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Phosphonated lipids as primary plasticizers for PVC with improved flame retardancy

Bocqué M.,[1] Lapinte V.,[1]* Courault V.,[2] Couve J.,[1] Cassagnau P.,[3] Robin J.J.[1]

[1]: Institut Charles Gerhardt Montpellier UMR-5253, CNRS, UM, ENSCM, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier cc1702, Place Eugène Bataillon 34095 Montpellier Cedex 5, France.

[2]: Serge Ferrari BP 54, 38352 La Tour-du-Pin Cedex, France.

[3]: Université Claude Bernard Lyon 1, UMR CNRS 5223, Ingénierie des Matériaux Polymères, 15 Boulevard Latarjet, F-69622 Villeurbanne, France

Correspondence to: Vincent Lapinte (E-mail: *Vincent.Lapinte@umontpellier.fr*)

Abstract

Bio-based plasticizers bearing moieties exhibiting flame retardancy properties (dimethyl (methyl oleate)phosphonate (PMO), diethyl (methyl oleate)phosphonate (PMO2), dimethyl (methyl linoleate)phosphonate (PML), dimethyl (dimethyl oleate)phosphonate (PDE)) were synthesized from methyl oleate, methyl linoleate and oleic diacid through free-radical addition of dialkyl phosphonates. Soft PVC were prepared from PMO, PMO2, PML and PDE primary plasticizers and compared to materials containing usual diisononyl phthalate DINP. Rheological behavior, thermal stability, mechanical properties and flame resistance performances of these PVC films were carefully investigated. The presence of the phosphonate group into the plasticizer structure explained the best thermal stability of the PVC films based on phosphonated plasticizer than that of based on DINP. Regarding all these results, PMO and PDE can be considered as efficient flame retardant primary plasticizers for PVC and can substitute phthalates in soft PVC based materials.

Keywords: bio-based; flame retardant; lipids; plasticizer; PVC.

1. Introduction

Poly(vinyl chloride) (PVC) is the second widespread manufactured and consumed thermoplastic in the world[1,2] owing to its low cost and its versatility in term of properties. The applications extend from highly rigid PVC (window profiles, computer housings, outdoor products, containers, blister packages) to flexible PVC (soft PVC) (wires and cables, flooring, wall coverings, roofing, food-wrap films, bottle caps, medical products, toys)[3]. Despite these advantages, the high melt viscosity of PVC induces a low processability. Additives including heat stabilizers, lubricants... are required to enhance the processing performance and the end-use properties. The most widely used additives are plasticizers[4,5] defined as "a substance or material incorporated in a material to increase its flexibility, workability or distensibility" by the council of the IUPAC (International Union of Pure and Applied Chemistry). The main candidates for PVC are the phthalate series even if since the early 1980s, they have been controversed due to their possible toxicity and their migration from PVC products[6] that represent a potential risk to human health[7]. To solve this problem, researches focused on alternative plasticizers based on citrate, adipate, azelate, sebacate, benzoate and other polymeric plasticizers, *etc.*[8-10]. Recently, an interest for natural-based plasticizers grew, especially for modified fatty acid derivatives (epoxidized oils[11-15], acetylated fatty esters[16,17], fatty acid polyesters[18], sulfonyl fatty esters,[19] glycerol esters[20] *etc.*), citrates[21] and sugar derivatives[22,23].

Additional properties such as UV resistance, electrical conductivity or fire retardancy must often be required for industrial applications. PVC is self-extinguishing since its chemical structure contains more than 50 % of chlorine. But, most of the organic additives are flammable and affect its fire resistance justifying the addition of flame retardant compounds. The most commonly flame retardant additives are antimony oxide, zinc borate, magnesium hydroxide, aluminum trihydrate and halogenated and phosphorus based compounds[24, 25].

Recently, Jia[26] described a PVC secondary plasticizer based on soybean oil containing a flame retardant phosphate moiety. Despite a good limiting oxygen index (LOI), the resulting soft PVC materials using these bio-based plasticizers exhibit lower mechanical properties and plasticizing efficiency than those using common observed with phthalates. Furthermore, the use of a primary plasticizer is needed to reach acceptable properties. Phosphorylation of lipids has already been widely described, including the synthesis of phosphorylated castor oil in presence of chlorodiphenylphosphine[27] or phosphoryl chloride[28] as described by De Espinosa and Liu, respectively. Guo detailed an alternative route between phosphoric acid and the epoxide rings of epoxidized soybean oil (ELO) [29] whereas Jia investigated the reaction epoxy-phosphorylated derivatives using diethyl phosphate with ELO[26] to design a secondary plasticizer for PVC. Knigh and Swem,[30] and Sasin[31] described the grafting of phosphorylated derivatives on vegetable oils by free-radical addition of dialkylphosphonates onto the lipidic double bonds. Based on this approach, a corrosion inhibitor additive was recently synthesized by Millet using dimethylphosphite on methyl oleate[32].

In this paper, we investigated the synthesis of primary PVC plasticizers combining a lipidic structure and phosphorus based moieties on the basis of our expertise on the chemical modification of triglycerides into lipidic polyols[33,34], polyamines[35,36], amphiphilic (macro)molecules[37-40]. The main goal of our researches was to get primary plasticizer exhibiting plasticization closed to that of DINP and simultaneously, flame retardancy avoiding the addition of any additives in PVC during compounding. Phosphonated groups are now well known for their ability to extinguish fire[41-43]. Thus, four phosphonated vegetable oil derivatives (PMO, PMO2, PML and PDE) were synthesized by free-radical addition of dialkyl phosphonates onto lipidic double bonds (Figure 1) into C9 or C10 position (and C12 or C13 position for PML). Soft PVC films were prepared from these bio-based plasticizers before evaluating their plasticizing efficiency and fire resistance.

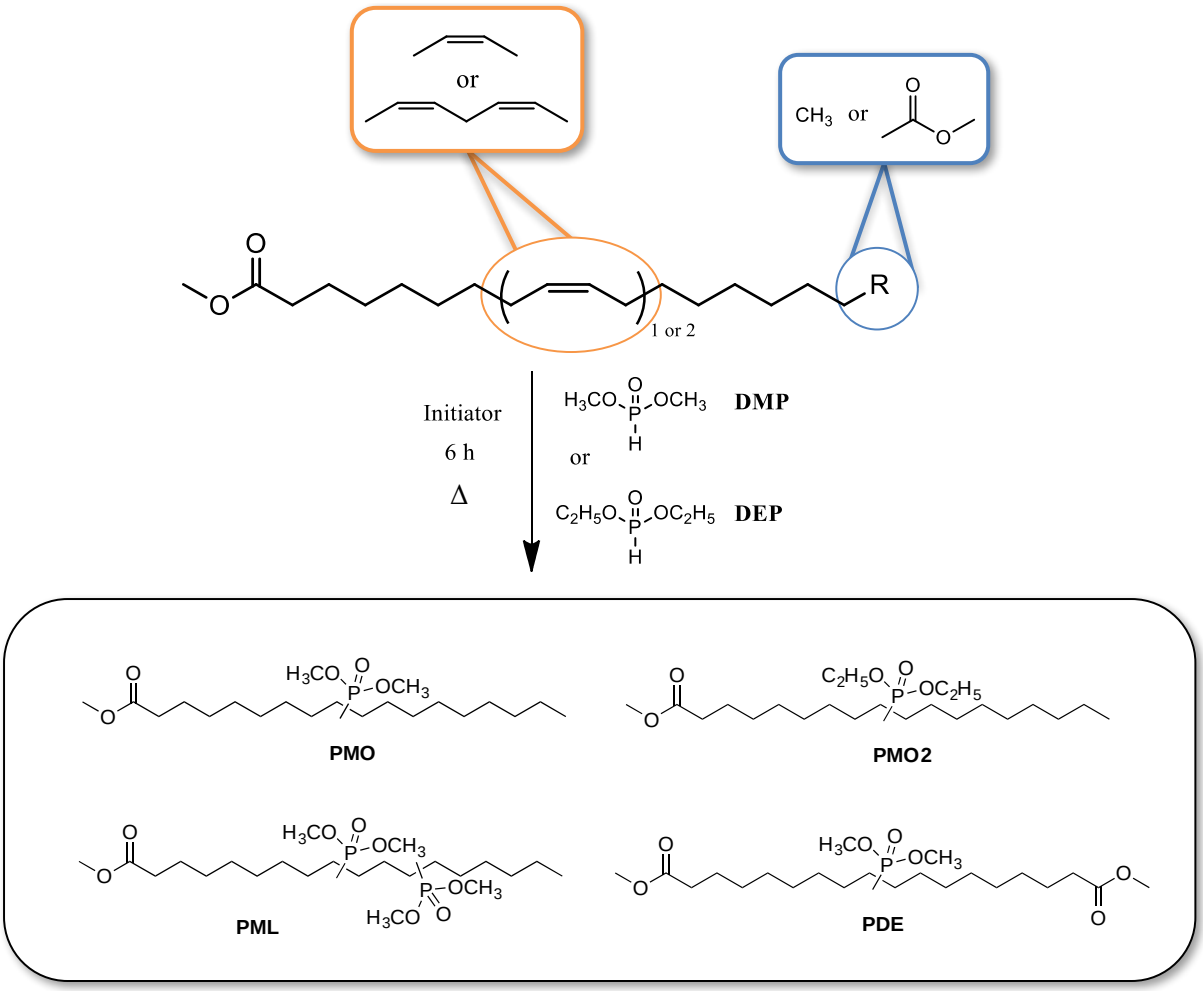


Figure 1. General chemical synthesis of PMO, PMO2, PML and PDE using MO, ML and DE.

2. Experiment

2.1. Materials

Methyl oleate (MO, purity 98.5 %, see Figure 1SI), methyl linoleate (ML, purity 80.9 %, see Figure 2SI) and C18:1 α,ω–diacid [(9Z)-octadec-9-enedioic acid] (purity 97.5 %, see Figure 3SI) (DA) were provided by Oleon and characterized by GC as detailed in 2.3.Methods section. PVC P70 resin and tin stabilizer T652 were provided by Serge Ferrari company. Dimethyl phosphate (DMP, 98%), diethyl phosphate (DEP, 98%), di-*t*-butylperoxyde (dtBP, 99%), *p*-toluenesulfonic acid monohydrate (98%) and methanol were purchased from Aldrich and used as received. *T*-butylperoxypivalate (tBPP) was supplied by AkzoNobel and used as received.

2.2. Synthesis of plasticizers

Phosphonation of MO and ML

MO or ML and the desired phosphonate (DMP or DEP; 3 equiv per double bonds present on the lipidic structures) were mixed in a glass flask (500 mL) and a nitrogen bubbling was performed for 30 min. The resulting mixture was heated under magnetic stirring at the desired temperature (75 °C or 141 °C) related to the peroxide (tBPP or dtBP, respectively). The radical initiator (0.1 equiv per double bond) was added and the reaction mixture was heated and stirred for 1 h. A second initiator addition (0.1 equiv per double bond) was achieved and the reaction mixture was stirred for a supplementary hour. Finally, a last addition of peroxide was done. The reaction mixture was stirred for 4 h, and at last, cooled at room temperature. The mixture was dissolved in the minimum amount of ethyl acetate, washed 3 times with brine, dried over anhydrous $MgSO_4$, filtered and solvent was evaporated under vacuum. PMO, PMO2 and PML were obtained in 96% (120.2 g, 0.2958 mol), 93% (30.5 g, 0.0702 mol) and 90 % yield (26.3 g, 0.05116 mol), respectively.

Dimethyl (methyl oleate)phosphonate (**PMO)** ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.83-0.88 (m, 3 H, C**H**$_3$), 1.24-1.27 (m, 22 H, C**H**$_2$ and C**H**$_2$-CH-P), 1.59-1.74 (m, 3 H, C**H**$_2$-CH$_2$-C=O and CH$_2$-C**H**-P), 2.25-2.30 (t, 2 H, CH$_2$-C**H**$_2$-C=O), 3.65 (s, 3 H, C**H**$_3$-O-C=O), 3.70-3.74 (d, 6 H, C**H**$_3$-O-P). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm): 37.75.

Diethyl (methyl oleate)phosphonate (PMO2) ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.85-0.90 (m, 3 H, C**H**$_3$), 1.25-1.39 (m, 33 H, C**H**$_2$, C**H**$_3$-CH$_2$-O-P and C**H**$_2$-CH-P), 1.61-1.74 (m, 3 H, C**H**$_2$-CH$_2$-C=O and CH$_2$-C**H**-P), 2.27-2.32 (t, 2 H, CH$_2$-C**H**$_2$-C=O), 3.66 (s, 3 H, C**H**$_3$-O-C=O), 4.03-4.13 (d, 4 H, C**H**$_2$-O-P). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm): 35.20.

Dimethyl (methyl linoleate)phosphonate (PML) ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.84-1.04 (m, 3 H, C**H**$_3$), 1.24-1.39 (m, 24 H, C**H**$_2$ and C**H**$_2$-CH-P), 1.58-1.71 (m, 6 H, CH$_2$-C**H**$_2$-C=O and CH$_2$-C**H**-P), 2.26-2.31 (t, 2 H, CH$_2$-C**H**$_2$-C=O), 3.65 (s, 3 H, C**H**$_3$-O-C=O), 3.70-3.74 (d, 6 H, C**H**$_3$-O-P). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm): 36.40-37.78.

Synthesis of phosphonated diester (PDE)

In a first step, D18:1 diacid (DA) were dissolved in chloroform ([DA] = 0.3 mol.L^{-1}) in presence of methanol (20 equiv). The mixture was vigorously stirred and *p*-toluenesulfonic acid monohydrate (0.2 equiv) was added. In a reverse Dean-Stark apparatus, the reaction mixture refluxed for 24 h. The organic solution was washed twice with distilled water and twice with brine, then dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to remove solvent and excess methanol. The dimethyl ester (DE) was obtained in 98 % yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.25-1.30 (m, 16 H, C**H**$_2$), 1.59-1.64 (m, 4 H, C**H**$_2$-CH$_2$-C=O), 1.99-2.01 (m, 4 H, C**H**$_2$-CH=CH-C**H**$_2$), 2.27-2.32 (t, 2 H, CH$_2$-C**H**$_2$-C=O), 3.66 (s, 6 H, C**H**$_3$-O-C=O), 5.32-5.35 (m, 2 H, C**H**=C**H**).

In a first step, phosphonated DE was dissolved in chloroform ([DE] = 0.3 mol.L^{-1}) in presence of methanol (20 equiv). The mixture was vigorously stirred and *p*-toluenesulfonic

acid monohydrate (0.2 equiv) was added. In a reverse Dean-Stark apparatus, the reaction mixture refluxed for 24 h. The organic solution was washed twice with distilled water and twice with brine, then dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to remove solvent and excess methanol. Dimethyl (dimethyl oleate)phosphonate (PDE) was yielded in 97 % (102.1 g, 0.227 mol).

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.24-1.37 (m, 22 H, C**H**$_2$ and C**H**$_2$-CH-P), 1.58-1.62 (m, 5 H, C**H**$_2$-CH$_2$-C=O and CH$_2$-C**H**-P), 2.26-2.31 (t, 2 H, CH$_2$-C**H**$_2$-C=O), 3.65 (s, 6 H, C**H**$_3$-O-C=O), 3.70-3.73 (d, 6 H, C**H**$_3$-O-P). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm): 37.46.

2.3. Methods

Nuclear magnetic resonance (NMR) spectra were recorded on a RMN BrukerAvance I 300 MHz. The chemical shifts were expressed in part per million (ppm), where (s) means a singlet, (d) a doublet, (t) a triplet, (m) a multiplet and (dd) a doublet of doublet. Chemical shifts (^{1}H NMR) were referenced to the peak of residual $CHCl_3$ at 7.26 ppm. Chemical shifts (^{13}C NMR) were referenced to $CDCl_3$ at 77 ppm.

The GC analysis were recorded on a Shimadzu GC-2010 Plus with RI detection. Samples were injected using a Supelco column (300 × 0.25 mm). The analysis was performed between 100 and 300 °C with a flow rate of 10 mL/min using acetonitrile as eluent.

The HPLC-MS analysis were recorded on a TSP/surveyor MSQ+ instrument in APCI$^+$ mode. Samples were injected using a Nucleosil 100-5C4 column (150 × 4.6 mm). The analysis were performed at 22 °C with a flow rate of 1 mL/min using isocratic elution with 20/80 acetonitrile/water.

Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal (ZnSe).

Size exclusion chromatography (SEC) was performed using a Waters 515 HPLC pump followed by a Water 2410 differential refractometer and a column set consisting of three 5µ PL-gel of 10^4, 10^3 and 500 angstroms. Chloroform was used as eluent at 0.8 $mL.min^{-1}$ at 35 °C and 200 µL of sample solution were injected. Calibration of the SEC equipment was carried out with polystyrene narrow standards (Agilent Standards, peak molecular weight range 162-1 238 000 $g.mol^{-1}$).

Calorimetric analyses were carried out using a Star1 differential scanning calorimeter (DSC) from Mettler Toledo® in order to determine the plasticizers melting points and the glass transition temperatures of PVC films. 10 mg of product was poured into an aluminum pan that was consecutively placed in the measurement-heating cell. An empty pan was used as reference. These calorimetric experiments were achieved under air atmosphere, from -70 to 25 °C with a heating rate of 10 $°C.min^{-1}$ for melting points, and from -100 °C to 150 °C with a heating rate of 15 $°C.min^{-1}$ for glass transition temperatures.

The thermal stability of the plasticizers and the PVC films was examined using a Q50 thermogravimetric analyzer (TGA) from TA Instruments®. The experiments consisted in registering the weight loss of the sample under air flow (25 $mL.min^{-1}$) as a function of temperature from the ambient up to 500 °C with a heating rate of 10 $°C.min^{-1}$.

To determine the gelation temperature, rheological analyses were performed using a dynamic rheometer (MCR 102 from Anton Paar®) equipped with parallel plate geometry (upper plate diameter ϕ = 25 mm and inner plate diameter ϕ = 40 mm). The liquid PVC (plastisol) formulation was inserted into the measurement plates at room temperature. The upper plate was lowered until contact with the sample with an average gap of 1 mm. The evolution gelation with temperature was monitored at an angular frequency of 6.28 $rad.s^{-1}$ from the variation of the linear complew shear modulus ($G^*(\omega)= G'(\omega)+jG''(\omega)$, $j^2=-1$). Such method has been described in a previous work.[45]

2.4. Sample preparation

A usual PVC plastisol formulation (around 30 wt.% plasticizer) consisted in mixing PVC, plasticizer and thermal stabilizer until obtaining a homogeneous mixture. The resulting paste was degassed under vacuum for 40 min. The mixture was spread out on a mirror or a glass plate, with a thickness of around 0.5 mm, using an Elcometer squeegee and heated at 190 °C in an oven for 10 min.

2.5. Sample characterization

Elongation at break and Young modulus of the films were measured on an Instron 3366L5885 tensile tester according to ISO 527-3:1995 standards. Films were cut into 10 strips of 1.5 x 10 cm and mounted between tensile grips with an initial grip spacing of 5 cm and cross-head speed of 200 $mm.s^{-1}$. The elongation at break is expressed as a percentage of the original length.

Cured plastisols' hardness was evaluated with a Shore A durometer (HBA 100-0 from Sauter).

Limited oxygen indices (LOI) were determined using an ILO Rheometrics apparatus. Fire was ignited from strips of PVC films (5 x 17 cm) under of a growing amount of oxygen. This test characterizes the combustion performance and is expressed by a unitless value. High numbers reveal great resistance to ignition since it means that higher amount of oxygen are needed to keep the flame alive.

3. Results and discussion

3.1. Phosphonation of vegetable oil derivatives

Herein, phosphonated lipidic derivatives (PMO, PMO2, PML and PDE) were synthesized by the free-radical addition of dimethyl phosphite (DMP) and diethyl phosphite (DEP) on methyl oleate (MO), methyl linoleate (ML) and diester (DE) (previously synthesized from the diacid D18:1 which is a dimer made from the metathesis of dec-9-enoic acid or oleic acid[46]) as shown in Figure 1. Two peroxide-type initiators: di-*tert*-butyl peroxide (dtBP) and *tert*-butyl peroxypivalate (tBPP) were investigated since they are well known for their hydrogen abstraction ability in the case of hydrogen phosphonate. They yielded in quantitative conversion rate the phosphorylated lipids at 141 and 75 °C, respectively.

The syntheses of PMO, PMO2, PML and PDE plasticizers were monitored by FTIR spectroscopy with the appearance of the characteristic peaks corresponding to P-O-C symmetric bending vibration at 1048 cm^{-1} and P-O-C stretching vibration at 813 cm^{-1}, as well as the total disappearance of =C-H bonds absorption band at 3009 cm^{-1}. An additional ^{1}H NMR study was achieved on PMO, PMO2, PML and PDE and is shown in Figure 2. The peak located at 0.8 ppm corresponding to the terminal methyl protons of fatty esters (-C$\underline{H}_3$ or H_a) was taken as reference for the conversion calculation whereas the triplet at 2.3 ppm corresponding to the fatty ester protons [-(C$\underline{H}_2$)-CO-] (H_b) was used for the PDE plasticizer. The typical peak attributed to methyl ester protons (CO-O-C$\underline{H}_3$) was located at 3.66 ppm. The addition of phosphorylated derivatives was monitored by the appearance of the -P-C$\underline{H}$- signal at 1.6 ppm as well the doublet at 3.70 ppm corresponding to the phosphonate group (-P-O-C$\underline{H}_3$) for PMO, PML and PDE products or the peaks at 1.3 ppm (-P-O-CH_2-C$\underline{H}_3$) and 4.1 ppm (-P-O-C$\underline{H}_2$-) for PMO2.

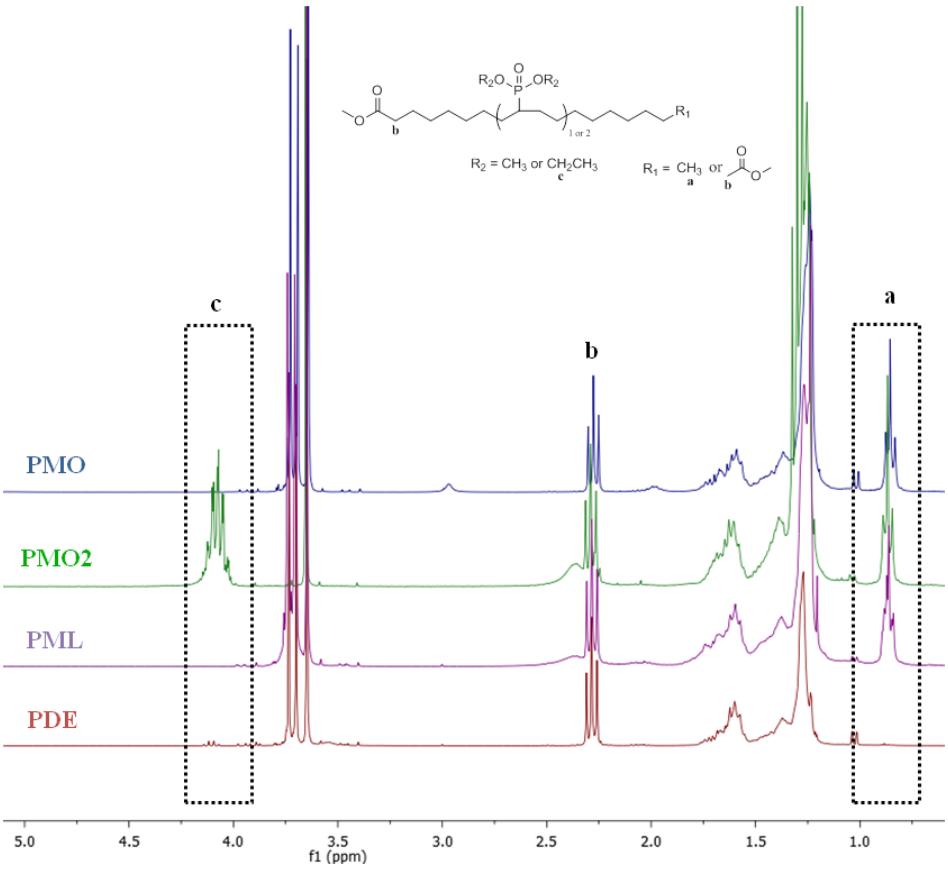


Figure 2. ^{1}H NMR spectra of PMO, PMO2, PML and PDE.

The chemical modifications of lipids were also monitored by SEC using chloroform as eluent (Figure 3). The shift of the SEC traces, before and after addition of phosphonates onto the unsaturations attested the total conversion into phosphorylated lipid as illustrated for DE. As expected, the trace of the resulting product shifted towards the lower elution time corresponding to the higher molecular weight even if the difference coming from the addition of a phosphonate group corresponded only to 110 g/mol. The molecular weight at the peak of the phosphorylated lipid followed the order of the theoretical ones: PMO > PMO2 > PDE > PML. In each case, we can observe a large peak and a smaller one in the area of higher elution time attributed to oligomers. This oligomerization was observed with all the chemical modifications of lipidic derivatives when the reaction was performed at high temperature

involving some oligomerization in radical way. This phenomenon was observed by Robin *et al.*[47]

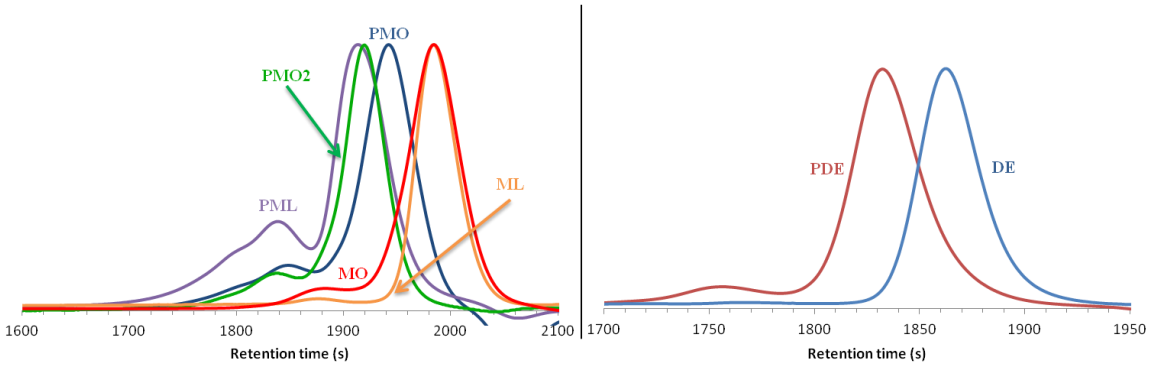


Figure 3. SEC chromatograms of PMO, PMO2, PML and PDE (left); of PDE related to virgin DE (right).

The zero shear viscosities of these compounds were measured at room temperature (T=25°C) to estimate the processability during the plasticization step. Actually, the viscosity was determined for the two most interesting candidates PMO and PDE (explained further in this study) as well as for the most commonly widespread plasticizer (DINP). The bio-based plasticizers, PMO and PDE, exhibit a lower viscosity (1.6 Pa.s and 2.4 Pa.s, respectively) than DINP (3.2 Pa.s). This behavior is in favor of a better processability of these compounds during plasticization.

3.2. Plasticization

The usual plasticization of PVC has already been fully described by several authors as summarized in our recent review[10]. The plasticization starts by mixing the small PVC particles into the liquid plasticizer, to obtain a paste called plastisol. The heating allows the solvation of PVC particles by the plasticizer[48-50] then above the PVC glass transition temperature (85 °C), PVC particles absorb the plasticizer in a great extent and the plastisol becomes a solid paste[51-53]. The extension of the heating at 190 °C triggers the fusion of PVC

micro-crystallites, high interactions between swollen plasticizer molecules and PVC polymer chains[54,56] producing, once cooled down, a flexible solid material. This complicated mechanism is based on a high compatibility between the plasticizer and PVC and explain why only few candidates are able to plasticize PVC. Several efficient lipidic plasticizers have already been reported but the question was to know if the modification of triglycerides by one or two phosphonate groups decreases the plasticizing effect of PVC? To study this aspect, our candidates were investigated as primary plasticizers of PVC. DINP plasticizer acts as reference with the elaboration of the sample A as shown in Table 1. Different soft PVC compositions based on our bio-based phosphonated plasticizers were prepared as described in the experimental part (samples B-E). To allow the comparison between the various formulations, 30 % plasticizer content, 2 % of stabilizer T652 and 50 g of PVC P70 were set for each ones.

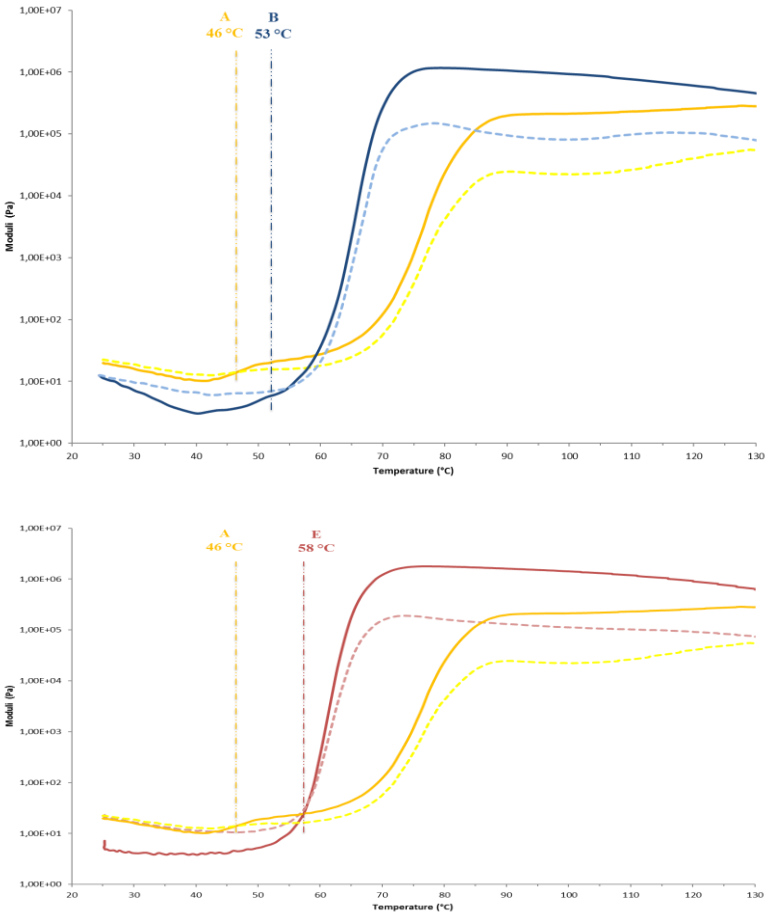
Table 1. Composition of PVC plastisol formulations.

Sample	PVC P70 (g)	DINP (g)	PMO (g)	PMO2 (g)	PML (g)	PDE (g)	Stabilizer T652 (g)
A (ref.)	50	25	0	0	0	0	1
B	50	0	25	0	0	0	1
C	50	0	0	25	0	0	1
D	50	0	0	0	25	0	1
E	50	0	0	0	0	25	1

As mentioned earlier, the gelation process of a plastisol is a complex process in which PVC particles and aggregates are swollen to form a gel structure. This process is governed by diffusion laws and highly depends on temperature and compatibility with the plasticizer. This phenomenon can be monitored by rheological measurements determining the evolution of the

storage and loss moduli, G' and G'' respectively, as a function of the curing temperature. The gelation temperature ($T_{gelation}$) of the plastisol can be defined as the crossover between complex modulus G'(ω) and G''(ω)[45]. This study was performed for the samples A to E as depicted in Figure 4. The gelation temperature ranged from 46 to 73 °C with an intermediate value for PDE (sample E) at 58 °C and a lower and higher value for the samples A and C, respectively.

At the end of the analyses, all G' moduli are located between 1.10^5 and 1.10^6 Pa and show some differences between the various samples. These variations will be magnified for mechanical properties and discussed.



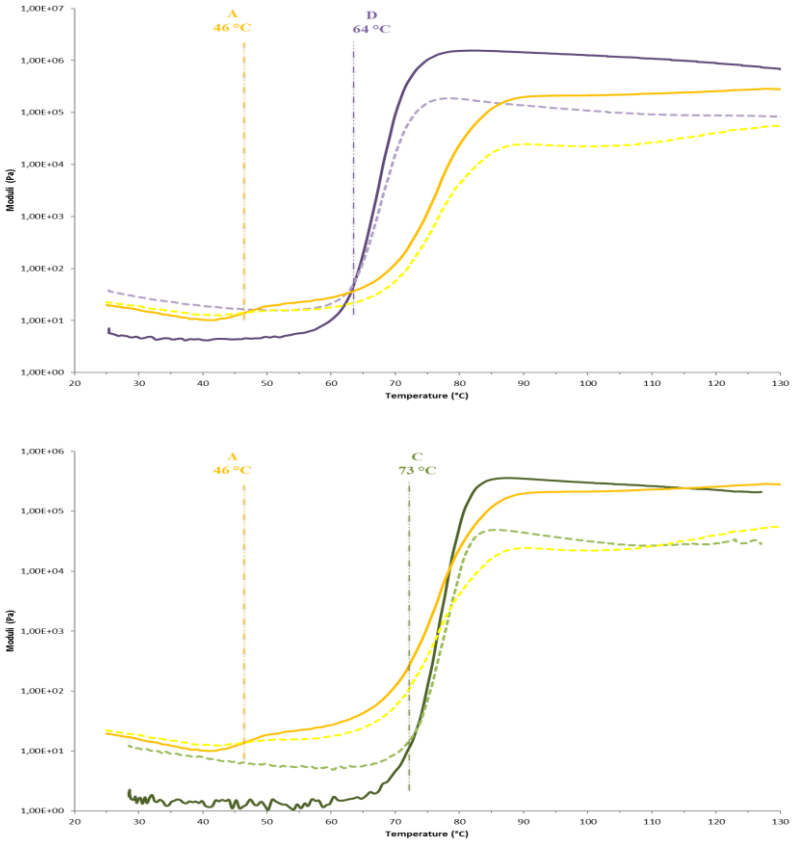


Figure 4. G' (full lines) and G" (dotted lines) as a function of temperature for various PVC plastisol formulations (5 °C/min).

3.3. Properties of soft PVC containing phosphonated lipidic plasticizers

The thermal properties of the plasticizers and of the resulting plastisols were investigated by calorimetric study (DSC) as shown in Figure 5. The melting point of the plasticizers ranged from -43 and -2 °C for DINP and PDE, respectively. These additives are liquid at room temperature favoring the swelling of PVC particles and the final plasticization of this resin. The thermograms of plasticized PVC revealed that all the additives were miscible with PVC aggregates since no melting of free plasticizer was observed (Figure 5). The plasticizing effect of the phosphonated lipids (PMO, PMO2, PML and PDE) on PVC films was confirmed by the decrease of the T_g values in comparison to that of PVC close to 85 °C. The chemical structure of the phosphonated lipidic plasticizers had only a slight influence

on the resulting material and final T_g ranged between -10 and -7 °C for the samples B to E. These low T_g suggested a convenient solubility of these plasticizers in PVC.

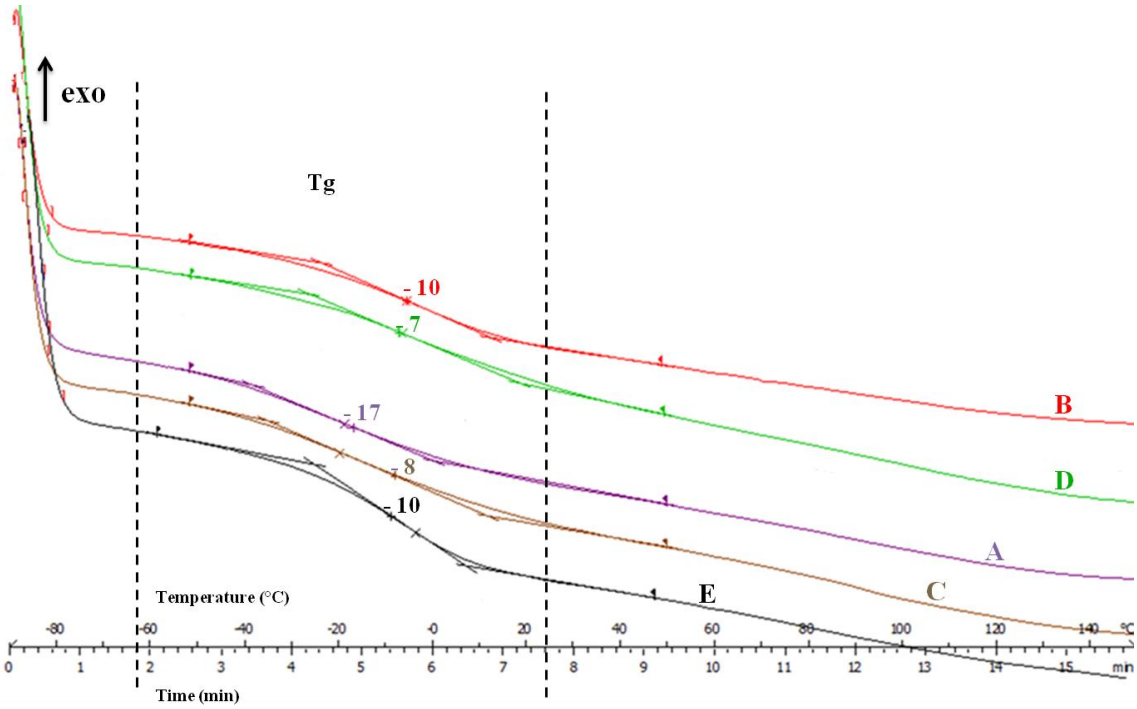


Figure 5. DSC thermograms of soft PVC corresponding to formulations A to E (10 °C.min^{-1}).

The thermal degradation of PMO, PMO2, PML, PDE and DINP plasticizers as well as PVC plastisol formulations A to E were studied by TGA and are reported in Figures 6 and 7, respectively. These thermogravimetric analyses were performed to highlight the plasticizers behaviors at the temperature corresponding to the curing of the plasticized PVC, that is to say 190°C. First of all, all the plasticizers decomposed according to the same three-stage thermal degradation profile with a fast degradation around 300 °C except for PDE which degraded later. At the curing temperature, only 2% of DINP were lost by evaporation versus 3-6% for the monophosphorylated lipidic plasticizers. The diphosphorylated one, PML, suffers a little more important degradation with 10% lost. Another piece of information deduced from the TGA study was the formation of a char layer around 15% observed at 500 °C for the

plasticizers bearing phosphonate groups. This effect is well known for phosphonate materials at high temperature[37,56] and missing for DINP. The degradation of dimethyl or diethyl phosphate into phosphonic acid triggered the formation of carbonization zones protecting the compound from further degradation. In conclusion, PMO2 owned the worst thermal stability compared to all the other bio-based plasticizers with a faster degradation. By contrast, PMO and more particularly PDE possessed the best thermal stability with the slowest degradation and the most important char layer formation at the end of the analysis.

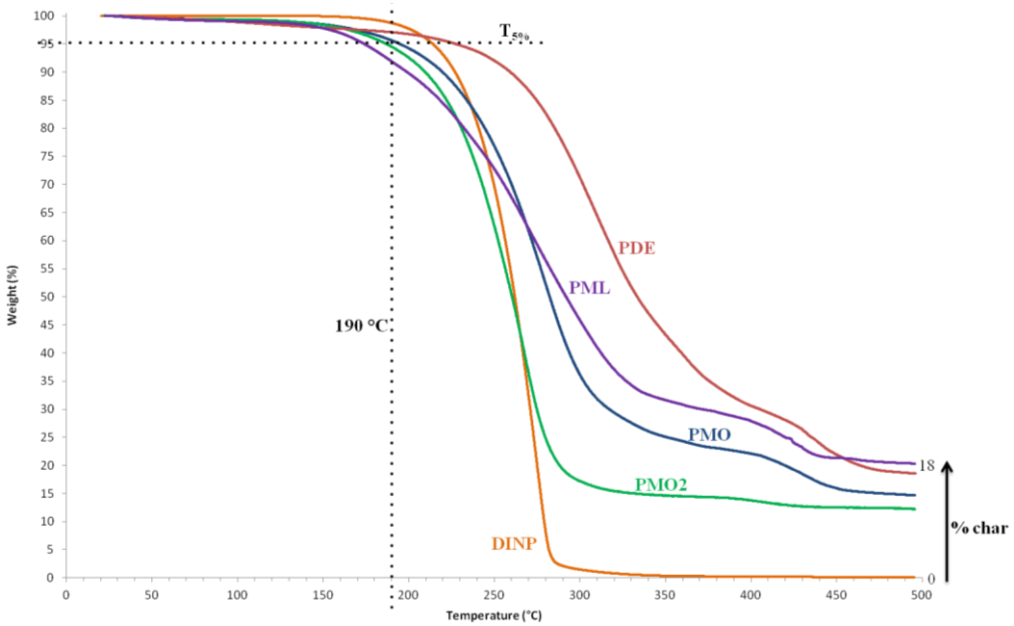


Figure 6. TGA analyses of plasticizers under air.

The TGA profiles of plasticized PVC revealed a thermal stability below 200 °C as illustrated in Figure 7. The large weight loss around 300 °C corresponds to the degradation of PVC and formation of HCl[24]. The samples degraded according to the same thermal profile, except for sample A (DINP) which possessed the worst thermal stability. In contrary, the sample E (PDE) was the most stable formulation with the same onset temperature of degradation than the unmodified PVC but with lower weight loss at the same temperature.

Finally, all soft PVC plasticized with the lipidic phosphonated compounds gave 27 % of char at 500°C whereas only 16% were produced by DINP.

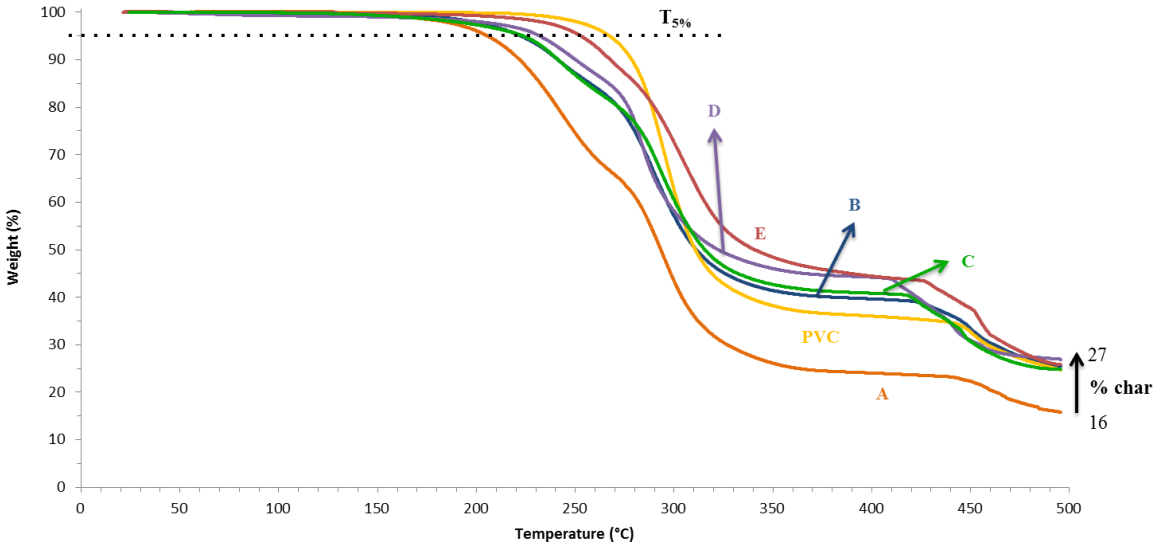


Figure 7. TGA analysis of cured PVC plastisols under air.

Plasticizers drastically impact the mechanical properties of PVC. The plasticizer efficiency is currently investigated by the tensile properties and Shore hardness[57]. Herein, all samples with a plasticizer content of 30% have similar Shore A values in the range of 89-99 as summarized in Table 2. They also gave good mechanical properties with an elongation at break ε ranged between 290% and that of DINP value (sample A) as shown in Figure 8. Among the phosphonated lipidic plasticizers, PMO and PDE (samples B and E respectively) lead to the highest elongation values. Moreover, PDE (sample E) has the highest plasticizing efficiency and flexibility compared to DINP and other bio-based plasticizers samples. Indeed, sample E exhibits lower Young modulus (9 related to 11-15 MPa) and tensile strength. In summary, the results show that the phosphonate group has an impact on the final properties of the plastisol. Hence, increasing the length of the phosphonate ester alkyl group or increasing the number of the phosphonate groups linked to the fatty chain diminishes the mechanical and

thermal properties. Moreover, raising the number of carboxylic ester improve these properties.

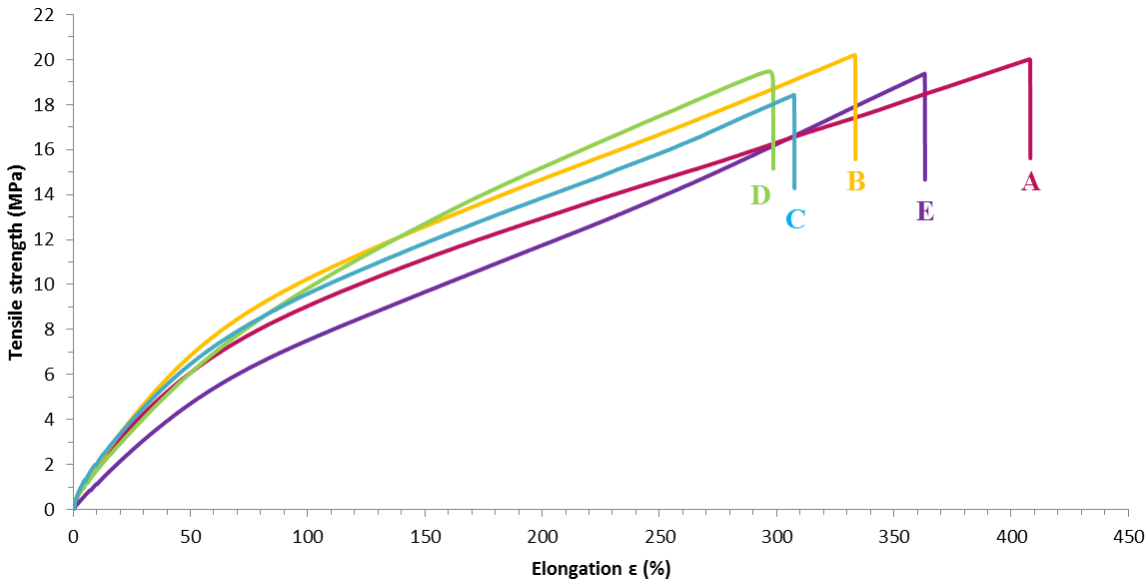


Figure 8. Tensile properties for soft PVC films with a plasticizer content of 30%.

Table 2. Mechanical properties of PVC films.

Sample	Elongation at break ε (%)	Young modulus E (MPa)	Tensile strength at break (MPa)	Shore A hardness
A (ref.)	405 ± 10	14 ± 0,8	20 ± 1	93 ± 2
B	320 ± 28	15 ± 0,4	20 ± 1,8	89 ± 2
C	300 ± 30	15 ± 2,2	19 ± 1	94 ± 1
D	290 ± 31	11 ± 1	18 ± 2,6	99 ± 1
E	365 ± 13	9 ± 0,5	18 ± 1,1	90 ± 2

The influence of the plasticizer content on the glass transition temperature and the mechanical properties was deeply investigated for the two best candidates, PMO and PDE

(Figure 9 and Table 3). As expected, T_g values decreased with plasticizer content increasing. This effect is magnified with PMO plasticizer going from -10 to -50°C for 30 to 50 % PMO content, respectively. Moreover, tensile properties (Young modulus and the tensile strength at break) logically decreased with the plasticizer content. Inversely, the elongation at break increased with the plasticizer content, especially for 50 % in plasticizer. PMO (full lines) gave higher Young modulus and tensile strength as well as lower elongation than PDE (dotted lines) while this trend slightly reversed for high percentage.

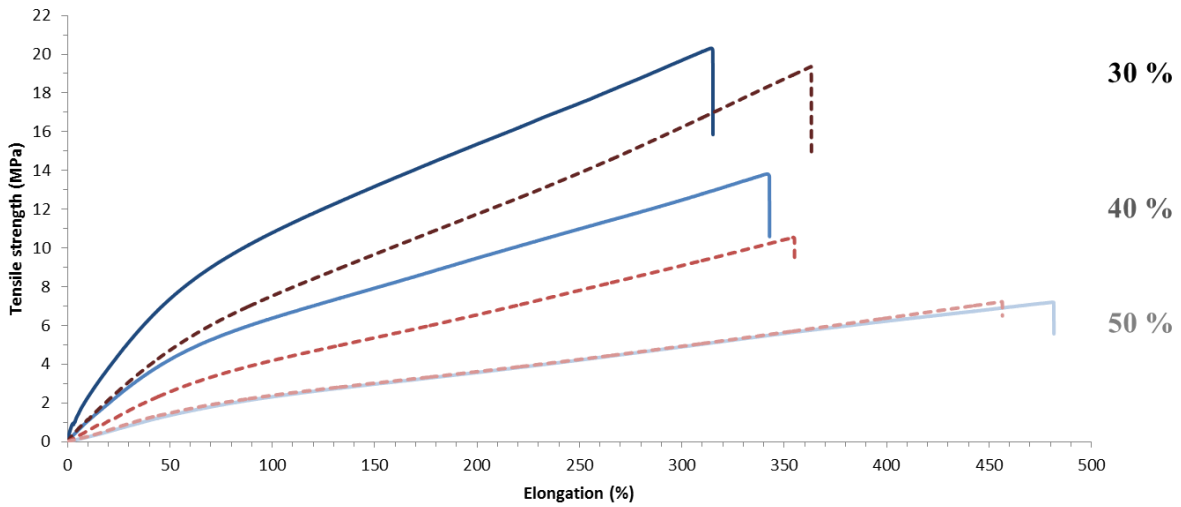


Figure 9. Tensile strength related to elongation for various plasticizer contents in PMO (full lines) and PDE (dotted lines).

Table 3. Influence of PMO and PDE content in PVC on mechanical properties.

Plasticizer	%	Tg(°C)	Elongation at beak (%)	Young Modulus E (MPa)	Tensile strength at break (MPa)	Shore A hardness
PMO	30	-10	320 ± 28	15 ± 0.4	20 ± 1.8	89 ± 2
	40	-30	340 ± 26	9 ± 0.5	14 ± 1.9	92 ± 1
	50	-50	480 ± 17	3 ± 0.3	7 ± 0.7	83 ± 2
PED	30	-10	365 ± 13	9 ± 0.5	18 ± 1.1	90 ± 2

	40	-20	350 ± 10	5 ± 0.3	11 ± 0.6	87 ± 1
	50	-40	440 ±2 6	3 ± 0.4	7 ± 0.8	77 ± 3

At last, the combustion performances of plasticized PVC films with PMO, PDE and DINP have been evaluated by the LOI test. It is first important to have in mind that rigid PVC possesses an oxygen index of 50[58]. As said before, this is due to the presence of chlorine. The addition of DINP lowers this value up to 23. Samples B and E both gave higher LOI values than the reference DINP with 27. Knowing that the materials exhibiting a LOI value above 26 are considered as efficient flame retardants with a self-extinguishing behavior[59,60], it can then be concluded that PMO and PDE are effective flame retardant plasticizers for PVC.

4. Conclusion

In this work, four phosphonated lipidic derivatives (PMO, PMO2, PML and PDE) were successfully synthesized in a one step process from methyl fatty (di)ester by free-radical addition of dimethyl phosphite or diethyl phosphite onto the double bonds. A rheological study revealed the diffusion of these bio-based additives into the PVC particles and their possible use as primary plasticizers in soft PVC films. PVC samples with similar thermal properties than DINP ones and better flame retardant properties were obtained. The presence of phosphonate groups allowed the formation of a char layer and the protection of the material against larger degradation. Mechanical tests highlighted a good plasticizing efficiency with a high elongation at break around 350 % and a lower Young modulus and tensile strength, especially PDE and PMO. Thus, PMO and PDE could efficiently substitute phthalates as primary PVC plasticizers with additional flame retardancy properties.

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