

Article

Green Plasticizers from Dimer Acids with Selected Esters Classified Through the Nile Red [E(NR)] Polarity Scale

Franco Cataldo 

Actinium Chemical Research Institute, Via Casilina 1626A, 00133 Rome, Italy; franco.cataldo@fastwebnet.it

Abstract: Dimer and trimer acids are interesting viscous liquids produced from fatty acids derived from renewable sources. The chemical structures of dimer and trimer acids are known and quite complex and are presented here, discussed and further elucidated through electronic absorption spectroscopy, FT-IR and Raman spectroscopy. Dimer and trimer acids have a number of applications in their original form or in the form of derivatives. In the present study, a series of esters of dimer and trimer acids with alcohols from renewable sources were synthesized for use as plasticizers for rubber and plastics. The polarity of the dimer and trimer acids as well as their esters with alcohols from renewable sources (dimerates and trimers) were systematically studied using a Nile red solvatochromic probe. The resulting E(NR) values were compared with the E(NR) values of the most common types of rubber and plastics. Compatibility and other physical properties expected from the E(NR) scale were studied and successfully confirmed in tire tread rubber compound formulations and in nitrile rubber and PVC matrices, confirming once again the sensitivity and the validity of the Nile red solvatochromic polarity scale for the development of new plasticizers. The validity of the liquids polarity measured with the Nile Red dye is supported by the correlation found between the E(NR) scale and the dielectric constants (ϵ) of carboxylic acids (including dimer and trimer acids, hydrogenated dimer acids and isostearic acid) and alcohols. A correlation was even found linking the E(NR) values with the ϵ values of thin solid films of rubbers and plastics. In the case of the esters the correlation of their E(NR) values was found with the length of the aliphatic chains of the alcohols used in the esterification.



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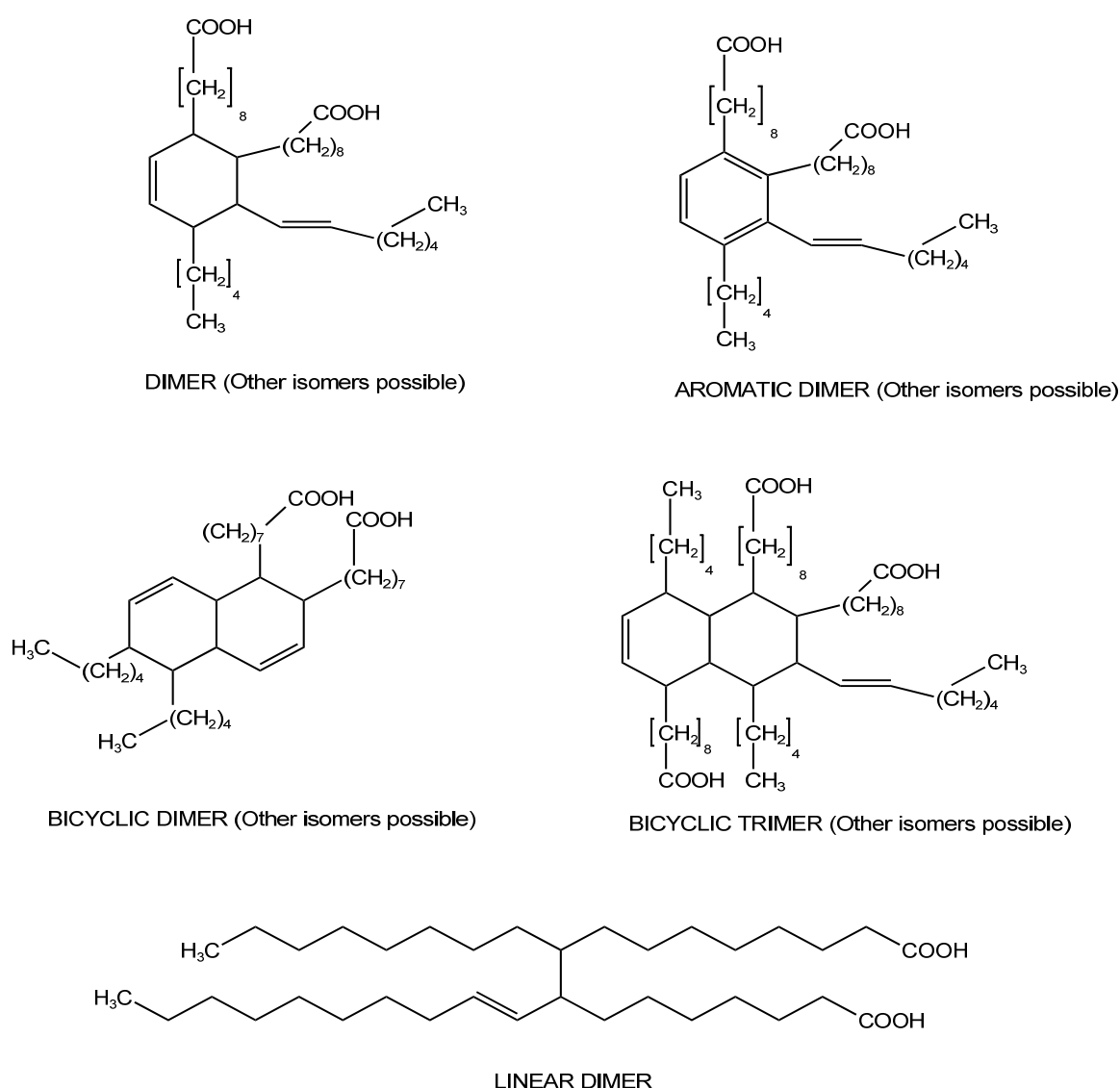
Keywords: dimer acid; trimer acids; dimerates; trimers; plasticizers; renewable sources; Nile red dye; solvatochromism; polarity probe; compatibility

1. Introduction

As discussed in a previous paper [1], there is great attention on and a demand for new plasticizers for rubber and plastics derived from renewable sources. In fact, the traditional petroleum-derived plasticizers typically used in the tire and rubber technical products industry are already partially substituted by vegetable oils (e.g., sunflower oil, soybean oil [2–4]) or by esters of fatty acids (e.g., methyl esters of fatty acids [5]).

Much less known are dimer acids, which are obtained from naturally occurring unsaturated fatty acids by a thermal treatment under pressure with variable amounts of clay (typically, montmorillonite clay is the catalyst of choice) [6–16]. The clay catalyst causes the dehydrogenation, hydrogen shift reaction and double bond conjugation of the treated fatty acids, favoring the subsequent Diels–Alder addition reaction and leading to dimer acids that are characterized by a 1,2,3,4-substituted-cyclohexene dimer structure,

as shown in Scheme 1, accompanied by a minor component of 1,2,5,6-tetrasubstituted-1,2,4a,5,6,8a-hexahydronaphthalene fatty acid bicyclic dimer, shown in Scheme 1 [6–12]. In addition to the dimer acids mentioned, which are generally the main products, trimer acids are produced that have, for example, the bicyclic structure 1,2,3,4,5,8-substituted 1,2,3,4,4a,5,8,8a-octahydronaphthalene (see Scheme 1) [6–12]. A linear dimer may also be present as a minor component (shown at the bottom of Scheme 1), which is mainly produced by a free radical mechanism [11]. Furthermore, a clay catalyzed hydrogen transfer reaction may lead to dehydrogenation of the 1,2,3,4-substituted cyclohexene ring, leading to the corresponding aromatic derivative, i.e., the 1,2,3,4-substituted benzene shown in Scheme 1. The earlier literature [6–12] claims that the key mechanism for the formation of dimers and trimers of fatty acids involves the Diels–Alder reaction and free radical mechanism for linear dimer formation. More recently, it has been suggested that an ionic mechanism, also promoted by clay, may contribute to dimer and trimer formation [13–16].

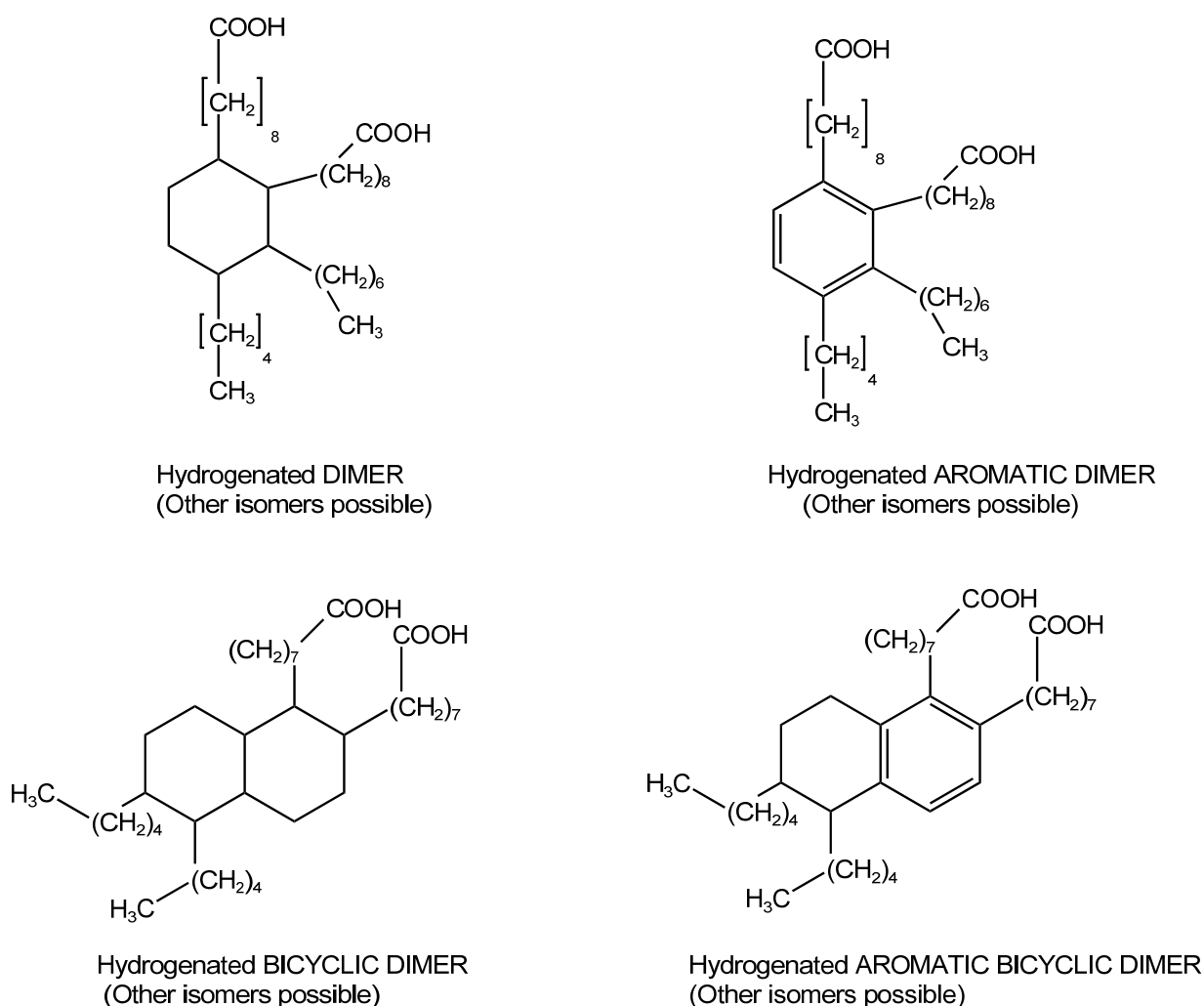


Scheme 1. Typical chemical structures of dimer and trimer acids; many other isomeric structures other than those shown can be conceived.

Dimer acids are isolated by distillation after the removal of the monomers and the isostearic acid (*vide infra*). The standard dimer acids available in the market are viscous liquids (8000–9000 cP at 25 °C), with a trimer content in the order of 20% [11].

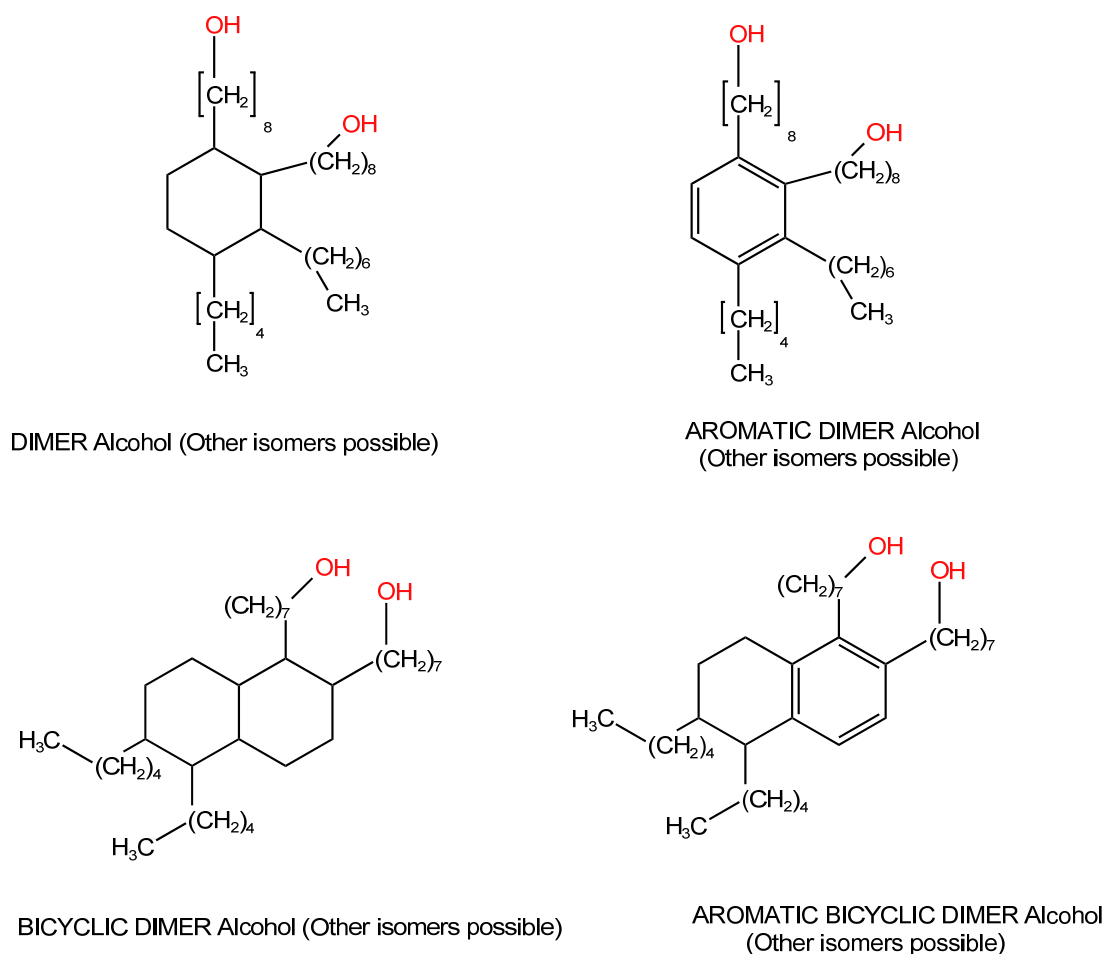
However, by an additional distillation step, the dimer content can be increased to >96%, and high purity dimer is a clear, viscous liquid (7100 cP at 25 °C). The distillation residue is mainly composed of trimers in the range of 55–70%, with the rest still composed of dimers [11]. The a trimer residue is, in general, a dark-colored liquid, characterized by an extremely high viscosity (23,000–30,000 cP at 25 °C) [11].

Both the 80/20 dimer/trimer and the high purity >96% dimer can be subjected to mild, catalytic hydrogenation. All the ethylenic double bonds are removed, but the aromatic rings present in the dimer mixture are preserved (see the Results Section for further insights) [11]. In Scheme 2, some chemical structures of hydrogenated dimers are shown. The hydrogenation does not significantly change the viscosity of these liquids but improves the color and the thermo-oxidative stability.



Scheme 2. Typical chemical structures of hydrogenated dimer acids; many other isomeric structures other than those shown can be conceived.

The hydrogenation can be pushed further to reduce the carboxylic functionalities into alcohol groups. In such a way, dimer alcohols are also produced, with the same structure as hydrogenated dimer acids but with –OH groups in place of –COOH groups. Examples of chemical structures present in dimer alcohols are shown in Scheme 3 [11].



Scheme 3. Typical chemical structures of hydrogenated dimer alcohols; many other isomeric structures other than those shown can be conceived.

The fields of application of dimer acids are numerous; for instance, they can be used as corrosion inhibitors in petroleum processing equipment, as additives in jet fuels, as synthetic lubricants and as a hardener in epoxy resins and nylon fibers [11]. Indeed, the most comprehensive review on the applications of dimer acids and their derivatives is provided in ref. [11]. Large volumes of dimer and trimer acids are employed in the synthesis of fatty polyamides [17,18], which are used in coatings as additives in flexographic inks and in hot melts. However, the main use of liquid fatty polyamides is in epoxy resin curing [17,19]. Furthermore, polyesters based on dimer acids have been developed [20]. Dimer acids are also employed to produce polyester polyols, suitable for the production of high-quality polyurethanes [12].

Esters of dimer acids have found applications as plasticizers for plastics, especially for PVC [11]. Very recently it was found that certain esters of dimer and trimer acids are also excellent plasticizers for rubber compounds, especially for passenger tire tread rubber compounds [21]. Esters of dimer and trimer acids made with alcohols from renewable sources are 100% from renewable sources since dimer and trimer acids are also fully derived from renewable sources. Furthermore, dimer and trimer acids are neither toxic nor irritants [11,17] and are not considered to be flammable materials [11]. The advantages offered by a series of selected dimer and trimer acid esters with alcohols from renewable sources in rubber tread formulations pertain to the viscoelastic properties of the resulting compounds, offering better dynamic properties with respect to the traditional petroleum-based plasticizers used by the tire industry, such as T-DAE (treated distillate aromatic extract) or MES (mild extract solvate), and also to vegetable oils such as sunflower oil [21].

In this paper, dimer acids are first characterized with electronic absorption spectroscopy and then with FT-IR and Raman spectroscopy. The polarity of a selection of esters of dimer and trimer acids and other plasticizers is studied with a Nile red polarity probe [1].

2. Materials and Methods

2.1. Materials and Equipment

Dimer acid samples were kindly supplied by Croda B.V. from their Dutch production plant in Gouda (Gouda, The Netherlands). Croda is now part of the Cargill Corporation, Minnetonka, MN, USA. The commercial dimer acid samples received are as follows: Pripol 1017 (approx. 80% dimer and 20% trimer), Pripol 1025 (hydrogenated dimer acids; it is the hydrogenated version of Pripol 1017), Pripol 1040 (approx. 80% trimer and 20% dimer) and Pripol 2030 dimer alcohols (the hydrogenation was pushed to the conversion level of all -COOH groups into -OH groups).

The dimer and trimer acid esters were prepared as detailed in ref. [21].

Glycerol formal alcohol as well as the fatty acid esters of glycerol formal and its epoxidized derivatives were donated by Fluos S.A.S. company, Samarate plant, Italy.

The FT-IR spectra were collected with a Nicolet iS50 spectrometer from Thermo Fischer (Waltham, MA, USA).

The Raman spectra were collected on a BWTek Inc (Newark, DE, USA) dispersive spectrometer model BWS415i using a laser source at 785 nm.

The electronic absorption spectra were recorded on a Shimadzu (Kyoto, Japan) model UV-2450 spectrophotometer operating with a resolution of 0.1 nm.

2.2. Determination of the Maximum Absorbance with Solvatochromic Dyes in Liquid Samples

An evaluation of the polarity of dimer acids and their derivatives with Nile red was performed following the procedure detailed in the previous paper [1].

3. Results and Discussion

3.1. Electronic Absorption Spectra of Dimer Acids and Hydrogenated Dimer Acids

Dimer acids are made from a mixture of fatty acids primarily derived from tall oil fatty acids, oleic acids and linoleic acids [17]. As shown in Figure 1, the electronic absorption spectra of a commercial dimer acid are rather complex, with a series of absorption bands at 215, 237, 267, 280, 301 and 328 nm. These electronic transitions are essentially due to the conjugated diene and triene moieties present in fatty acid chains and, moreover, to a benzene ring conjugated with a double bond, as shown in Scheme 1.

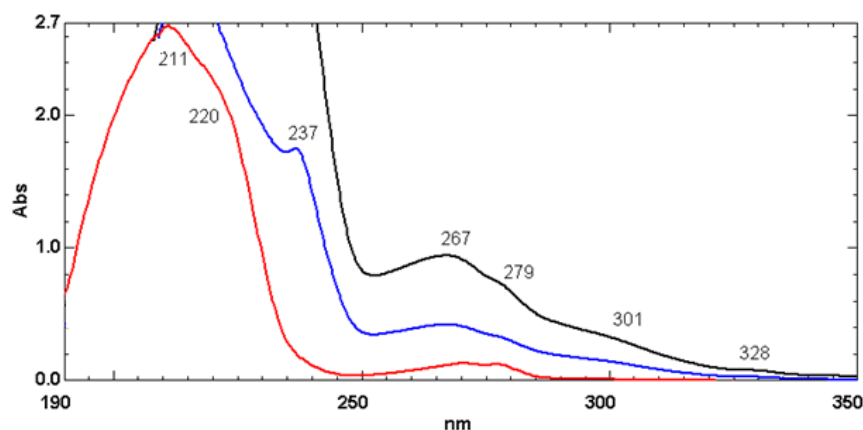


Figure 1. Electronic absorption spectra in n-hexane: hydrogenated dimer acids 1.17×10^{-3} M (red trace); dimer acids (blue trace 1.1×10^{-5} M and black trace 2.3×10^{-5} M).

As shown in Figure 1 and, especially, in Figure 2, the hydrogenation of dimer acids causes the removal of all the electronic transitions at longer wavelengths, with the exclusion of a benzenoid band characterized by two maxima at 270 and 277 nm (Figure 2). A similar electronic absorption spectrum is also displayed by the dimer alcohol, obtained when hydrogenation is pushed further, not only saturating the ethylenic double bonds but also converting the carboxylic functionalities into hydroxy groups. The benzenoid band in Figure 2 confirms that only the aromatic rings originally present in the dimer have survived the hydrogenation step, leading to the chemical structures shown in Schemes 2 and 3. The skeleton of the aromatic rings present in the hydrogenated dimer acids and in dimer alcohol is that of 1,2,3,4-tetraalkyl-substituted benzene. The simplest 1,2,3,4-tetraalkyl-substituted benzene is 1,2,3,4-tetramethylbenzene or prehnitene. For the latter hydrocarbon, the molar extinction coefficient of the strongest band (i.e., that at 270 nm) is reported at $301 \text{ M}^{-1} \text{ cm}^{-1}$ [22]. By using hydrogenated dimer acids and dimer alcohol solutions in *n*-hexane at the known concentration C_{total} , it is possible to make an estimation of the concentration of the aromatic fraction $\%C_{\text{arom}}$ in these commercial products using the Lambert–Beer law:

$$C_{\text{arom}} = A\epsilon^{-1}b^{-1} \quad (1)$$

where A is the absorbance at 270 nm, ϵ is the molar extinction coefficient ($301 \text{ M}^{-1} \text{ cm}^{-1}$) and b is the pathlength of the cuvette (1 cm).

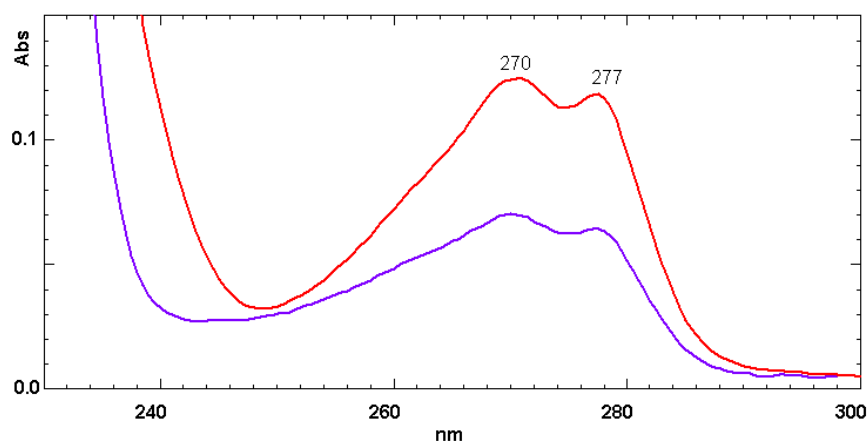


Figure 2. Electronic absorption spectra in *n*-hexane. Hydrogenated dimer acid concentration weighing $1.17 \times 10^{-3} \text{ M}$ (red trace); using $\epsilon = 301 \text{ M}^{-1} \text{ cm}^{-1}$ at 270 nm, the aromatic concentration is $4.15 \times 10^{-4} \text{ M}$; hence, the aromatic fraction is 35.5%. Dimer alcohol weighing $7.73 \times 10^{-4} \text{ M}$ (violet trace); using $\epsilon = 301 \text{ M}^{-1} \text{ cm}^{-1}$ at 270 nm, the aromatic concentration is $2.87 \times 10^{-4} \text{ M}$; hence, the aromatic fraction is 30.1%.

Thus, the aromatic fraction is then determined:

$$\%C_{\text{arom}} = (C_{\text{arom}}/C_{\text{total}}) \times 100 \quad (2)$$

where both C_{arom} and C_{total} are expressed in $\text{mol} \cdot \text{L}^{-1}$. From these determinations, it can be concluded that the aromatic fraction in commercial hydrogenated dimer acids (and hence in dimer acids) is 35.5%, and a little bit lower in the case of dimer alcohols, where the aromatic fraction is found at 30.1%.

It is interesting to make a comparison of our results with those reported by earlier investigators [23], who made a similar estimation of the aromatic fraction content of hydrogenated dimer acids produced on a lab scale (not a commercial product, as in our case). They concluded that the aromatic fraction is in the range of 20–25% [23]. The lower aromatic content reported is explainable by the different origins of the hydrogenated dimer

acids and the fact that their samples were hydrogenated on a lab scale. Furthermore, in the current determination, we have correctly used the molar extinction coefficient of prehnitene, the correct hydrocarbon, while they have adopted the ϵ value of durene, which is more than double the value of the ϵ of prehnitene [24].

3.2. Raman Spectroscopy on Dimer Acids and Hydrogenated Dimer Acids

Dimer and trimer acids and hydrogenated dimer acids display essentially the same band pattern in the infrared spectra (see the FT-IR spectra in Figure 3). Even the spectrum of oleic acid, taken as a reference, appears practically identical to the spectra of dimer and trimer acids (Figure 3). The unique distinctive feature in the oleic acid infrared spectrum is the weak band at 3005 cm^{-1} due to ethylenic $=\text{CH}$ stretching. In all cases, the infrared spectra of the oleic, dimer, trimer and hydrogenated dimer acids are dominated by the $\text{C}=\text{O}$ stretching of the COOH group at about 1710 cm^{-1} , while the $\text{C}=\text{C}$ stretching expected at 1600 cm^{-1} is not detectable in the infrared spectra.

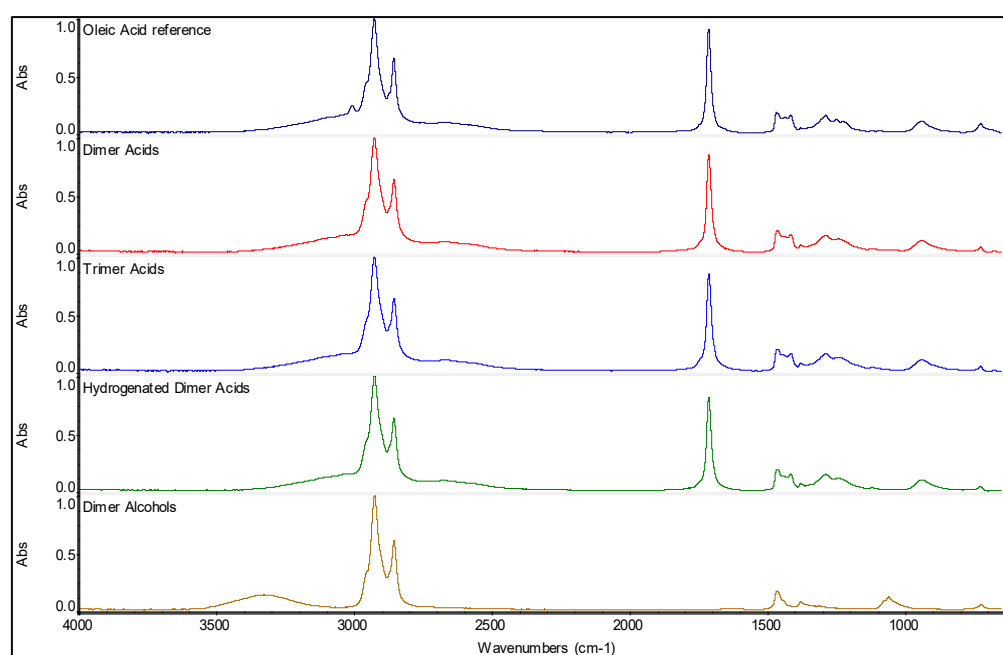


Figure 3. Normalized FT-IR spectra in ATR from top to bottom: oleic acid (reference); dimer acids; trimer acids; hydrogenated dimer acids; dimer alcohols.

FT-IR spectroscopy is very useful in the identification of dimer alcohol (see Figure 3 at the bottom). Hydrogenation has completely removed the $\text{C}=\text{O}$ stretching band, and the presence of the OH groups is confirmed either from the ν_{OH} at 3328 cm^{-1} or from the $\text{C}-\text{O}$ bending at 1057 cm^{-1} .

Raman spectroscopy is a very useful tool for the analysis of lipids thanks to its complementarity to infrared spectroscopy [25]. For the first time, the Raman spectra were successfully recorded in dimer acids, hydrogenated dimer acids and dimer alcohol, as shown in Figure 4. Dimer acid shows only the $\text{C}=\text{C}$ stretching band at about 1655 cm^{-1} , while the carboxylic $\text{C}=\text{O}$ band is very weak and not detectable with our instrumentation. The hydrogenated dimer acid shows a strong reduction in the intensity of the $\nu_{\text{C}=\text{C}}$ band, as shown in Figure 4 (compare a vs b), with respect to pristine dimer acids. As expected, in the Raman spectrum of dimer alcohol (bottom of Figure 4c), there is no more evidence of the $\nu_{\text{C}=\text{C}}$ band.

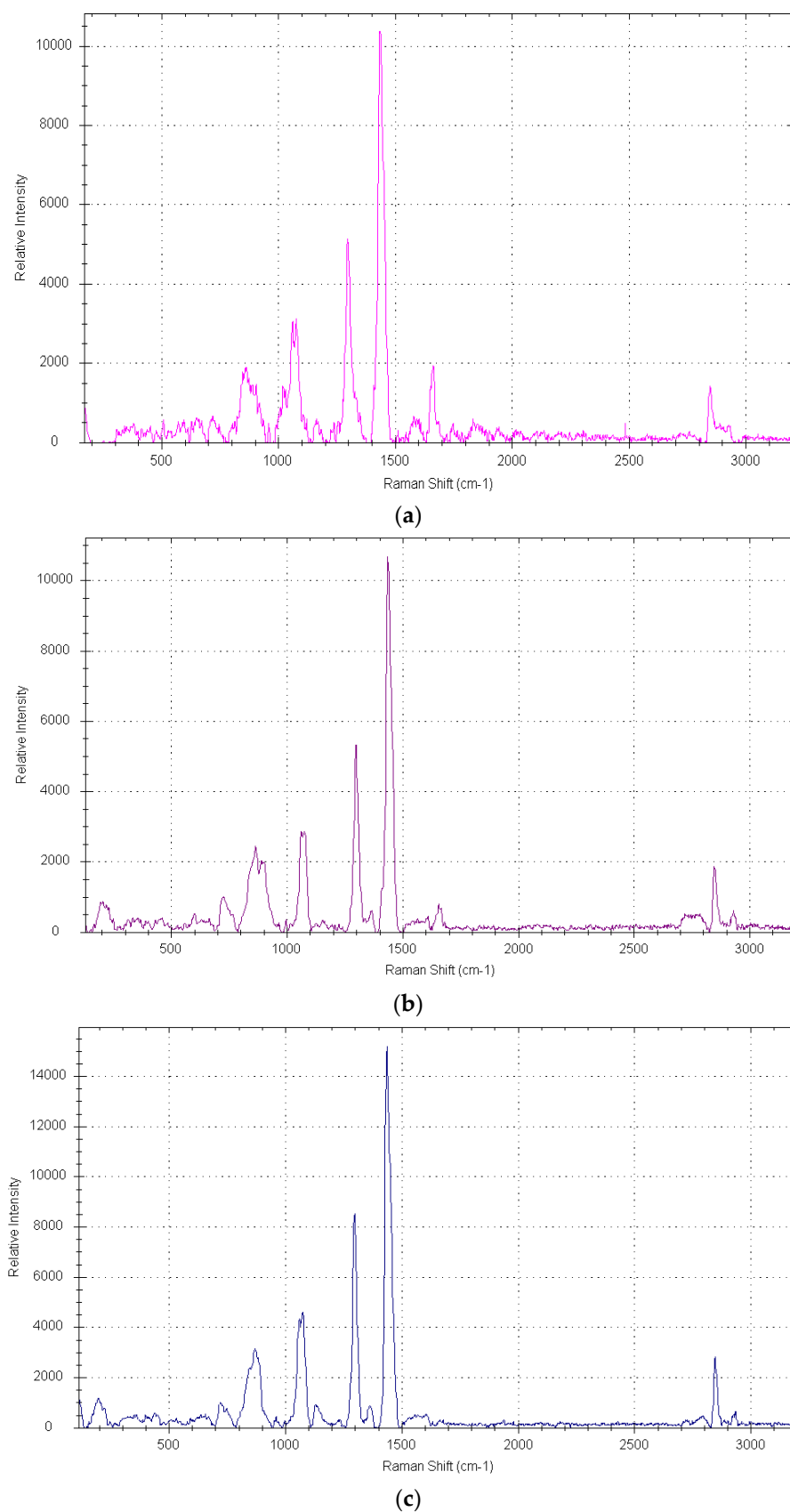


Figure 4. Raman spectra: (a) dimer acids; (b) hydrogenated dimer acids; (c)—dimer alcohols.

We have also tried to record the Raman spectrum of trimer acids. We were successful in obtaining a Raman spectrum of this substrate but at a relatively low quality due to

fluorescence since the trimer is a dark viscous liquid. The Raman spectrum of trimer acids is completely comparable to that of the dimer acid in Figure 4a.

Regarding the other Raman lines observed in the spectrum of the dimer acids, it is interesting to notice that these bands are very similar to those observed, for instance, in the Raman spectrum of oleic acid (Figure 5a). In the case of oleic acid, the cis-C=C stretching band is very strong, even stronger than that observed in the spectrum of dimer acids. However, also in the Raman spectrum of oleic acid, the C=O stretching is not detectable (Figure 5a). The C=O stretching band appears in the Raman spectrum at about 1740 cm^{-1} only in ester ethyl oleate (Figure 5b) and is easily distinguished from the C=C stretching band. All esters, including the glycerides of oleic acid, show both the $\nu_{\text{C=C}}$ and $\nu_{\text{C=O}}$ bands in the Raman spectra.

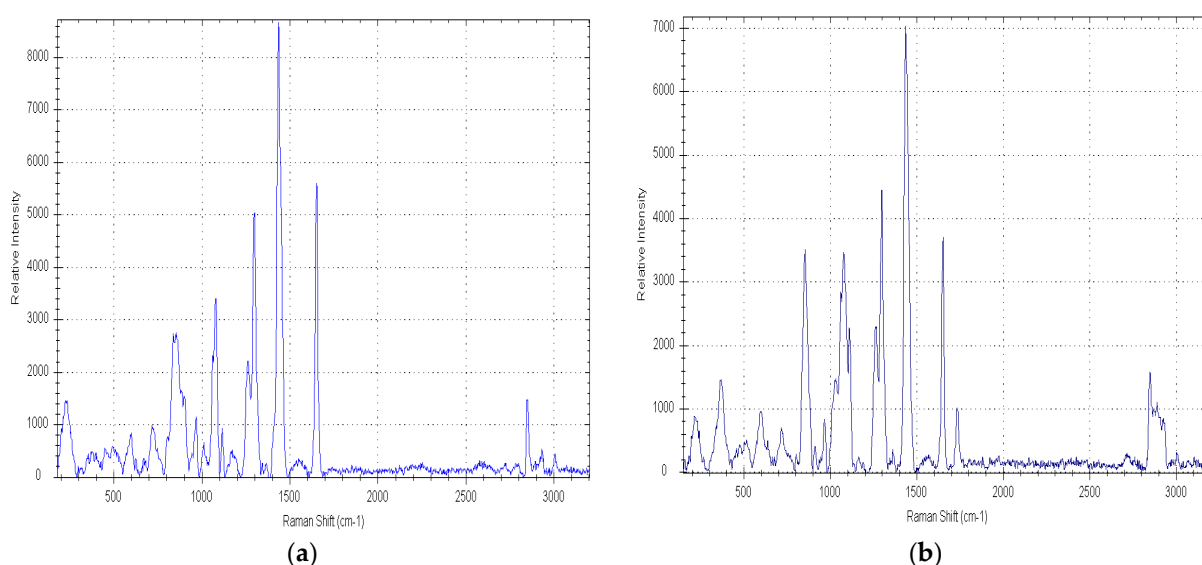


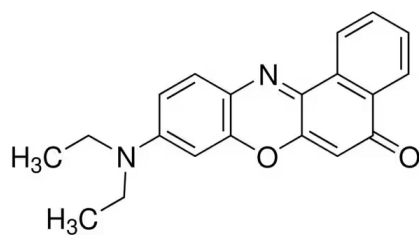
Figure 5. Raman spectra: oleic acid (a); ethyl oleate (b).

Following the assignment made by other authors in the case of the Raman spectra of fatty acids [25], Raman bands (Figures 4 and 5) in the range of $1500\text{--}1400\text{ cm}^{-1}$ are due to the scissoring and twisting vibrations of the CH_2 groups, while the CH_3 groups display the same types of vibration at about 1300 cm^{-1} . The $=\text{CH}$ bending mode is reported at 1265 cm^{-1} , but it is evident only in the Raman spectra of oleic acid and ethyl oleate. In the range of $1200\text{--}1040\text{ cm}^{-1}$, the skeletal optical modes due to $\nu_{\text{C=C}}$ appear [25].

3.3. Dimer Acids and Their Esters as Plasticizers Evaluated in the Nile Red Polarity Scale $E(\text{NR})$

3.3.1. Dimer Acids and Other Carboxylic Acids Evaluated with the Nile Red Polarity Scale $E(\text{NR})$

In the previous work [1], it was shown that one of the best ways to measure the polarity of plasticizers is to use Nile red dye (see Scheme 4 for the chemical structure) instead of Reichardt's $E_{\text{T}}(30)$ dye. The main problem with 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (i.e., $E_{\text{T}}(30)$ dye) is its sensitivity to acids. Even the trace residual acidity present in ester plasticizers (or other liquids) causes protonation of the phenolate oxygen anion, leading to the disappearance of the long-wavelength solvatochromic charge transfer (CT) band of the $E_{\text{T}}(30)$ dye, hindering any possible measurement. Other problems hindering the wider application of Reichardt's $E_{\text{T}}(30)$ dye are connected with its insolubility in certain liquids. The use of Nile red dye and the known correlation found between the $E(\text{NR})$ scale and $E_{\text{T}}(30)$ may represent a solution to evaluating the polarity of esters, plasticizers, carboxylic acids and other “difficult” liquids or certain polymers experimentally [1].



Scheme 4. Nile red dye, i.e., 9-diethylamino-5H-benzo[α]phenoxazinone.

Another powerful alternative to the above-mentioned experimental approaches is represented by a sophisticated semi-empirical approach proposed by Acree and Lang [26] that permits the estimation of the $E_T(30)$ values of certain “difficult” liquid and solid substrates where the experimental polarity measurement is inaccessible for a number of reasons.

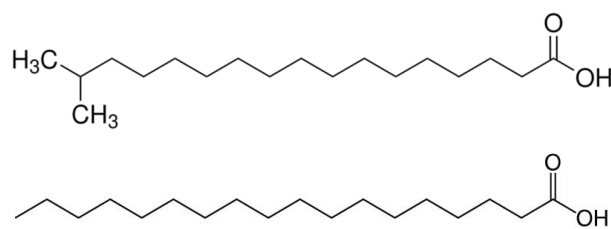
Remaining with the purely experimental approach of polarity measurement, the use of Nile red dye represents the tool of choice for difficult substrates. Nile red dye is soluble in innumerable media, is completely insensitive to acidity and exhibits positive solvatochromism in different liquid media in contrast with the negative solvatochromic behavior of Reichardt’s dye. A drawback of Nile red dye is that the absorption band of NR is less sensitive to the polarity changes of liquids than the absorption band of Reichardt’s dye. This is manifested in smaller solvatochromic shifts as a change in the polarity of the given liquid, requiring higher sensitivity spectrophotometers.

Another advantage offered by Nile red solvatochromic dye compared with Reichardt’s $E_T(30)$ dye is the possibility of measuring the polarity of liquid carboxylic acids. As shown in Table 1, a series of liquid carboxylic acids was studied with Nile red solvatochromic dye, including dimer and trimer acids, hydrogenated dimer acids and even isostearic acid (see Scheme 5 for the chemical structure). The latter compound is formed during the dimerization reaction when tall oil fatty acids (or other mixture of fatty acids) are heated with a montmorillonite catalyst. Isostearic acid is then separated from dimer acids, and it is characterized by a branched fatty acid chain instead of a linear one, as in the case of common stearic acid, as shown in Scheme 4 [6–12]. The unique property of isostearic acid is that it is liquid at ambient temperatures, while stearic acid is a solid with a melting point at about 70 °C. All the $E(NR)$ data in Table 1 were measured in the present study, with the exclusion of formic, acetic and propionic acids, whose $E(NR)$ values were taken from ref. [27].

Table 1. Polarity of liquid carboxylic acids measured with Nile red dye and the corresponding dielectric constant (or relative permittivity) ϵ .

Liquid Carboxylic Acid	λ (nm)	$E(NR)$ kcal/mol	References or Notes on the $E(NR)$ Values	Dielectric Constant ϵ (*)
Oleic acid	524.2	54.54	this work	2.34
Isostearic acid	525.2	54.44	this work	2.3 (**)
Dimer acids	528.7	54.08	this work	2.6 (**)
Hydrogenated dimer acids	528.7	54.08	this work	2.5 (**)
Trimer acids	531.5	53.79	this work	2.9 (**)
Propionic acid	542.4	52.71	Ref. [27]	3.3
Acetic acid	557.2	51.31	Ref. [27]	6.2
Levulinic acid (γ -ketovaleric acid)	595.5	48.01	this work	19
Lactic acid 90%	596.6	47.92	this work	22
Formic acid	634.0	45.10	Ref. [27]	54.5

(*) from refs. [28,29]; (**) estimated values, see text.



Scheme 5. Chemical structure of isostearic acid (**top**) versus the structure of stearic acid (**bottom**).

To show the validity of the E(NR) measurements in the case of these liquid carboxylic acids, an attempt was made to correlate the E(NR) values with the dielectric constants (ϵ) of these liquids. Fortunately, the dielectric constants (or relative permittivity) of the carboxylic acids studied in Table 1 are known [28,29], with the obvious exception of the dimer, trimer, hydrogenated dimer and isostearic acids. Since the dielectric constants of fatty acids are fully known [28,29], it was assumed that the dielectric constants of the dimer, trimer, hydrogenated dimer and isostearic acids were similar to the ϵ values of oleic, stearic and palmitic acids, with some minimal corrections derived from the E(NR) measurements. As shown in Figure 6, this approach has led to an interesting correlation between the E(NR) of liquid carboxylic acids and ϵ through a power law:

$$E(\text{NR}) = 57.09 \epsilon^{-0.058} \quad (3)$$

with an excellent R^2 value of 0.996.

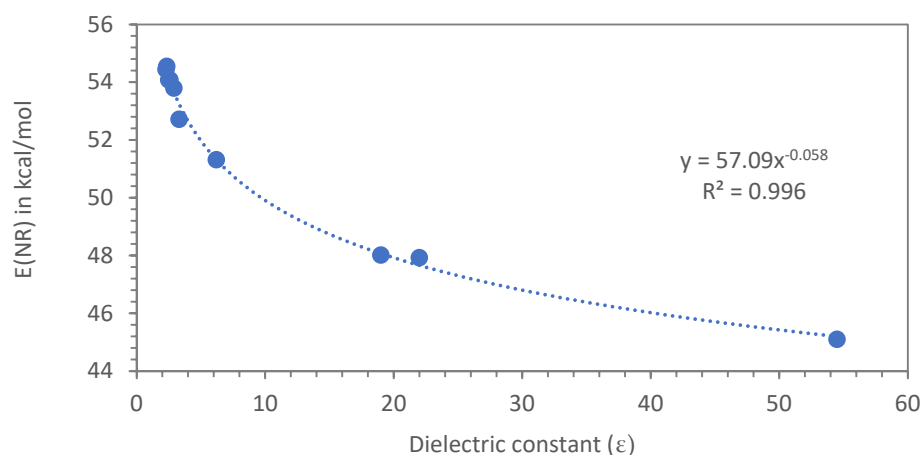


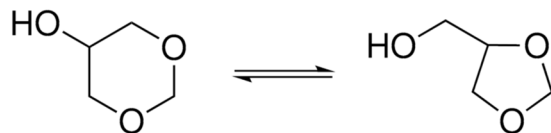
Figure 6. Correlation between the E(NR) values and the dielectric constant (or relative permittivity) of the liquid carboxylic acids.

3.3.2. Dimer Alcohols and Other Alcohols Evaluated with the Nile Red Polarity Scale E(NR)

Because of the interesting results obtained with liquid carboxylic acids in terms of E(NR) values and their correlation with the dielectric constants of the corresponding acids, a selection of alcohols typically used to produce ester plasticizers were subjected to the same methodological approach.

Table 2 shows the E(NR) values of selected alcohols measured in this work or derived from ref. [27]. The dielectric constant values were taken from refs. [28,29]. The dielectric constant of dimer alcohols was not found in the literature and was estimated as similar to that of 1-octanol (i.e., 11.3) since its structure recalls that of dimer alcohols (see Scheme 3) or t-butanol because dimer alcohols share a similar E(NR) value to t-butanol (see Table 2). Glycerol formal (see Scheme 6) is another interesting alcohol, similar to dimer alcohols, since it is >95% derived from glycerol from renewable sources, which is then reacted with

one molecule of formaldehyde to produce glycerol formal (see structure in Scheme 6). Thus, it has been assumed that glycerol formal maintains the same dielectric constant value as glycerol, i.e., 46.5 [28]. This assumption is also justified from the experimental value of the E(NR) transition, which places glycerol formal just between ethylene glycol and methanol (see Table 2).



Scheme 6. Chemical structure of glycerol formal.

Table 2. Polarity of selected alcohols measured with Nile red dye and the corresponding dielectric constant (or relative permittivity) ϵ .

Alcohol	λ (nm)	E(NR) kcal/mol	References or Notes on the E(NR) Values	Dielectric Constant ϵ (*)
1-Dodecanol	534.7	53.47	this work	8.1
2-Methyl-2-propanol (t-butanol) (***)	536.5	53.29	this work	10.5
Dimer alcohol	536.5	53.29	this work	10.4 (**)
2-Propanol (isopropanol) (***)	539.2	53.03	Ref. [27]	18.3
1-Nonanol	541.0	52.85	this work	9.2
1-Octanol	544.0	52.56	Ref. [27]	10.3
2-Ethylhexanol (***)	544.8	52.48	this work	7.6
1-Propanol	545.6	52.40	Ref. [27]	20.1
3-Methyl-1-butanol (***)	545.7	52.39	this work	15.6
1-Pentanol	547.2	52.25	this work	16.2
1-Butanol	547.6	52.21	Ref. [27]	17.8
Tetrahydrofurfuryl alcohol (***)	548.2	52.16	this work	13.6
Ethanol	548.3	52.15	Ref. [27]	24.3
2-Methyl-1-butanol (***)	548.3	52.15	this work	15.6
Methanol	549.6	52.02	Ref. [27]	32.6
Glycerol formal	559.5	51.10	this work	46.5 (**)
Ethylene glycol	565.2	50.59	Ref. [27]	41.4
Water (***)	593.2	48.20	Ref. [27]	80.0

(*) from refs. [28,29]; (**) estimated values, see text; (***) included in Figure 7 but excluded from Figure 8.

Figure 7 shows the attempt to correlate the E(NR) values of all the selected alcohols in Table 2 with the relative dielectric constants of each alcohol. This time, the correlation can be considered reasonably good, although not as good as in the case of the carboxylic acids studied in Figure 6. In fact, this time, $R^2 = 0.890$, and the linear equation linking E(NR) with ϵ is the following:

$$E(NR) = -0.063\epsilon + 53.54 \quad (4)$$

It is reasonable to think that the dispersion of values in Figure 7 is due to the relatively large variety of chemical structures of the alcohols considered. As reported in Table 2, if all the alcohols with non-linear structures and water (all marked with three asterisks) are excluded from the E(NR) vs. ϵ correlation, then the best fit of the data is offered by a power

law equation (similar to that found for carboxylic acids) with $R^2 = 0.831$, and Equation (4) is turned into the following Equation (5):

$$E(\text{NR}) = 56.06 \epsilon^{-0.024} \quad (5)$$

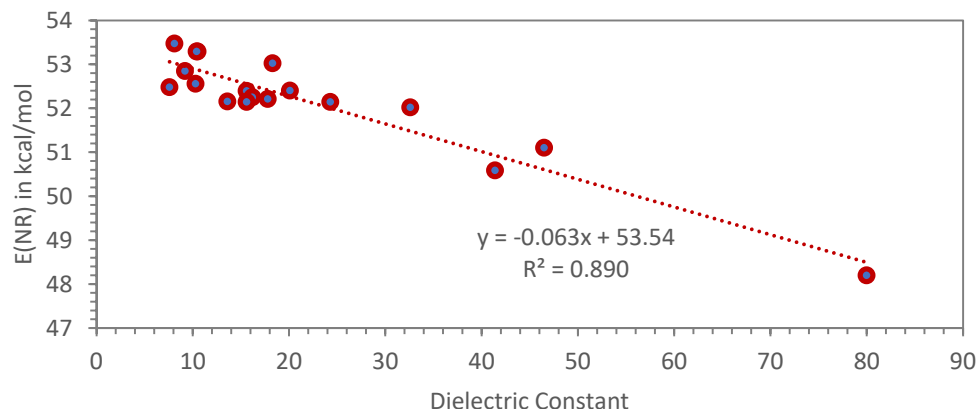


Figure 7. Correlation between the E(NR) values and the dielectric constant (or relative permittivity) of all the alcohols listed in Table 2, including water.

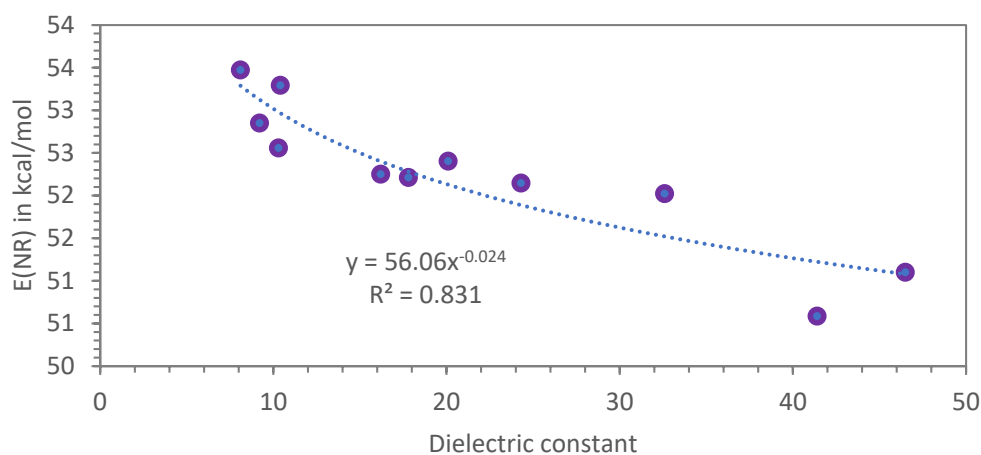


Figure 8. Correlation between the E(NR) values and the dielectric constant (or relative permittivity) of selected “linear” alcohols listed in Table 2 (those without three asterisks).

3.3.3. Plasticizers Evaluated with the Nile Red Polarity Scale E(NR)

A series of new plasticizers were synthesized according to the procedure detailed in ref. [21]. The new plasticizers are essentially the esters of the dimer or trimer acids and hence named “dimerates” or “trimerates”, respectively, and shown in bold in Table 3. The other plasticizers and esters reported in Table 3 are shown for reference to see how the dimerates and trimerates are positioned in the E(NR) scale. Furthermore, Table 3 shows another two “new” plasticizers, which are the fatty acid esters of glycerol formal (see Scheme 5), an alcohol derived from renewable sources as the resulting esters of fatty acids [30,31]. Unfortunately, it is not possible to try to make a correlation between the E(NR) values of the plasticizers reported in Table 3 and the corresponding dielectric constant of these liquids. The reason is that for many of the plasticizers reported in Table 3, the ϵ values are not available from the literature and, moreover, the dimerate and trimerate esters are little known. A similar comment applies also to the fatty acid esters of glycerol formal.

Table 3. Polarity of selected plasticizers measured with Nile red dye.

Plasticizers	λ (nm)	E(NR) kcal/mol	References or Notes on the E(NR) Values
T-DAE (treated distillate aromatic extract)	--	56.20	Ref. [1]
Oleyl oleate	508.1	56.27	Ref. [1]
Ethyl oleate	521.3	54.85	Ref. [1]
MES (mild extract solvate)	521.5	54.83	Ref. [1]
Methyl esters of fatty acids (brassica)	522.0	54.77	Ref. [1]
Methyl esters of fatty acids (cocco)	522.7	54.70	Ref. [1]
Diethyl adipate (diethylhexyl adipate)	523.0	54.67	Ref. [1]
Soybean oil	524.1	54.55	Ref. [1]
NYTEX Bio (Naphthenic oil and vegetable oil mixture)	525.4	54.42	Ref. [1]
Lauryl dimerate	526.0	54.36	This work
Nonyl dimerate	526.2	54.34	This work
Lauryl trimerate	526.2	54.34	This work
Amyl dimerate	526.6	54.29	This work
Ethylhexyl dimerate	526.7	54.28	This work
Glycerolformal esters of brassica fatty acids	526.8	54.27	This work
Isoamyl dimerate	527.1	54.24	This work
Butyl dimerate	527.1	54.24	This work
Ethyl dimerate	527.7	54.18	This work
Sunflower oil (high oleic)	528.2	54.13	Ref. [1]
Ethyl trimerate	528.4	54.11	This work
Diisododecyl adipate	528.5	54.10	Ref. [1]
Dimer acids	528.7	54.08	This work
Hydrogenated dimer acids	528.7	54.08	This work
Diethyl azelate	528.7	54.08	Ref. [1]
Methyl undecenoate	529.6	53.99	Ref. [1]
PEG dioleate	531.5	53.79	Ref. [1]
Tetrahydrofurfuryl dimerate	531.9	53.75	This work
PEG monoleate	533.4	53.60	Ref. [1]
Ethyl levulinate	536.4	53.30	Ref. [1]
Dimer alcohol	536.5	53.29	This work
Di(ethylhexyl)phthalate	537.0	53.24	Ref. [1]
Epoxidized glycerolformal ester brassica fatty acids	538.2	53.12	This work

Thus, a way to follow the change in polarity of the dimerates and trimerates is shown in Figure 9, where it is possible to see that the polarity of this family of esters is reduced by the length of the aliphatic chain of the alcohol used for esterification with a general equation:

$$E(\text{NR}) = 0.022 n + 54.11 \quad (6)$$

and with n the number of carbon atoms in the alcohol. These results are completely intuitive since the maximum polarity (lowest E(NR) values) are observed in free carboxylic acids, dimer acids and hydrogenated dimer acids, with a linear and measurable increase in

E(NR) on passing to ethanol ($n = 2$), butanol ($n = 2$) and so on in the resulting esters. With $R^2 = 0.859$, the correlation is reasonably good.

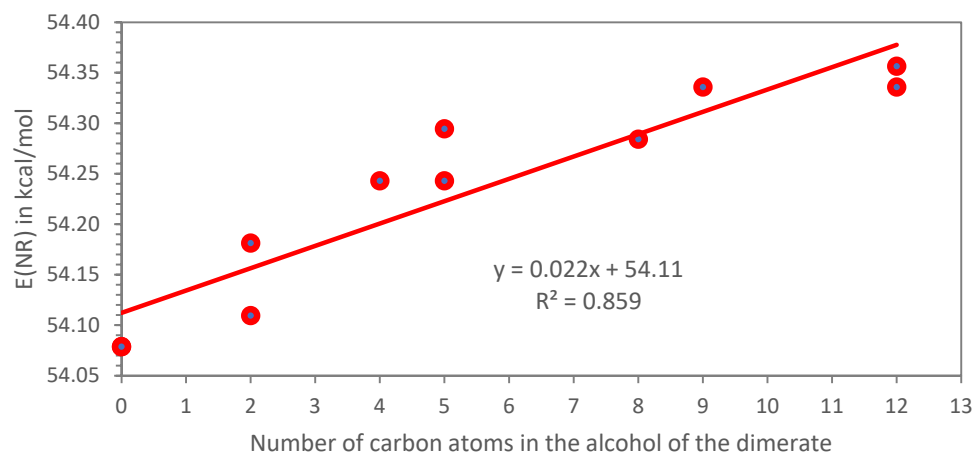


Figure 9. Correlation between the E(NR) values of dimerates and trimerates listed in Table 3 and the number of carbon atoms present in the alcohol of the ester.

The trimerates are considered only in a couple of cases, i.e., as ethyl and as lauryl (C_{12}) esters. In both cases, as well as in the case of the free trimer acids (see Table 1), this class of compound becomes more polar than the corresponding dimerate esters and dimer acids. This experimental fact is completely reasonable since trimer acids have three free carboxylic acid functionalities in contrast with the two functionalities displayed by dimer acids. The same reasoning applies in the case of the corresponding esters, i.e., three ester groups for the trimerates and only two ester groups for the dimerates.

4. Discussion of the Application of Dimerates, Trimerates and Other Esters

Dimerates and trimerates and the fatty acid esters of glycerol formal were developed in order to offer a new series of plasticizers, mainly for the rubber but also for the plastics industries. These new esters were designed to be derived from renewable sources and with the aim of substituting them for the traditional petroleum-based plasticizers used in the rubber industry, like T-DAE (treated distillate aromatic extract) and MES (mild extract solvate) [21,30,31]. Furthermore, the mentioned esters of dimer acids were considered biodegradable, and indeed, they present a reasonably good level of biodegradability [32].

In a previous work [1], the discussion was extensively focused on new plasticizers, which can substitute partially or completely for the traditional petroleum-based plasticizers, and their evaluation through the Reichardt's or Nile red polarity scales. It was shown that a solid correlation between the two scales does exist, and furthermore, Nile red dye is much more suitable than Reichardt's dye $E_T(30)$ for the study of the polarity of ester liquids. Dimerates and trimerates, particularly the former, show polarity levels at the E(NR) scale that make them compatible with the typical polymer matrices used by the rubber and, in particular, the tire industries, i.e., polybutadiene, polyisoprene (or natural rubber) and styrene–butadiene copolymers. Table 4 shows a summary of the E(NR) values of rubber and certain common plastics.

From the data in Table 3, it appears immediately evident that the most suitable dimerate ester candidates to be studied as replacements for petroleum-based MES, in addition to the methyl esters of fatty acids [5], soybean oil and the commercial product Nytex Bio, which is a mixture of naphthenic and vegetable oil, are lauryl (C_{12}), nonyl (C_9) and amyl (C_5) dimerates. Of course, ethylhexyl dimerate is also a candidate, but

2-ethylhexyl alcohol is synthetic and not naturally sourced. On the other hand, lauryl alcohol is derived, for example, from the naturally occurring and renewable palm kernel or coconut oil after fractionation and hydrogenation [33]. 1-Nonanol is industrially produced from the ozonolysis of oleic acid (a widely available and naturally sourced compound), followed by the hydrogenation of the resulting 1-nonanal [34]. Finally, amyl alcohol is naturally occurring from fermentation processes involving corn, molasses, potatoes or other similar substrates and known as fusel oil [35].

The above-mentioned dimerates with E(NR) values closer to those of polybutadiene (BR), polyisoprene (NR) and styrene–butadiene copolymer (S-SBR) rubbers (see Table 4) were indeed selected, synthesized and tested successfully as plasticizers in substitution of both the petroleum-based plasticizers (e.g., MES of Table 3) and vegetable oil plasticizers (Table 3) used in passenger tire tread formulations, with important advantages in winter performance and other tire tread properties [21]. Compatibility between the selected dimerate esters and the rubber matrix was found to be excellent and in agreement with the expectation from the E(NR) scale.

In addition to dimerates, the fatty acid ester of glycerol formal was successfully tested in a tire tread formulation [30,31]. The glycerol formal ester is positioned in the E(NR) scale just between the amyl and ethylhexyl dimerates from one side and the isoamyl and butyl dimerates from the other side (see Table 3). Even in this case, compatibility with the rubber matrix was found to be excellent, and the plasticizing effect and winter performance of the vulcanizate were found to be much better than the results with the reference traditional petroleum-based plasticizers and vegetable oils [30,31].

Furthermore, an epoxidized version of the glycerol formal ester of fatty acids has been developed to provide special compatibility with more polar polymer matrices like nitrile rubber (NBR) and polyvinylchloride (PVC), which have E(NR) values of 53.07 and 52.21 kcal/mol (Table 4) compared with 53.12 kcal/mol for the epoxidized glycerol formal ester of fatty acids (Table 3). Thus, epoxidation is able to shift the glycerol formal ester from 54.27 kcal/mol down to 52.21 kcal/mol in the epoxidized version (Table 3). As expected, the compatibility of the latter, the epoxidized version, with NBR and PVC is simply excellent [30,31]. Another interesting feature to be noticed in Table 3 regards the fact that the E(NR) value of the epoxidized glycerol formal ester (i.e., 53.12 kcal/mol) is equal to or better than the E(NR) value of (diethylhexyl)phthalate (i.e., 53.24 kcal/mol), the most widely used plasticizer in the past but being currently phased out because of concerns regarding its toxicity and its behavior as a xenohormone [36,37].

Table 4. Polarity of selected rubbers and plastics measured with Nile red dye.

Polymers	λ (nm)	E(NR) kcal/mol	References or Notes on the E(NR) Values	Dielectric Constant ϵ (*)
Polibutadiene (BR)	502.0	56.96	Ref. [1]	2.3
Polyisoprene (IR or NR)	503.2	56.82	Ref. [1]	2.4
Styrene–butadiene copolymer (S-SBR) with styrene 21% & vinyl 50%	509.0	56.17	Ref. [1]	2.5
Polystyrene (PS)	512.0	55.84	Ref. [1]	2.5
Epoxidized natural rubber (ENR-25)	526.4	54.32	Ref. [1]	3.0
Polymethylmethacrylate film (PMMA)	535.0	53.44	Ref. [1]	3.6
Poly(lactic acid) (PLLA)	535.0	53.44	Ref. [1]	3.5 (**)
Nitrile rubber (NBR) with 33% ACN	538.8	53.07	Ref. [1]	3.66
Polyvinylchloride (PVC)	547.6	52.21	This work	3.7

(*) Data from ref. [38]; (**) from ref. [39].

Thus, the epoxidized glycerol formal ester of fatty acids is one of the most interesting and effective potential replacements for (diethylhexyl)phthalate, both in a nitrile-based rubber matrix and in plasticized PVC.

The validity of the liquid polarity measured by Nile red dye and through the resulting E(NR) scale is supported not only from the previous work [1] but also by the correlation found between the E(NR) scale and the dielectric constants of carboxylic acids (Table 1, Figure 6) and alcohols (Table 2, Figures 7 and 8). In the case of the esters, the correlation of their E(NR) values with the length of the aliphatic chains of the alcohols used in the esterification was found (Table 3 and Figure 9).

Because of these exciting results, the correlation between the E(NR) values measured in solid polymer thin films containing Nile red dye and the dielectric constant of the relative polymers was also studied using the data in Table 4. As shown in Figure 10, in this case, a nice, linear correlation was also found linking E(NR) measured in rubber and plastics with their ϵ values:

$$E(\text{NR}) = -2.776 \epsilon + 63.13 \quad (7)$$

with the excellent $R^2 = 0.975$. Thus, even in the solid state, Nile red dye remains an excellent polarity probe of the medium in which it is dispersed or dissolved, irrespective of the physical state of the given medium, whether liquid or solid.

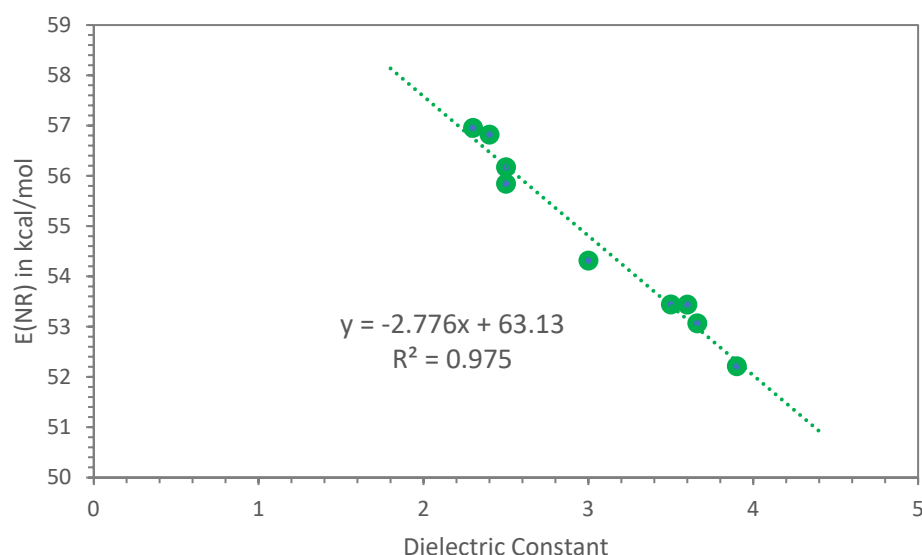


Figure 10. Correlation between the E(NR) values and the dielectric constant (or relative permittivity) of all the rubber and plastics listed in Table 4.

5. Conclusions

Dimer and trimer acids are relatively little-known liquids with relatively complex structures, as discussed in the introduction. Through the study of the electronic absorption spectra of pristine dimer acids and hydrogenated dimer acids, it was possible to conclude that in commercial dimer acids, the aromatic fraction is 35.5%. By contrast, in the case of dimer alcohol, the aromatic fraction was found at a level of 30.1%.

With FT-IR spectroscopy, dimer and trimer acids are practically indistinguishable from the band pattern of a common fatty acid like oleic acid. Of course, dimer alcohols are clearly distinguishable and easily identifiable with respect to either dimer acids or oleic acids.

It was found that Raman spectroscopy is a useful tool for the analysis and easy identification of dimer acids with respect to hydrogenated dimer acids, oleic acids and dimer alcohols. The stretching band of the ethylenic double bonds was found to be a highly diagnostic value in Raman spectroscopy.

Using the solvatochromism of Nile red dye, it was possible to study the polarity of a series of carboxylic acids, including dimer and trimer acids and hydrogenated dimer acids and isostearic acid (all from renewable sources), as shown in Table 1. The validity of this measurement was also confirmed by the correlation found between the E(NR) scale of the carboxylic acids studied and their dielectric constant (or relative permittivity). The experimental data were fitted with a power law, Equation (3).

Because of the success of the E(NR) polarity scale with a series of carboxylic acids, a series of alcohols (including dimer alcohol and glycerol formal, both from renewable sources) was also studied in the same way (see Table 2), and in this case, a fair correlation between the E(NR) scale and the dielectric constant of the alcohols considered was found. A linear correlation was found, as shown by Equation (4). However, when selecting alcohols with linear structures, the correlation of E(NR) with ϵ assumes a form of a power law of Equation (5).

A series of esters produced from raw materials from renewable sources were synthesized. These esters were made from dimer or trimer acids (both from renewable sources) and alcohols from renewable sources, such as lauryl, 1-nonyl and amyl alcohols. Other alcohols were also considered as dimerate and trimerate esters, as shown in Table 3. Furthermore, the fatty acid ester of glycerol formal (another alcohol from renewable sources) was considered as well as its epoxidized derivative. Table 3 shows the classification of all these plasticizer esters and other plasticizers used for rubber and plastics based on the polarity E(NR) scale using Nile red dye. Unfortunately, it was not possible to study a correlation between the E(NR) values of the plasticizers shown in Table 3 and their dielectric constant for the simple reason that the ϵ values of most of the plasticizers are not available from the literature data. Instead, a reasonable linear correlation (Equation (6)) was found between the E(NR) values of the dimerate and trimerate esters listed in Table 3 and the number of carbon atoms present in the alcohol chain of the ester.

Finally, a linear correlation (Equation (7)) was found between the E(NR) values measured in a series of polymers in the solid state (as thin solid films) and the relative dielectric constant of the polymers, confirming that Nile red is a powerful polarity probe effective not only in the liquid phase but also in the solid state.

The correlation between the E(NR) values and the dielectric constant of the medium is really intriguing and deserves further investigation.

The typical approach for the selection of the most compatible plasticizer for a given polymer was also shown. In general, it is necessary to select a plasticizer with the same E(NR) value as the polymer:

$$E(NR)_{\text{plasticizer}} \leq E(NR)_{\text{polar polymer}} \quad (8)$$

For polar polymers are also suitable those plasticizers having lower E(NR) values than polymers, i.e., plasticizers which are more polar than polymers.

On the other hand, for a non-polar polymer (e.g., hydrocarbon polymers)

$$E(NR)_{\text{plasticizer}} \geq E(NR)_{\text{non-polar polymer}} \quad (9)$$

are also suitable those plasticizers having higher E(NR) values than that of the polymer, i.e., plasticizer with less polarity than the polymer.

The success of this approach has already been tested in the development of new plasticizers from renewable sources for rubber and plastics.

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