plasticized flexible PVC.[65,66]

2.2.2. The Environmental Effect of Traditional Plasticizers. Phthalate plasticizers are the main class of the plasticizers widely used in the common products and easily released into the environment. As they are not strongly bonded to the products, leaching and evaporation take place over the duration of use and affect the environment. As a result, PVC plasticized with phthalate plasticizers has limited applications in flooring, cosmetics, home furnishing, and toys.[64,67,68] Also, traditional phthalate plasticizers can easily liberate from materials via volatilization, scratch, leaching in liquids, and direct diffusion of the materials to dust on the surface of the material, which causes environmental pollution and creates the risk to human health[69−72] as depicted in Figure 6.

Numerous phthalate plasticizers have been revealed to cause harmful effects to the health of animals.[73−75] Also many authors have been studying the toxic effect of the phthalate plasticizers on humans. For illustration, antiandrogenic effects have been related to internal phthalate concentration because of its high and wide volume of use as reported by Bustamante-Montes et al.[76] and Huang et al.[77] Fatty foods such as butter, milk, and meats are the main sources of DEHP plasticizers and another phthalate in human society.[78,79] Phthalate is suspected of disrupting human hormones and generating numerous chronic diseases in children such as allergies and asthma.[80,81]

The softened PVC materials containing phthalate are also used as flooring materials, and this is a significant source of indoor phthalate dust. On the basis of a few investigations, phthalated PVC as flooring has caused health related issues from the uptake of phthalate via infants. Many phthalates (benzyl butyl phthalate (BBzP) metabolite) have been found

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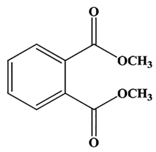
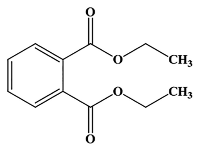
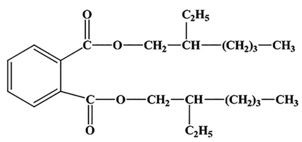
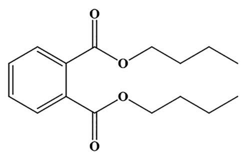
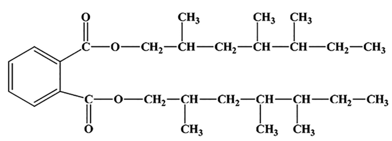
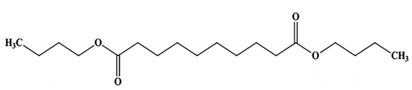
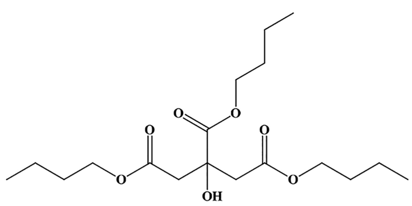
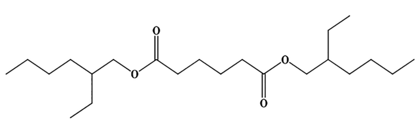
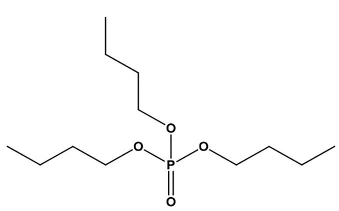
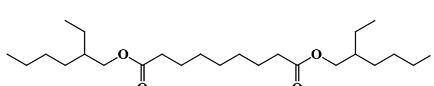
Table 1. Name and Chemical Structure of the Generally Employed Plasticizers for PVC[63]

Plasticizers name	Chemical structures
Dimethyl phthalate	
Diethyl phthalate	
Di-(2-ethylhexyl) phthalate	
Di-n-butyl phthalate	
Diisodecyl phthalate	
Di-n-butyl sebacate	
Tri-n-butyl citrate	
Di-(2-ethylhexyl) adipate	
Tributyl phosphate	
Di-(2-ethyl) azelate	

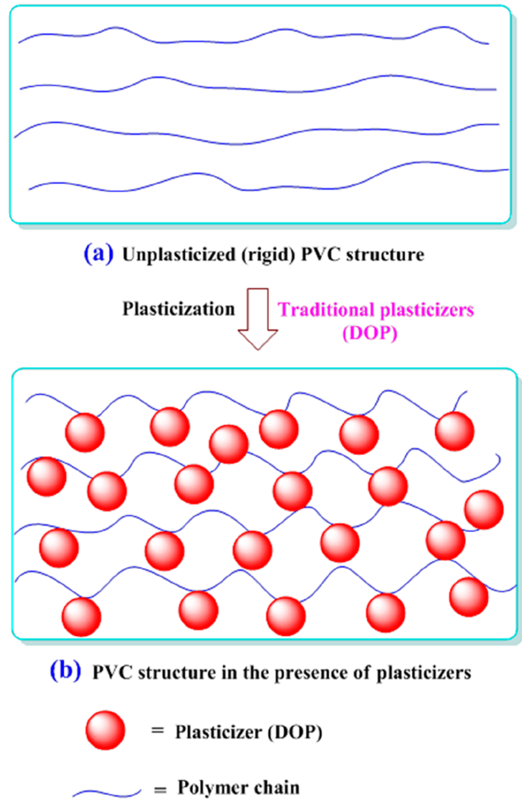


Figure 4. Chemistry of traditional plasticizers with PVC.

to be present in the urine of infants that live with floors made from PVC. Therefore, the use of phthalate plasticizers is restricted in some countries such as Canada and the United States to set limits on the concentration of diethylhexyl phthalate DEHP, diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP) in childcare items.[82]

2.3. Biobased Plasticizers. Currently, there is growing attention in the utilization of renewable resources such as plant oils, cardanol, citric acid, sugar, curcumin, and succinate esters in the development of new biobased plasticizers. Because they are environmentally friendly and have low migration and toxicity, biobased plasticizer make a good alternative to the phthalate plasticizers. There is an increasing demand for biobased plasticizers as shown in Figure 7.[83]

2.3.1. The Biobased Plasticizers Effect on Mechanical and Thermal Properties of PVC. Chen et al.[65] synthesized epoxidized castor oil based diglycidyl phthalate (ECODP) plasticizers as shown in Figure 8 and incorporated them into PVC. Comparative studies of the plasticization effect of the biobased (ECODP) plasticizers and traditional dioctyl phthalate (DOP) plasticizer were conducted.

The tensile strength (TS), modulus, and elongation (%) of the PVC films before and after heat aging are described in Figure 9 panels a,b and c,d. PVC films plasticized with traditional DOP, biobased (ECODP), and the various ratios, such as 0/40, 10/30, 20/20, 30/10, 40/0, of both (ECODP/DOP) plasticizers were studied, and their properties were compared. The biobased plasticizers based PVC materials exhibited higher tensile strength, modulus, and elongation before and after heat aging.

Figure 9b demonstrated that the DOP plasticizers containing PVC film exhibited lower elongation, tensile

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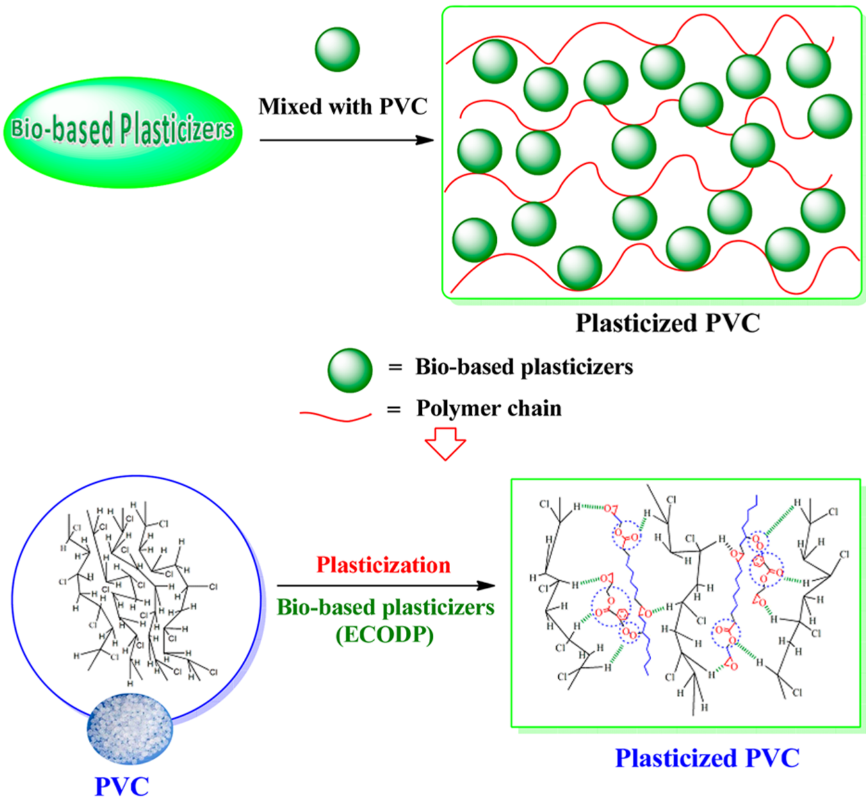

Figure 5. Chemistry of biobased plasticizers with PVC.

strength, and modulus compared to the biobased ECODP plasticizers based PVC film before and after heat aging. Further, the plasticization of PVC film by different ratios of ECODP/DOP plasticizers enhanced the tensile strength, modulus, and elongation. The elongation revealed a remarkable enhancement of flexibility with plasticizers having a higher percentage of ECODP than DOP. This is due to the lubrication effect of PVC chains from the longer ECODP alkyl chains. The lubrication decreases the polymer interaction force and enhances the free space of the polymer amorphous area which results in increasing the flexibility of the PVC blend network.[85,86]

It can be seen that by employing a lower percentage of ECODP, the flexibility becomes identical to that of the higher percentage of DOP. On the other hand, the mechanical properties demonstrated higher variation after heat aging, and slight change was seen in the mechanical performance of the ECODOP plasticized film after aging (heat). These investigations show that biobased ECODP plasticizers raise the flexibility and thermal stability of the PVC films. Hence, biobased plasticizers could be a suitable alternative to traditional phthalate-based DOP plasticizers.

Similarly, the thermal properties of the ECODP and DOP plasticized PVC are depicted in Table 2. The ECODP plasticized PVC demonstrated higher thermal degradation than DOP plasticizers, representing a higher thermal stability of ECODP.

Table 2 reveals the initial decomposition temperature (T_{onset}) (T_5, T_{10}, and T_{50}) and residue at 400 °C (R_{400}). Contrasting with that of DOP plasticized PVC, the T_{onset}, T_5, T_{10}, and T_{50} of ECODP was enhanced 98.4, 69.5, 89.6, and 114.3 °C, correspondingly. With the addition of the plasticizers, the residue % R_{400} value of the DOP and ECODP increased from 0.50plasticization effect to 39.87%, respectively. This indicate that the ECODP exhibits higher thermal stability owing to the benzene ring, diglycidyl ester, and epoxy groups.[87]

On the other hand, with the addition of plasticizers with a particular ratio of ECODP/DOP with PVC film, all the samples demonstrated two steps of thermal degradation behavior. The initial degradation starts at ∼250−350 °C. This is ascribed to the thermal degradation of the plasticizers and chlorination of PVC. The second thermal degradation starts at ∼430−500 °C relative to the development of aromatic compounds, and the data are summarized in Table 2. The residue values of the PVC films are enhanced with the addition of the ECODP/DOP plasticizers with different ratios due to the presence of multiglycidyl ester groups and an epoxy group of the ECODP, in which the the HCl is reduced and the thermal stability of the PVC film is hindered.

Chen et al.[66] also synthesized novel plasticizers from cardanol and epoxide cardanol glycidyl ether (ECGE) as depicted in Figure 10. They studied the effect of ECGE combined with the traditional plasticizers such as dioctyl phthalate (DOP) on the mechanical and thermal properties of PVC films plasticized with various ECGE/DOP ratios, that is, 0/40%, 10/36%, 20/32%, and 30/28.

Figure 11 panels a and b indicated the tensile strength, modulus, and elongation of the plasticized PVC samples. Incorporation of the ECGE plasticizer content (10%, 20%, and 30% of total plasticizers) into the PVC materials enhanced almost all the properties of the PVC films. The tensile strength (TS) of the PVC matrix was enhanced by the increase of the ECGE content. The 30% ECGE based PVC film exhibited a

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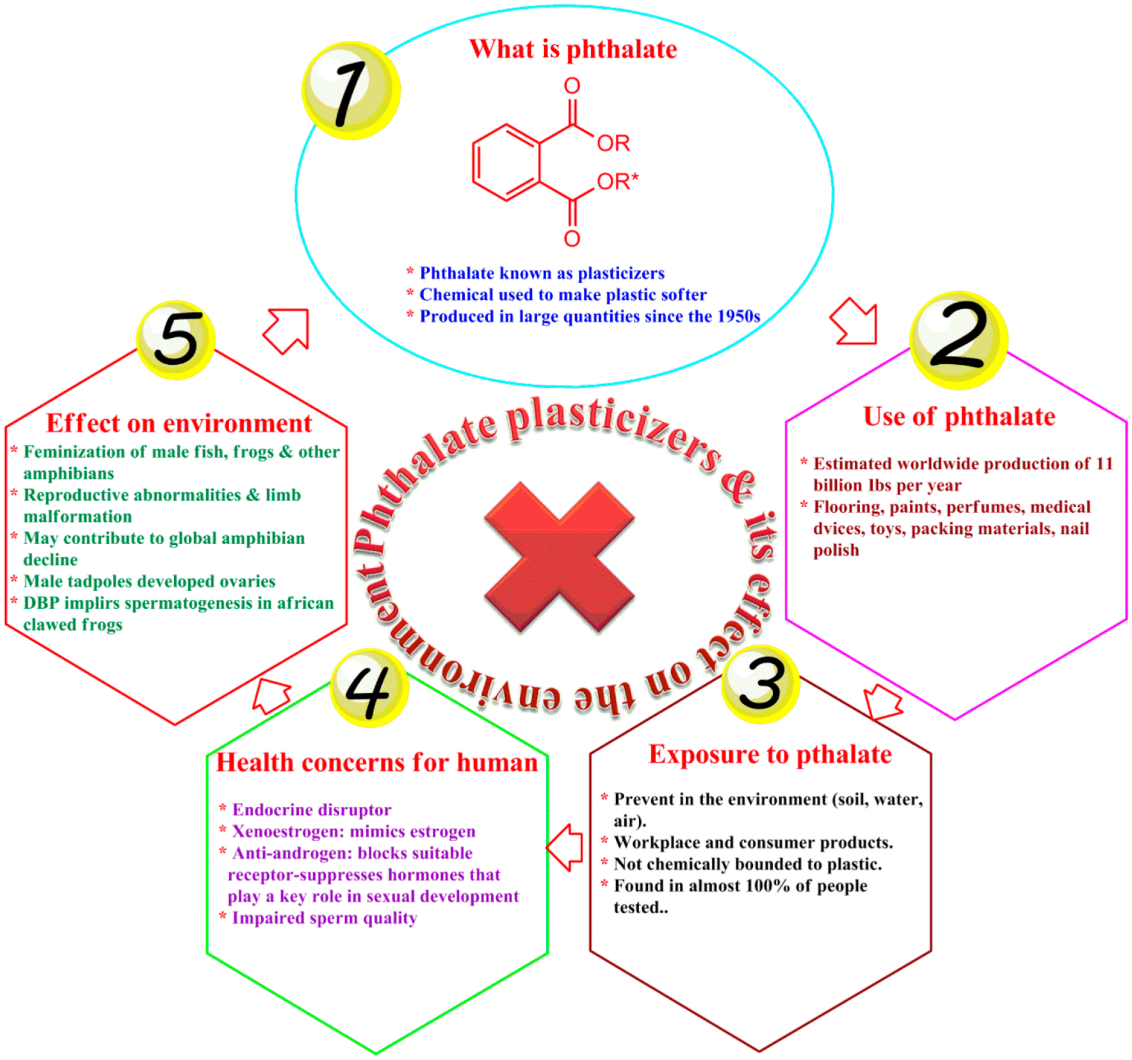

Figure 6. Phthalate plasticizers and their effect on the environment.

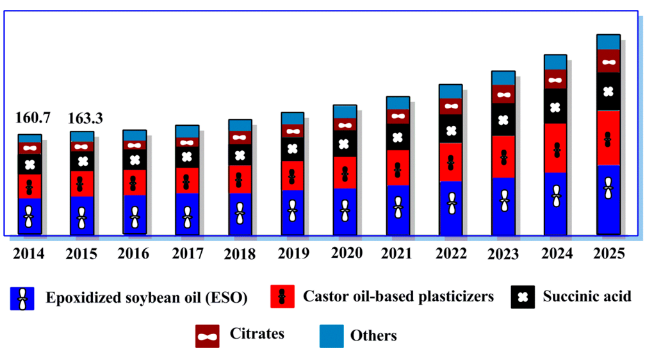

Figure 7. Biobased plasticizers market revenue for 2016 (USD million).[84]

maximum TS of 24.38 MPa compared to the DOP (22.90 MPa) plasticizers which indicated the strength of the plasticizers polarity and as well alter the plasticizers proportions. The ECGE plasticizer bestows not only an important enhancement in flexibility but also a toughness other than improvement in the TS of the PVC films.

Furthermore, compared with DOP, ECGE plasticized film exhibits better tensile strength and elongation but lower modulus properties due to the higher molecular weight characteristic of the plasticizers. The higher content of the ECGE exhibited more polar groups such as aromatic benzene ring, epoxy, glycidyl ether, and long alkyl chains. The plasticizers polar groups interact by the polar parts of the PVC molecules, decrease the PVC−PVC interactions between the polymer chains as depicted in Figure 12, and enhance the gap among polymer molecules.

On the other hand, the movement of the alkyl chains of ECGE also produces more free volume in the matrix. After the addition, the 10% and 20% ECGE enhanced the elongation 969.19%, 981.58%, respectively, compared to the DOP plasticized PVC. Further, additions of 30% ECGE caused the elongation (%) to slightly reduce to 981.53%; this is due to the flexible alkyl chains of ECGE. As a result, the ECGE demonstrated higher plasticization efficiency than DOP and the 20% ECGE based film exhibited a higher elongation (%) value. This indicated that a lower percentage of plasticizer (ECGE) is needed to get a similar elongation value as a DOP based PVC film.

In the case of the modulus, after incorporation of the ECGE plasticizers, the modulus was reduced compared to the DOP based PVC film owing to the decreased rigidity with the addition of ECGE as revealed in Figure 11a. This is ascribed to the higher efficiency of ECGE on raising the free volume of the

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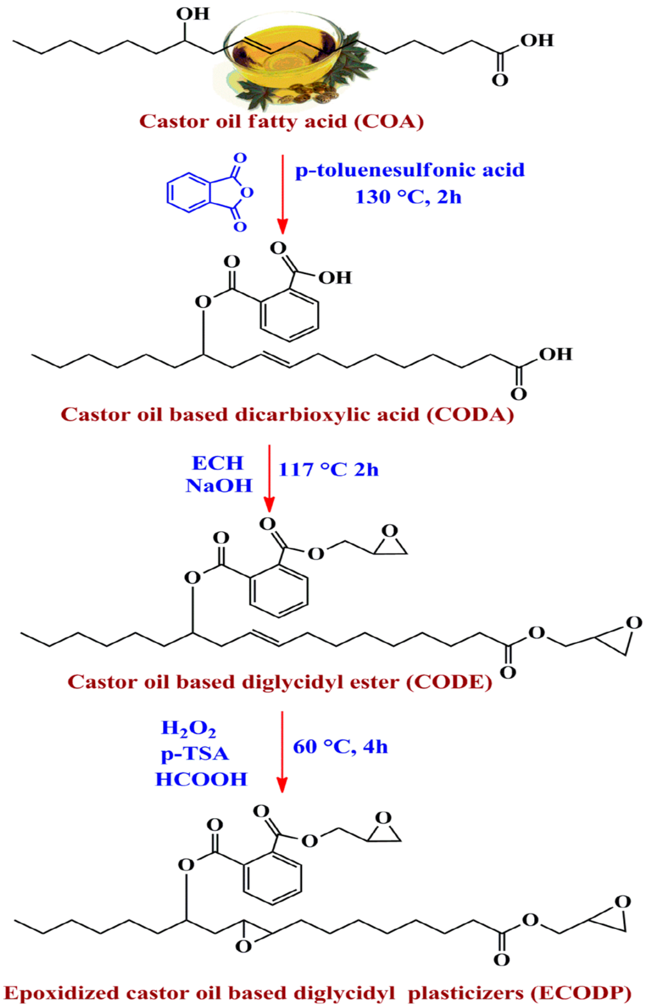

Figure 8. Synthesis of castor oil based diglycidyl plasticizers.

matrix. Conversely, the addition of the higher content of ECGE enhanced the modulus of PVC films. This indicates that the higher content of ECGE provides the plasticization effect of PVC with a comparatively high stage of rigidity.

Thermogravimetric analysis shows the thermal stability of the PVC films as depicted in Table 3 as well as the T_{onset}, $T_{10\%}$, and $T_{50\%}$ weight loss thermal degradation temperature. Evidently, the addition of the ECGE content increases the thermal stability of PVC films of 27.77 °C and 16.87 °C in $T_{10\%}$ and $T_{50\%}$, respectively, compared with DOP plasticized PVC films. This is attributed to several epoxy groups of the ECGE which scavenge the hydrochloric acid and restrict the degradation.

Further, Chen et al.[88] synthesized the soybean oil-based epoxidized glycidyl ester of fatty acids (EGESOFa) and tung oil based tung-maleic triglycidyl esters (TMTE) plasticizers, respectively, and their addition into the PVC films and substitution of traditional plasticizers such as dioctyl phthalate (DOP) were investigated. The results demonstrated that the soybean oil-based plasticizers enhanced the mechanical and thermal stability of PVC blends and somewhat or absolutely substituted the DOP. Further, EGESOFa could provide PVC with well-balanced properties of strength, hardness, and flexibility. Thus, soybean oil (SO) based plasticizers exhibited better potential properties compared to the traditional plasticizers (i.e., DOP).

Stuart et al.[89] synthesized three types of succinic-based plasticizers such as diethylhexyl succinate, didecyl succinate, and didodecyl succinate, for which the plasticization effect was investigated. These are nontoxic and sustainable and potentially used for the replacement of the traditional plasticizers (i.e., phthalate plasticizers). Synergistic effects take place when the interaction among the two materials is improved via the inclusion of a third part. As a result, the higher molecular weight (MW) succinic diesters exhibited lower MW and were more effective as plasticizer for PVC compared to the single succinic diesters.

Wang et al.[90] prepared the hydroxyl (−OH) and nitrogen (N_2) groups including tung-oil based ester plasticizers such as GEHTMA_1, GEHTMA_2, GEHTMA_3, and GEHTMA_4 (glycidyl ester hydroxyl congaing tung-maleic anhydride) from tung-maleic anhydride (TMA) employed to plasticize PVC. They studied the comparative properties of the traditional plasticizers, for example, dioctyl terephthalate (DOTP). The biobased GEHTMA_3 plasticizers with PVC provided good mechanical properties. On the other hand, with the incorporation of GEHTMA_3 plasticizers into the DOTP (PVC-DOTP-GEHTMA_3), the plasticized PVC demonstrated improved mechanical and thermal stability, and the migration resistance properties contrasted to that of the PVC-DOTP networks. The PVC-28DOTP-12GEHTMA_3 formulation reveals a higher TS and elongation from 32.19 MPa to 345.20%, correspondingly, and greater thermal stability. This is due to the molecular interaction of GEHTMA_3, DOTP, and PVC.

Yin et al.[91] synthesized three various kinds of biobased plasticizers such as oligo(isosorbide adipate (OSA), suberate oligo(isosorbide suberate (OSS), and isosorbide dihexanoate (SDH). These synthesized plasticizers were blends with polyvinyl chloride and were compared with the traditional phthalate plasticizer (DIOP) PVC blend. As a result, the 40 wt % SDH plasticized PVC films revealed comparable tensile strain as to that of the traditional plasticizers (DIOP) based PVC film, whereas the other isosorbide plasticizers exhibited lower tensile strain. The PVC plasticized by 20 wt % DIOP and three different types of isosorbide plasticizers revealed a comparable tensile strain.

Conversely, the PVC plasticized with 40 wt % SDH and DIOP plasticizers exhibited elastomeric stress−strain behavior, and no yield point was obtained until the break. However, the 40 wt % OSA and OSS plasticized PVC demonstrated lower T_g, lower tensile strain, and higher tensile stress than an SDH or DIOP plasticized PCV film. The structure of the OSS plasticizer is more flexible compared to that of the OSA plasticizer, and for that reason the OSS revealed lower T_g but higher tensile strain. Further, the OSA and OSS plasticized PVC demonstrated higher thermal stability compared to the bio SDH and traditional plasticizers (DIOP). Finally, the isosorbide synthesized plasticizers appeared to be a better substitute for traditional plasticizers. Yin et al.[92] also reported glucose esters based green plasticizers for PVC which reduced the environmental problems that came from the traditional phthalates plasticizers.

Jia et al.[93] developed rosin-based plasticizers that exhibited a similar branched chain structure (e.g., alkane chain and benzene ring) that contrasted to the phthalate plasticizers. The first dehydroabietic acid reacts with oxalic dichloride to form a chloride dehydroabietic (CD). Further reactions proceeded with castor oil methyl ester, cardanol, and tributyl

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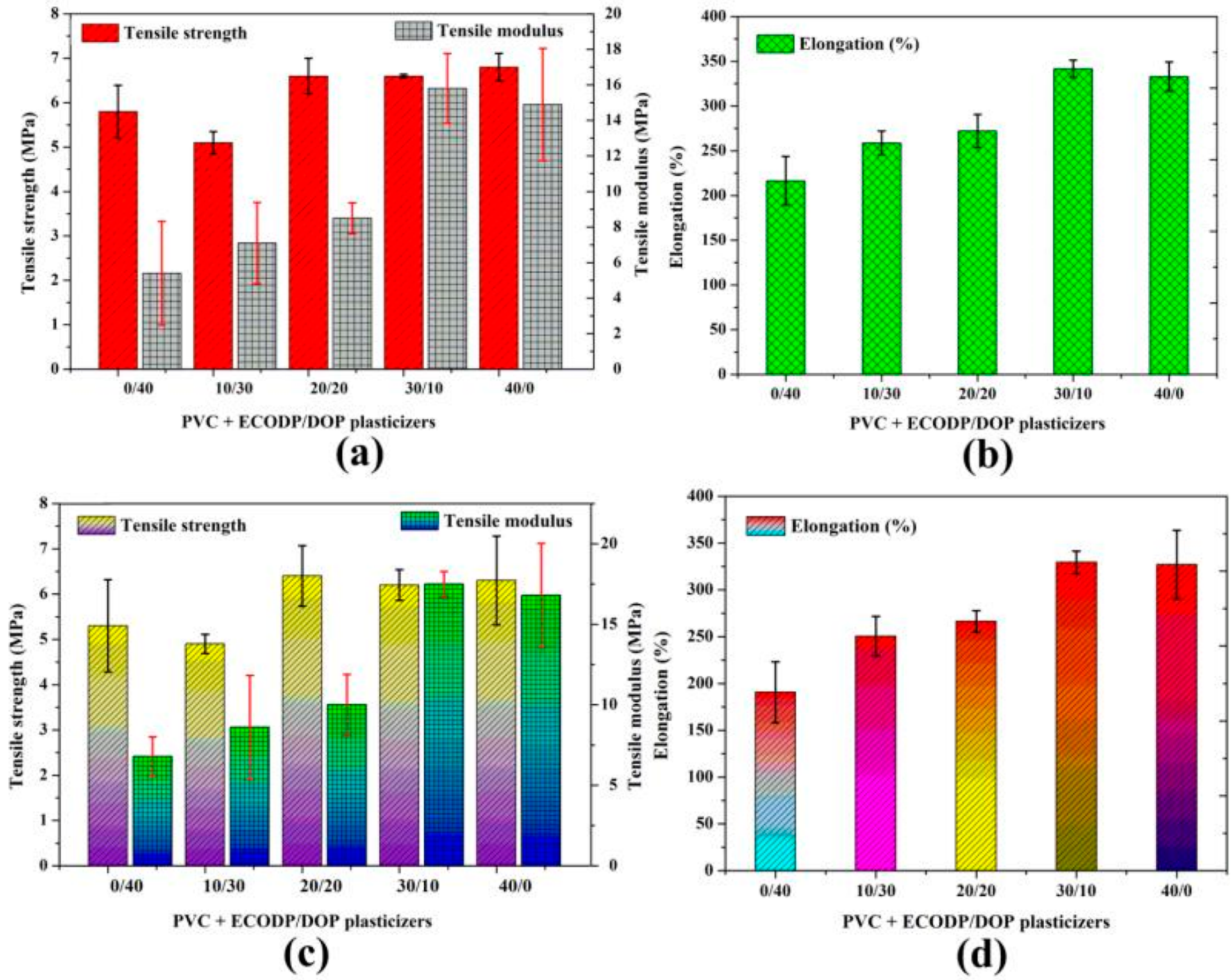

Figure 9. Mechanical properties of PVC + ECODP/DOP plasticizers (a, b) before aging and (c, d) after aging.[65]

Table 2. Thermal Properties of PVC Film with Two Different Plasticizers[65]

sample code	T_g (°C)	T_{onset} (°C)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	R_{400} (%)
DOP		224.3	208.2	223.1	263.4	0.50
ECODP		322.7	277.7	312.7	377.7	39.87
PVC + 0%ECODP/40%DOP	41.46	256.2	240.5	255.5	300.5	27.92
PVC + 10%ECODP/30%DOP	34.51	257.6	246.6	262.5	311.8	29.30
PVC + 20%ECODP/20%DOP	35.88	269.1	263.9	275.1	320.9	31.61
PVC + 30%ECODP/10%DOP	40.82	271.0	269.9	278.5	322.3	34.88
PVC + 40%ECODP/0%DOP	45.41	280.9	279.4	287.5	330.8	35.23

citrate to obtain rosin-based plasticizers with dissimilar chain structures such as cardanol-rosin ester plasticizer (ECR), castor oil methyl ester−rosin ester plasticizer (ECMR), and tributyl citrate-rosin ester plasticizer (ECTR) respectively, as shown in Figure 13.

Figure 14 provides information about the TS and elongation (%) to analyze the plasticization effect of the developed plasticizers. The results demonstrated that the ECTR plasticizers exhibited the highest plasticization effect compared to the ECR and ECMR plasticizers. The TS of all PVC films reduces steadily with the incorporation of more amounts of plasticizers (rosin-based) with PVC, while the elongation (%) of all PVC films enhanced regularly. This is due to the decline of the entanglement of the PVC chains, and the chains being more flexible after blending with the rosin-based plasticizers.

The elongation (%) of ECMR and ECR enhances from 180% to 307% and 180% to 279%, respectively, and ECTR reveals a better elongation (%) of 108%−346%. The TS values of ECMR, ECR, and ECTR decrease, respectively, but for the similar wt ratio ECTR provides the best plasticizing properties.

The thermal properties of plasticized PVC films show that first step of the two-step thermal degradation starts from 260 to 350 °C, which is ascribed to the pyrolysis of PVC chlorination.[94,95] The second step of the degradation starts from 400 to 540 °C owing to the demolition of chains, forms cross-linking, cyclization, and scission compounds.[96] Conversely, with the addition of ECMR into the PVC matrix, the thermal stability of the PVC films reduces with the enhancement of ECMR. For that reason, the thermal stability of ECMR is poor at a higher temperature (i.e., 250 °C) due to the benzene ring of the ECMR being entirely degraded. The

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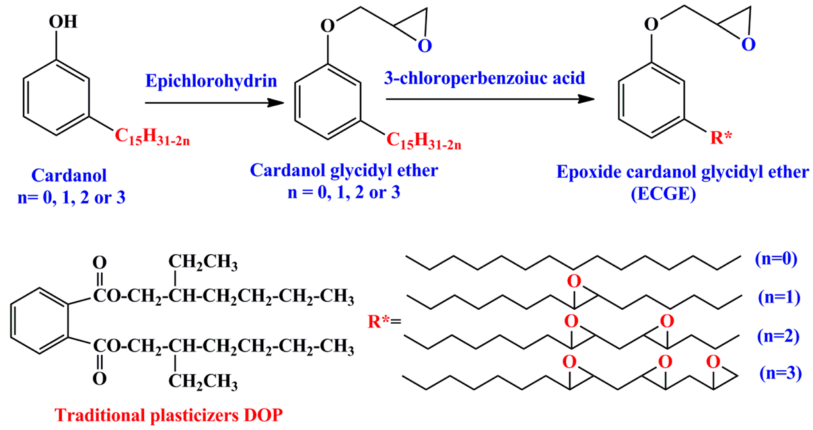

Figure 10. Synthetic route of cardanol-based ECGE plasticizers.

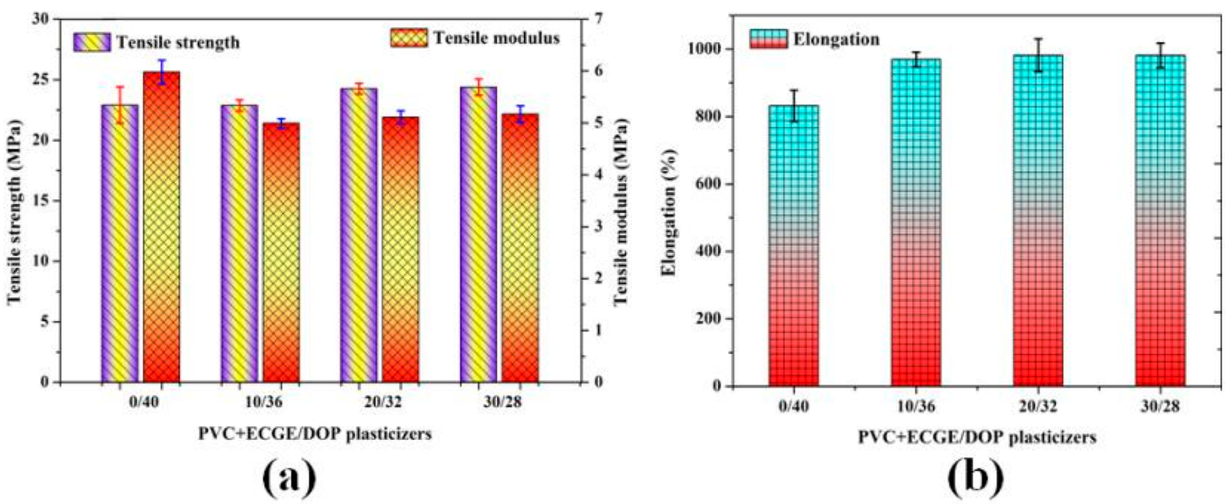

Figure 11. Mechanical properties of the ECGE/DOP plasticized PVC: (a) tensile strength, and (b) elongation (%).[65]

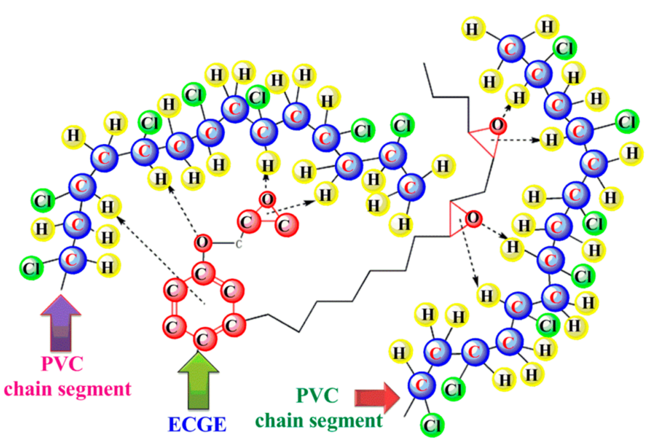

Figure 12. Schematic representation of the chemical interaction of plasticizers (ECGE) and PVC system.

plasticization efficiency of rosin-based plasticizers such as ECMR, ECR, and ECTR is 69.7%, 57.8%, and 85.5% respectively.

Feng et al.[97] synthesized biobased citric acid based plasticizers (AC-FAME-CAE) for PVC, employing waste cooking oil and citric acids as the main material as shown in Figure 15. The mechanical properties of the PVC films such as TS, modulus, and elasticity declined after incorporation of the plasticizers, and elongation (%) was enhanced with the increase of AC-FAME-CAE, DOP, and ESO plasticizers content. These results show that all the plasticizers have different plasticization capability. On the other hand, the AC-FAME-CAE plasticized PVC films with various phr values such as 20, 30, 40, exhibited better tensile properties compared to the ESO plasticized PVC film with 30 and 40 phr content. Both plasticizers revealed higher tensile properties with 30 and 40 phr content compared to the DOP plasticizer added with the same 30, 40 phr to PVC resin. It is confirmed that the AC-FAME-CAE is a great potential plasticizer for PVC composites and better alternative to phthalate plasticizers.

Table 3. Thermal Properties of the ECGE and DOP Plasticized PVC Films[66]

sample	T_{onset} (°C)	T_{10} (°C)	T_{50} (°C)
PVC + 0%ECGE/40%DOP	194.01	242.57	291.28
PVC + 10%ECGE/36%DOP	198.68	251.63	303.03
PVC + 20%ECGE/32%DOP	199.86	256.24	305.10
PVC + 30%ECGE/28%DOP	200.03	263.46	308.15

The initial thermal stability (5 wt % loss) of PVC films plasticized with three different plasticizers AC_40, ESO_40 and DOP_40 is 248, 247, and 233 °C, respectively. The AC-FAME-CAE is very compatible with PVC compared to other

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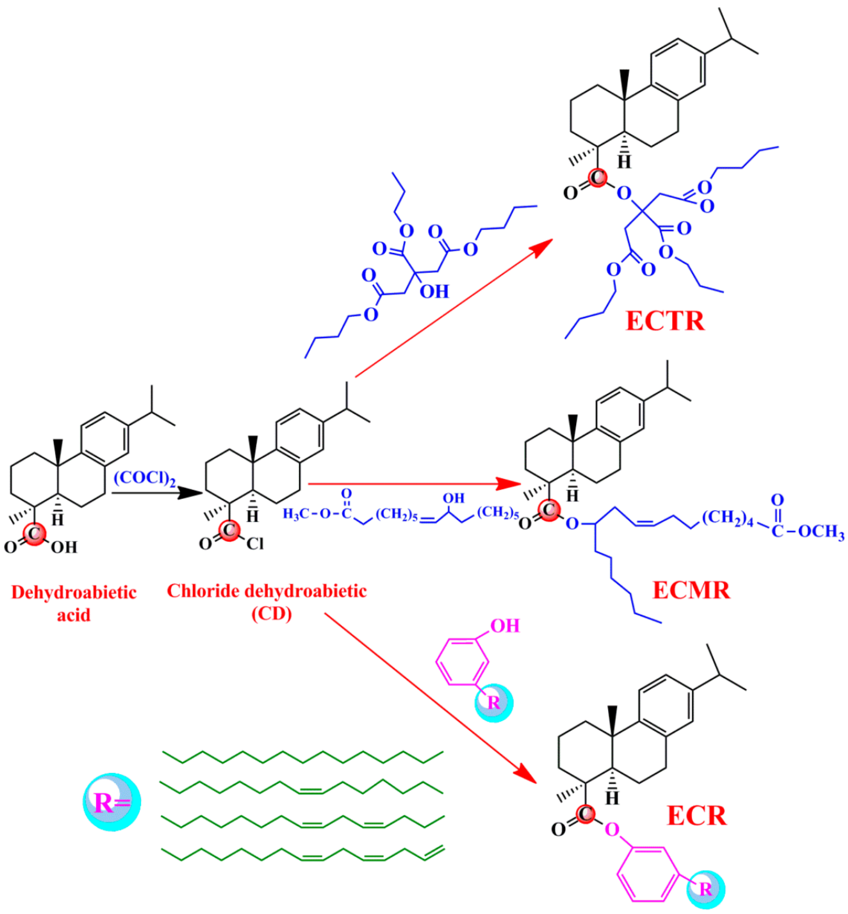

Figure 13. Schematic representations of rosin-based plasticizers.

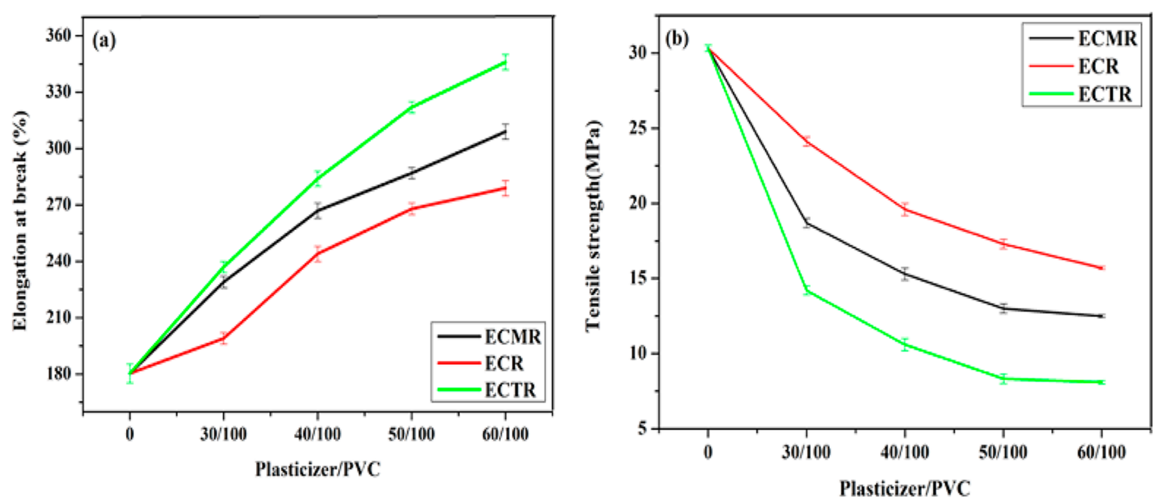

Figure 14. Mechanical properties of PVC materials: (a) elongation (%); (b) tensile strength. Reprinted from ref 93. Copyright 2019 American Chemical Society.

plasticizers. This is due to the strong bonding of several polar bonds, the C−Cl band of PVC reduced the dehydrochlorination of PVC films. According to the TGA results the thermal stability of AC-FAME-CAE_40 plasticizers is higher than that of ESO and DOP at 600 °C due to the char residue % of AC_40, ESO_40, and DOP_40 being higher at 7.7%, 5.6%, and 3.3%, respectively.

Further, Jia et al.[98] exploited the triethyl citrate for the preparation of biobased citrate plasticizers which were used to modify the PVC materials. The modulus of elasticity, elongation at break (%), and thermal stability was enhanced compared to that of the DOP plasticized materials.

Other Plasticizers. Pyeon et al.[99] synthesized the non-phthalate plasticizers from camphor (1′,7′,7′-trimethyl[1,3]-dioxolane-2,2′-bicyclo[2.2.1]heptanes-3′,2′′[1,3]dioxolane]-4,4′′diyl)(methylene) dioctanoate (CDO) (Figure 16) plasticized with flexible PVC and studied its compatibility with PVC, thermal and mechanical properties, and its application to

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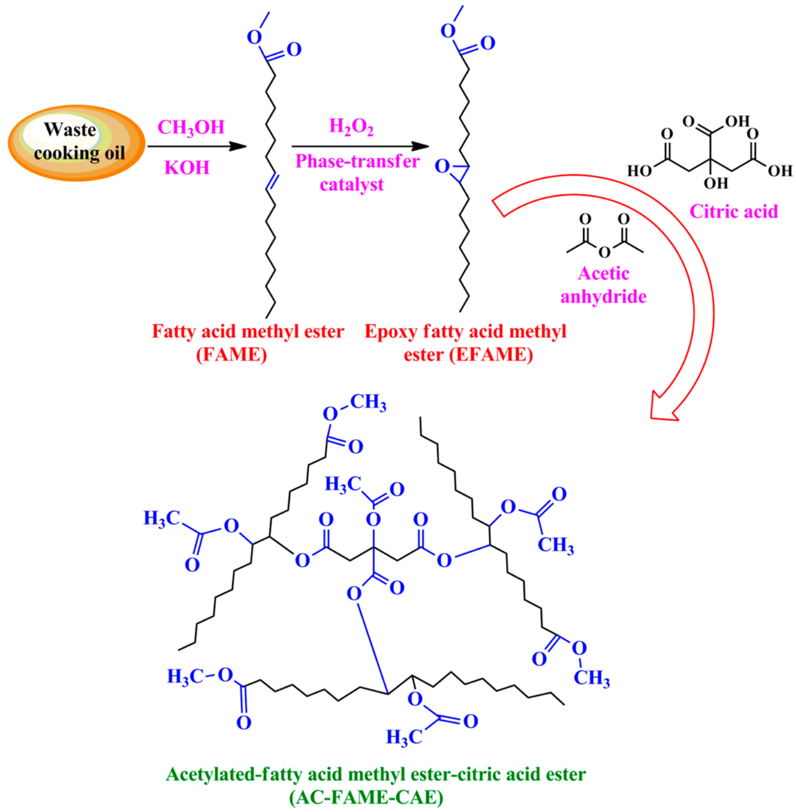

Figure 15. Synthesis route of citric acid based plasticizers (AC-FAME-CAE).

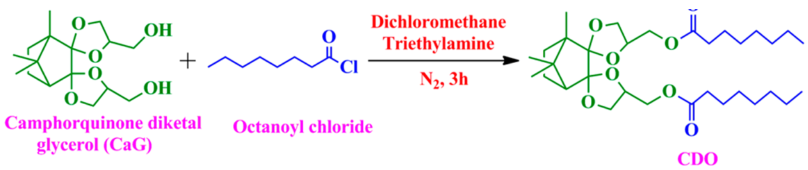

Figure 16. Synthesis route of camphor based plasticizers (CDO).

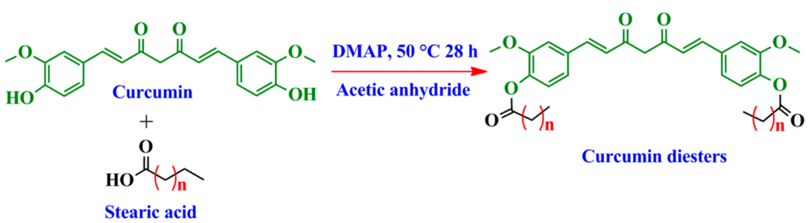

Figure 17. Synthetic routes of curcumin-based plasticizers.

replace the commercial phthalate plasticizers. As a result, 20% CDO showed a tremendous compatibility when incorporated with PVC materials achieving enhanced TS, elongation (%), thermal stability, and glass transition temperature due to the presence of strong and bulky groups. The leaching resistance of CDO in PVC matrix was higher than that of DOP. This is due to the bulky and rigid character of CDO and its pincer-like structure, unlike DOP trapped in PVC matrix, and increased the properties of plasticized PVC. The results confirmed that the CDO has a great potential to develop the application of PVC and substitute the traditional DOP plasticizers for the production of environmentally friendly materials.

The curcumin-diester based green plasticizer was synthesized from curcumin and stearic acid by the esterification reaction in the presence of dimethylaminopyridine (DMAP) base as shown in Figure 17. The developed plasticizers exhibited lower cytotoxicity and better leaching resistance compared to the traditional dibutyl phthalate (DBP) plasticizers reported by Saltos et al.[100]

Howell et al.[101] also synthesized tartaric acid based plasticizers revealing a better compatibility with PVC, low migration, good plasticization effect, and no effect on the thermal stability of the polymer. These materials demonstrated better properties as substitutes for phthalate plasticizers.

The multifunctional natural plasticizers were prepared from a cardanol glycidyl ether (CEG) derivative via a two-step reaction by Chen et al.[102] Further, CEG was included into the PVC matrix and compared with commercial diisononyl

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phthalate (DINP) and bis(2-ethylhexyl) benzene-1,4-dicarboxylate (DOTP) plasticizers, respectively. The SEM and DMA analyses confirmed that the CEG is compatible with PVC. On the basis of the thermal analysis, the CEG/PVC system demonstrated higher thermal stability, extensive processability, higher exudation resistance, and better elongation properties in contrast to the DINP/PVC and DOTP/PVC systems. CEG has great potential to reduce the dependence on petro-based plasticizers. On the other hand, Jia et al.[103,104] also reported that the biobased glycerol monooleate-based polyester plasticizers for PVC materials are a better alternative to commercial plasticizers.

2.3.2. Environmental Effect of Biobased Plasticizers. The use of biobased plasticizers into the PVC materials has demonstrated many advantages, such as being nontoxic and having better compatibility with low migration ability. Because these are derived from renewable resources such as plant oils, cardanol, isosorbide, citric acid, etc., easily available, and biodegradable, there are no environmental and health issues.[55,105−110] Figure 18 shows the environmental effect of the traditional and biobased plasticizers.

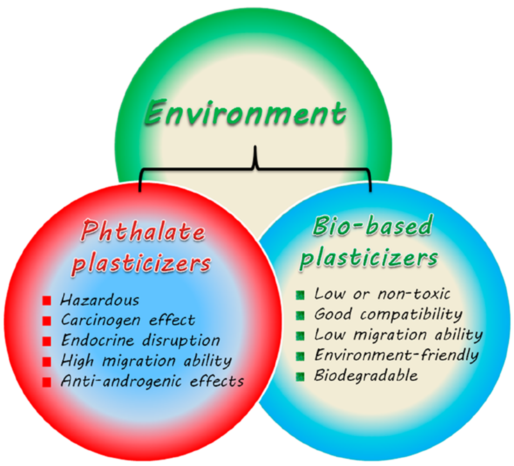

Figure 18. Effect of traditional and biobased plasticizers on the environment.

3. FUTURE SCOPE

Utilization of the new class of biobased plasticizers is a growing interest of researchers and industries that wish to develop new biobased materials from renewable resources. The biobased plasticizer exhibits a huge potential to substitute or reduce the use of traditional plasticizers based products and plays a significant role in the current market. But their development cost is very high and they do not get the benefit of the economic scale. However, the demand for the biobased materials use in various applications is growing rapidly and they particularly have great potential in PVC compounding.

4. CONCLUSIONS

There is an increasing awareness of health and the environment associated with leachable phthalate-based plasticizers as they are very toxic. Recently, their application in some areas was limited because of growing environmental and health safety concerns, and a large amount of scientific data provides evidence of real threats concerning health problems related to the use of traditional plasticizers. On the other hand, these disadvantages encourage researchers to develop novel biobased plasticizers that are environment-friendly and have lower toxicity and low migration levels. Recently, various researches and industries have shown their interest in the development of biobased plasticizers. The use of such types of biobased plasticizers demonstrates less leachability, volatility, toxicity, and good compatibility with PVC and also increases the mechanical and thermal properties of the PVC materials. These advantages indicate that the biobased plasticizer is the best substitute for traditional plasticizers.

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Notes

The author declares no competing financial interest.

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