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Catalyzed ring opening of epoxides: Application to bioplasticizers synthesis

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ABSTRACT

The ring opening of mono, di or tri-substituted epoxides by acetic anhydride to corresponding diacetates is catalyzed by weak bases such as hydrotalcite in the carbonated form. This reaction is performed at 423 K without solvent and the solid catalyst is reused after simple regeneration for 4 runs with constant conversion. Ring-opening of methyl oleate epoxide leads to the formation of useful diacetate methyl oleate.

Starting from vegetable oils, polyacetate derivatives are prepared in three catalytic steps (methanolysis, epoxidation then ring opening). Plastisol was prepared by mixing these products with PVC and their rheological properties were evaluated. The recorded data show that they can act as bioplasticizer with similar behaviour as phthalate reference.

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1. Introduction

Polyvinyl chloride (PVC) is one of the oldest and most common plastics in use today because of the low cost, durability, and versatility with respect to fabrication and property modification. It finds uses in one or both of two general forms: unplasticized or plasticized PVC [1]. The latter one is widely used for numerous applications such as household goods, cable covering, toys or as a substitute for leather and introduced in clothes or various furnishings. Plasticized PVC contains up to 50% plasticizers as an additive to increase the flexibility, softness, processability and pliability of the end product. Plasticizers are typically a high boiling, organic liquid that reduces the glass temperature of the polymer where the polymer changes from brittle to flexible [2]. Thus, the addition of plasticizer reduces the tensile strength and elastic modulus of PVC but increases the elongation at tensile failure at ambient temperature. The alkyl phthalate family represents the main PVC plasticizers currently used in industrial processes. However, their use is restricted in some applications (toys, food contact, medical devices) because they eventually migrate out of plastics [3,4]. Moreover, they are suspected to disrupt human endocrine activity. So there is a tendency to the use of alternative plasticizers especially prepared from renewable raw materials. Recently, Polysorb ID37[®],

an isosorbide diester developed by Roquette, showed excellent plasticizing properties [5]. Danisco reported a plasticizer produced from castor oil that makes plastic products soft and flexible and that is fully biodegradable [6]. Tall-oil derivatives were also described as PVC plasticizers [7].

Large range of applications of oleochemicals in polymers has been reported mainly as stabilizers or lubricants [8–12]. The catalytic transesterification of vegetable oils with methanol to FAME is now well established as well as the epoxidation of the unsaturated fatty derivatives yielding to the production of reactive substrates that can react with many nucleophiles leading to the opening of the strained epoxide ring (Scheme 1) [13–16].

In previous communications, we reported the solvent-free ring opening of epoxides by acetic anhydride catalyzed by quaternary ammonium salts [17]. The diacetylation of 1,2-epoxydodecane took place in good to excellent yields in a catalytic reaction in solvent free conditions. Among the studied catalysts, tetrabutyl-ammonium chloride and acetate were the best ones reaching full conversion at 373 K after 6 h. The replacement of soluble catalysts by solids would provide cleaner and safer processes, due to the reduction of salts, easier separation of the products and recycling of the catalyst which is necessary for environmental preoccupations. Some functionalized polystyrene resins bearing ammonium groups were previously evaluated, however, they exhibited much lower activities (only 85% after 48 h). Considering these results, we studied alternative heterogeneous catalysts able to perform this transformation. Herein, we report the development of basic solids to catalyze the ring open-

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Scheme 1. Synthetic route from vegetable oil to bioplasticizer.

ing reaction of oxirane with acetic anhydride. More specifically, we compare a strong base such as Mg–La–mixed oxides [18,19], with mild bases such as Mg–Al hydrotalcites [20–22], and the mixed oxides obtained by calcinations, that are well known as basic catalysts for a broad range of reactions. Furthermore, we wish to present the development of this ring-opening reaction to epoxides derived from fatty esters. The influence of the nature of vegetable oils and the reaction conditions will be detailed as well as some properties of the product.

2. Experimental

1,2-Epoxydodecane, methyl oleate and acetic anhydride were purchased from Aldrich. Novance kindly provided two types of fatty ester namely Lubrirob 926.65 containing mainly methyl oleate and Lubrirob 301.01 containing mainly methyl linoleate (Scheme 1).

2.1. Synthesis and characterization of the solid bases

Hydrotalcites (HDT–CO₃, Mg/Al=3) and Mg–La mixed oxides (Mg/La=3) were prepared by precipitation of a mixture of nitrate salts at a constant pH=10, according to previous reports [23]. Hydrotalcites were activated at 723 K in an air flow using a temperature ramp of 2.5 K/min and maintained at this temperature for 1 h, while Mg–La mixed oxides were calcined at 923 K. HDT-calc and Mg–La-calc were thus obtained. These calcined solids were eventually rehydrated overnight at room temperature in a flow of nitrogen saturated by water, giving HDT–OH and Mg–La–OH.

The surface area of the Mg–La mixed oxide is $38 \text{ m}^2 \text{ g}^{-1}$ after calcination at 923 K ($60 \text{ m}^2 \text{ g}^{-1}$ before calcination). The as-prepared HDT shows a surface area of about 90 m² g⁻¹, while the surface area of HDT-calc is $280 \text{ m}^2 \text{ g}^{-1}$, and that of HDT-OH about $50 \text{ m}^2 \text{ g}^{-1}$. The basic strength of the solid and the number of basic sites were determined by microcalorimetry at room temperature, using CO₂ as probe molecule. Coupling microcalorimetry and volumetry allows to determine the number of basic sites adsorbing CO₂, and their strength measured by the adsorption enthalpy, i.e. the energy of the interaction of the probe with the surface.

2.2. Epoxydation of methyl oleate [24-26]

In a round bottom flask, 3 g of methyl oleate (10 mmol) and 0.1 ml of formic acid (3 mmol) were heated at 40 °C. 2.6 ml of 35% H_2O_2 (30 mmol) were then added dropwise and the solution was heated to 3.5 h at 70 °C. The solution was cooled to room temperature. The epoxide was extracted by Et_2O (30 ml) and the organic layer was washed with H_2O (30 ml), Na_2CO_3 sat (30 ml) and NaCl sat (30 ml) and dried (MgSO₄). After evaporation, quantitative yield of epoxide was obtained which was used in the following step without purification. NMR data are in accordance to literature.

2.3. Epoxydation of Lubrirob 926.65 (OLE)

In a round bottom flask, 100 g of Lubrirob 926.65 (OLE) and 3.8 ml of formic acid (100 mmol) were introduced. 104 ml of 35% H_2O_2 (30 mmol) were then added dropwise (30 min) and the solution was heated to 10.5 h at 70 °C (complete conversion monitored by GC analysis). The solution was cooled to room temperature. The epoxide was extracted by Et_2O and the organic layer was washed with H_2O (30 ml), Na_2CO_3 sat (30 ml) and Na_2SO_3 sat until elimination of peroxide. The organic phase was dried over $MgSO_4$ and the solvent was evaporated to yield 86% of pale yellow liquid (OLE-ox) which was used in the following step without purification.

The same procedure was applied for Lubrirob 301.01 (LIN) unless 2 equiv. of formic acid and H_2O_2 were added (yield 60%, LIN-ox). NMR and GC analysis are detailed in supplementary materials.

2.4. General method for ring opening reaction of 1,2-epoxydodecane with hydrotalcite

In a typical experiment, the reaction was carried out in a 5 ml closed vial equipped with a magnetic stirrer. A mixture of 1 mmol (0.2 g) of 1,2-epoxydodecane, 1.2 mmol $(120 \,\mu\text{J})$ acetic anhydride and 20 mg catalyst $(10 \,\text{wt\%})$ was introduced into the vial. Dodecane was introduced as internal standard. The reaction mixture was heated to the desired temperature (typically 373 K) under stir-

ring for 24 h. After cooling, an aliquot was treated with water and extracted with ether. The organic layer was dried over $MgSO_4$ and analyzed by GC (column HT5, 60 m).

2.5. General method for ring opening of epoxized oils catalyzed with Bu₄NCl

In a typical experiment, 100 g of OLE-ox, 108 ml (1.1 mol) of Ac_2O and 5.5 g of Bu_4NCl were added in a 500 ml round bottom flask and heated for 18 h at 130 °C (complete conversion by GC analysis). The solution was cooled down, extracted with AcOEt. The organic layer was washed with H_2O , Na_2CO_3 and then NaCl sat. The brown solution was then filtered on active carbon (Acticarbon L3S) then dried over MgSO₄. After evaporation of the solvent, 228 g of slightly yellow liquid were obtained (OLE-ac).

2.6. Analysis of fatty ester derivatives

The composition of the mixture was determined by GC analysis using a DB-23 column (60 m) with methyl myristate as external standard (Scheme 1).

The following data are obtained (supplementary materials):

LUBRIROB 926.65: methyl palmitate (6%), methyl stearate (2%) methyl oleate (59%), methyl linoleate (21%), methyl linolenate (9%).

LUBRIROB 301.01: methyl palmitate (6%), methyl stearate (3%) methyl oleate (32%), methyl linoleate (57%), methyl linolenate (2%).

2.7. Rheological properties

The plastisol formulation was 50 parts (by weight) of plasticizer per hundred of PVC. Viscoelastic properties were measured with a dynamic stress rheometer of TA Instruments (AR 2000). Rheology measurements were carried out in the oscillatory mode with a parallel-plate geometry (diameter = 25 mm). The thickness of the sample (gap of the parallel plate) was about 1 mm. Furthermore, a programmed heating rate (\cong 5 °C/min) at a constant frequency (ω = 6.28 rad/s) was carried out from room temperature (*T*) 150 °C to follow the complete of gelation of various PVC plastisols. Finally, the complex shear modulus ($G^*(\omega) = G'(\omega) + jG''(\omega)$) was recorded versus temperature.

2.8. Procedure for recycling the catalyst

The first run was performed from 800 mg 1,2-epoxydodecane, Ac_2O (1.2 equiv.) and 80 mg catalyst (10%). At the end of the reaction (24 h), the mixture was cooled to room temperature, the solid was filtered. Several treatments were evaluated. Treatment 1: the catalyst was reused without treatment. A mixture of 800 mg of 1,2-epoxydodecane, 1.2 g acetic anhydride were introduced into the vial containing the used catalyst. The reaction mixture was heated at 373 K; treatment 2: the catalyst was washed with AcOEt, then ether and air dried at room temperature; treatment 3: the catalyst was washed with ether, air dried at room temperature and calcined (723 K); Treatment 4: the catalyst was washed with ether (10 ml), then treated with saturated NaHCO₃ (30 ml). After filtration, the solid was air dried.

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Ring-opening of epoxydodecane by tertiary amine.

Entry	Catalyst	<i>T</i> (K)	Cat (mol%)	Conv. (%)	Sel (%)
1	NEt ₃	373	5	93	94
2	(C ₁₂ H ₂₅) ₃ N	373	5	87	92
3	(C ₁₂ H ₂₅) ₃ N	373	20	98	90
4	C_5H_5N	373	5	97	95
5	C_5H_5N	353	5	69	99

Reaction conditions: 1 equiv. 1,2-epoxydodecane, 1.2 equiv. Ac₂O, catalyst, 5 h.

3. Results and discussion

3.1. Ring opening of epoxydodecane with base

Initially, the acylation of 1,2-epoxydodecane to the corresponding diester product was used as a model reaction (Scheme 2). We have previously shown that ammonium quaternary salts were very efficient for this reaction [17]. Considering the mechanism, we anticipated that the reaction could be catalyzed by bases so, evaluation of the corresponding amine was carried out using the same reaction conditions: 373 K in the presence of a slight excess of acetic anhydride (1.2 equiv.) and under solvent free conditions (Table 1).

Tertiary amines were very efficient to catalyze this reaction. Almost complete conversions were achieved in the presence of 5% triethylamine, fatty amine or pyridine (entries 1, 2 and 4). Whatever the tertiary amines, high selectivity towards diacetate (>90%) was obtained, the only by-product analyzed being the monoacetate derivative. These results are in the same range to those obtained with ammonium salts (97% conversion at 5 h [17]). Pyridine is the most efficient catalyst and the reaction can be performed selectively at 353 K but the conversion decreased (entry 5). However, due to toxic properties of this aromatic amine, its use should be avoided.

In parallel, several inorganic bases were evaluated for this reaction and we found that hydrotalcite exhibited significant activity achieving an almost complete conversion (95%) after 24 h. The reaction was selective towards the diacetate, and only small amount of monoacetate was formed. Considering this interesting result and the easy availability of this catalyst family, we optimized the reaction conditions with a range of solid oxides with different basic strengths (Table 2).

The results of the determination of basic strengths of hydrotalcites and Mg–La mixed oxide by microcalorimetry are reported in Fig. 1. As-synthesized HDT, evacuated at 373 K, thus still in the carbonate form, appears as a weak base, adsorbing CO₂ with an enthalpy of about 80 kJ mol⁻¹. The number of active sites is about 150–200 μ mol/g. Mg–La mixed oxide decarbonated at 923 K is a strong base but with very low number of basic sites, adsorbing about 10 μ mol/g of CO₂ with an enthalpy >140 kJ mol⁻¹. Calcined, then hydrated hydrotalcite (HDT–OH) adsorbs about 250 μ mol/g with a constant heat of adsorption of 100 kJ mol⁻¹. Rehydration of the solid shifts then the type of basicity from Lewis to Brönsted with only marginal changes of basicity [27]. By contrast, Mg–La mixed oxide appears to be a stronger base, and this series of catalysts permits to investigate the effects of basicity on the catalytic properties.

The following parameters were studied: temperature of the reaction, amount of catalyst, nature and activation of mixed oxides (Table 2). The catalytic properties of the hydrotalcites (Mg/Al



Scheme 2. Catalyzed-ring opening of epoxides.

Entry	Catalyst	S_{BET} (m ² g ⁻¹)	Basic sites (µmol/g) ^a	<i>T</i> (K)	Cat. (wt%)	<i>t</i> (h)	Conv. (%)	Sel _{24 h} (%)
1	HDT-CO ₃	90	110	373	10	5/24	67/90	87
2				373	1	24/72	25/80	73
3				353	10	24	79	71
4	HDT-calc	280	400	373	10	5/24	28/77	83
5	HDT-OH	50	420	373	15	5/24	63/87	97
6	$Mg-La-CO_3$	60		373	10	5/24	10/28	70
7	Mg-La-calc	38	25	373	10	5/24	6/20	71
8	Mg-La-OH	-	-	373	10	5/24	18/70	71

 Table 2

 Influence of mixed oxide pre-treatment on the conversion of epoxide.

Reaction conditions: 1 equiv. 1,2-epoxydodecane, 1.2 equiv. Ac₂O, catalyst; HDT-CO₃ used as received; HDT-calc: after thermal treatment at 723 K (see Section 2); HDT-OH: after rehydration (see Section 2).

^a Refers to number of basic sites with adsorption enthalpy higher than 40 kJ mol⁻¹).

ratio=3) are compared to those of stronger basic Mg–La mixed oxides (ratio Mg/La=3). All these solid catalysts are subjected to different activation treatments. The original mixed oxides are prepared in the carbonate form ($-CO_3$). Decarbonatation occurs after thermal treatment at 723 K for 1 h (-calc), finally the latter ones are treated in a stream of nitrogen saturated with water to give the hydrated form (-OH) [20,27].

The preliminary optimization of reaction conditions has been performed with the as-synthesised hydrotalcite Mg/Al = 3 (HDT-CO₃). Full conversion was achieved at 373 K after 24 h reaction time in the presence of 10 wt% solid (Table 2, entry 1). The reaction can be performed at 353 K without affecting strongly the reaction rate (entry 3). As expected, decreasing the amount of catalyst lead to a lower reaction rate, the conversion reaching only 80% after 72 h (entry 2). In order to compare the activity of the different solids, the reaction was carried out at 373 K in the presence of 10% weight of basic solids (Table 2, entries 1, 4 and 5). After thermal activation (HDT-calc) and rehydration (HDT–OH), the solids exhibited different behaviours the former one being much less active.

The kinetics of the catalyzed ring-opening of epoxide have been determined on HDTs subjected to the different treatments. In all cases, the diacetate is the main product of the reaction (>90%), the by-product being the hydroxyl monoacetate [17]. The evolution of the conversion with time is reported in Fig. 2.

The comparison after 3 h on 10% and 1% HDT–CO₃ shows that the conversion is roughly proportional to the catalyst amount, which means the process operates in the chemical regime. Several experiments performed with 20 mg of catalyst exhibit reproducibility better than 90%, thus showing that hydrotalcite has a homogeneous composition.

It is clear that HDT-CO₃ and HDT-OH presented similar performances, while, HDT-calc is much less active. After 5 h reaction time, 67, 63 and 28% yield of diacetate are achieved with HDT-CO₃, HDT-OH and HDT-calc respectively (Table 2, entries 1, 5 and 4). One important point which has to be taken into account in basecatalyzed reaction is the acidity of the reactant. Indeed, when the reactant is a ketone (pK ca. 19-20), strong basic sites are necessary to deprotonate the substrate, while moderate strength is enough to activate an acid anhydride. The calcined hydrotalcite is the solid with the highest surface area $(280 \text{ m}^2 \text{ g}^{-1})$ and it also possesses a large number of basic sites (ca. 400 µmol/g). Nevertheless, it exhibits the lowest performance for the considered reaction. Indeed, after the calcination of synthesized hydrotalcite, the basic sites are Lewis sites which are not the most suitable for the ring opening of epoxide with acetic anhydride [27]. On the other hand, as-synthesized hydrotalcite (HDT-CO₃) or rehydrated one (HDT-OH) are solids with moderate surface area $(50-90 \text{ m}^2 \text{ g}^{-1})$ and 100-420 µmol/g Brönsted basic sites (Table 2). In the presence of traces of water, the carbonates can be hydrolyzed to hydrogenocarbonates which are Brönsted bases [28]. We suggest that the present reaction is mainly catalyzed by Brönsted type basic sites.

The role of the basic sites was confirmed by the use of Mg–La mixed oxides. These solids are strong bases but with a small number of sites compared to hydrotalcites (25μ mol/g, entry 7, Table 2)[23]. After 5 h, the calcined form which is considered as the most basic one, yielded very low conversion (entry 7). This mixed oxide has however a very low number of sites compared to HDT, as illustrated in Fig. 1, and the higher strength does not compensate this small amount of basic sites. After rehydration, Brönsted basic sites are formed and the conversion increased from 20% with the calcined sample to 70% with the hydrated one (entries 7 and 8), in agreement with the proposal of a higher activity of Brönsted sites.



Fig. 1. Differential enthalpies of adsorption of CO_2 on (a) HDT- CO_3 evacuated at 373 K, (b) HDT calcined at 773 K, then evacuated at 773 K, (c) HDT calcined at 773 K, hydrated at RT, evacuated at 373 K, and (d) Mg-La mixed oxide calcined at 923 K, stored in air, evacuated at 773 K.



Fig. 2. Influence of the pretreatment of hydrotalcite on the kinetic of the ring opening. Reaction conditions: 1 equiv. 1,2-epoxydodecane, 1.2 equiv. Ac₂O, catalyst, 373 K.



Scheme 3. Schematic representation of the role of hydrotalcite in ring epoxide opening.

Considering the reaction mechanism (Scheme 3a), it can also be assumed that strong bases such as Mg–La mixed oxides interact too strongly with acetic anhydride or some intermediate acetic derivatives, that could act as poison. High basicity is not necessary for the ring-opening of epoxides therefore it is more convenient to use solids with a larger number of Brönsted basic sites as present in rehydrated hydrotalcite. The interest of hydrotalcite lies in their role as acid–base bifunctional catalyst [29]. In the present work, the mechanism could be a concerted reaction with nucleophilic attack of the acetate on the epoxide activated by Mg²⁺ cations (Scheme 3b). Similar concerted mechanism was reported by the group of Kaneda in the condensation of epoxide with CO₂ [30].

The comparison with usual liquid bases can be done under similar reaction conditions, after 5 h of reaction: in the presence of 5 mol% NEt₃, the conversion reached 93% (entry 1, Table 1), corresponding to a TOF \approx 4 h⁻¹, while in the presence of 10 wt% HDT-CO₃, the conversion reached 67% (entry 1, Table 2) that is TOF \approx 60 h⁻¹ indicating that these solids are very efficient for that reaction. The best performance achieved with solid catalysts could be attributed to the concerted mechanism described in Scheme 3.

The possibility of reuse of the catalysts for the ring opening of 1,2-epoxydodecane was then studied starting from the assynthesized HDT-CO₃ solid (Fig. 3). At the end of the reaction, the mixture was cooled down and the catalyst was separated by filtration and reused in a new run. A significant decrease in conversion was observed under those conditions and the conversion reached only 25% in the second run (treatment 1). Attempts to wash the solid with ether to remove potential organics absorbed on the surface failed as well (treatment 2). As expected, the calcination at 723 K did not allow reusing the solid (treatment 3, <20%). Finally, after the first run, the solid was filtered, washed with ether, treated with aqueous solution of NaHCO₃ in order to obtain the initial hydrotalcite (treatment 4). This treatment was successful as sim-



Fig. 3. Reuse of the catalysts. Reaction conditions: 1 equiv. 1,2-epoxydodecane, 1.2 equiv. Ac₂O, 10% HDT, 373 K, 24 h. Treatment 1: the catalyst was reused without treatment; treatment 2: the catalyst was washed with ether and air dried at room temperature; treatment 3: the catalyst was washed with ether, air dried at room temperature and calcined (723 K); treatment 4: the catalyst was washed with ether, then NaHCO3.

ilar conversion and selectivity were achieved for the second run (>90%). It is assumed that this work up reactivates the hydrotalcite to the active carbonate form. Following this un-optimized treatment, this catalyst was found to be reusable without appreciable loss in activity for at least 4 runs.

3.2. Ring opening of substituted epoxides

The performances of the catalysts for the ring opening of 2,3epoxynorbornene 1, limonene epoxide 2, α -pinene oxide 3 and methyl oleate epoxide 4 were tested (Fig. 4). For comparison, NBu₄Cl reported as efficient catalyst for this reaction was also evaluated (Table 3).

Regardless of the treatment of hydrotalcite, in the presence of the cyclic epoxides 1–3, a mixture of products was obtained, showing that the catalyst is not stereoselective. As a general feature, we observed that HDT-calc exhibited the lowest activity while similar conversions were observed with HDT-CO₃ or HDT-OH solids (entries 2–4). An increase of temperature allowed an improvement of conversion. For the less reactive α -pinene oxide 3, almost complete conversion was achieved after 24 h at 403 K in the presence of HDT-OH solid (entries 6 and 7).

Due to their readily availability, HDT could be applied to the ring opening of methyl oleate epoxide 4 providing access to the corresponding diacetate that could find application as bioplasticizers [31,32]. The most active catalyst (HDT–OH) was evaluated for this reaction. For this disubstituted cis-epoxide, only 60% conversion was achieved at 373 K for 24 h in the presence of 10% catalyst (entry 8). Increasing the temperature allowed almost complete conversion using either HDT–OH or HDT–CO₃ (entries 9 and 10). The reaction was very selective only small amount (<5%) of monoacetate being detected as a by-product. As observed for the previous substrates, the performance of HDT-calc was lower (entry 11).

 Table 3

 Acvlation of epoxide catalyzed with HDT-OH.

Acylation of epoxide catalyzed with HD1-OH.							
Entry	Substrate	Catalyst	<i>T</i> (K)	Conv (%)			
1	1	HDT-OH	373	85			
2	2	HDT-CO ₃	373	100			
3		HDT-calc	373	36			
4		HDT-OH	373	98			
5		Bu ₄ NCl	373	88			
6	3	HDT-OH	373	72			
7		HDT-OH	403	100			
8	4	HDT-OH	373	61			
9		HDT-OH	403	94			
10		HDT-CO ₃	403	99			
11		HDT-calc	403	71			
12		Bu ₄ NCl	373	83			
13		Bu ₄ NCl	423	97			

Reaction conditions: 1 equiv. epoxide, 1.2 equiv. Ac_2O, catalyst 10 wt.% HDT or 5 mol% Bu₄NCl, 24 h.



Fig. 4. Structure of the epoxides evaluated in this work.

We have previously shown that NBu₄Cl was also efficient catalyst for the ring opening of 1,2-epoxydodecane [17]. Indeed, we evaluated this ammonium salt for the ring opening of di or trisubstituted epoxides. Some results are reported in Table 3 indicating that high conversions were achieved in the presence of 5 mol% of homogeneous catalyst (entries 5 and 13) but at 403 K.

Then, we carried out the ring opening of epoxides synthetized from vegetable oil. Hydrotalcite catalyst was evaluated for the ring opening of epoxidized fatty ester and compared with homogeneous ammonium salts. We investigated different sources of vegetable oil having from 1 to 3 double bonds in the fatty chain (Table 4). In the following, two types of fatty ester are considered: OLE containing methyl oleate as the main constituent (58%) and LIN constituted of mainly methyl linoleate (57%) (Scheme 1). The epoxidation of fatty ester was carried out using Prileschajew reaction conditions (HCOOH, cat. H_2O_2) [24]. After 10 h at 343 K, complete conversion was achieved.

The reaction conditions necessary to get complete conversion using different anhydride and catalyst are reported in Table 4. Hydrotalcites were active for the ring opening of OLE-ox (Table 4, entry 1). However, to reach complete conversion, an excess of Ac_2O was used and the reaction was carried out for 24 h at 403 K. Using NBu₄Cl as catalyst, complete conversion was achieved after 6 h at 403 K with 1.2 equiv. of anhydride. This latter catalytic system was used to synthesize large scale of substituted oil (Scheme 1) for the evaluation of their physicochemical properties. In order to establish the influence of the chain length not only acetic anhydride was used as reactant but also heavier anhydride from propionic up to valeric (Table 4). With these anhydrides the reactions were carried out overnight for complete conversion.

3.3. Physicochemical properties of fatty ester derivatives

To evaluate the physicochemical properties of the potential plasticizers synthetized from vegetable oils, we prepared plastisol which is a liquid suspension of PVC particles finely dispersed in the liquid plasticizer matrix (1 part of plasticizer and 2 parts of PVC) at room temperature. When the PVC plastisol is heated, the plasticizer diffuses into the resin particles up to give a homogeneous mass corresponding to the gelation [33,34]. The most commonly used methods for characterizing gelation behaviour are the determination of the gelation temperature where a significant change is brought about by heating. The storage modulus G' and loss modulus G'' were recorded as the function of the temperature [35–37].

Table 5Gelation temperature and maximal storage modulus for selected plastisol.

Entry	Plasticizers	$T(^{\circ}C)_{gelation}$	$G'_{\rm max}~(imes 10^5~{ m Pa})$	$T_{G'_{\max}}$ (°C)
1	DINP	80	3.6	125
2	OLE	80	1.3	150
3	LIN	78	1.3	150
4	OLE-ox	52	8.3	100
5	OLE-ac	72	4.3	130
6	LIN-ac	64	4.7	120

All the samples were miscible with PVC indicating a good compatibility of the plasticizers. In Fig. 5a and b, storage modulus G' and loss modulus G'' of plastisol prepared from oleate derivatives (OLE) were recorded as a function of the temperature. For comparison, a reference plastisol was prepared from phthalate derivative (DIPN).

At room temperature, the storage modulus and loss modulus values of commercial fatty ester (OLE) are one order of magnitude lower than the phthalate indicating low plastic properties probably due to modest interactions between fatty ester and PVC. The properties of the epoxide derivative (OLE-ox) largely used as stabilizer in PVC were also determined. With such compound, the gelation temperature (52 °C) corresponding to the transformation from the liquid paste to solid is too low (Table 5, entry 4).

After acylation (OLE-ac) the storage modulus and loss modulus profiles are very similar to those recorded for phthalate plasticizer with a $G'_{\rm max}$ of same order of magnitude (4 × 10⁵ Pa) at 125–130 °C. The gelation temperatures are 80 °C and 72 °C for DIPN and OLE-ac respectively (entries 1 and 5).

The properties recorded with LIN series (supplementary material) are similar to those reported with OLE series both for the non-substituted substrate (entries 2 and 3) and for peracetylated one (entries 5 and 6). Moreover, the plastisol was stable and after one month storage, similar profiles were recorded (Fig. 5a and b).

The ring-opening of OLE-ox was carried out with several anhydrides and the properties of the resulting products were evaluated (Fig. 6). The higher the chain length is, the higher the viscosity of the product is. Moreover, the maximum storage modulus is lower for butyric or valeric derivatives and has been reached for a higher temperature corresponding to unfavourable gelation properties.

To summarize, the viscoelastic properties of plastisol prepared with LIN-ac and OLE-ac exhibited similar properties to fossil-based phthalate derivatives and are good candidates to replace the latter one. Further works are under progress to determine extended physicochemical properties.

Table 4

Reaction conditions used to get complete conversion of epoxide.

Epoxide	Composition	$(\text{RCO})_2 O(n \text{ equiv.})$	<i>t</i> (h)	Catalyst
		Ac ₂ O(2)	24	10 w% HDT-CO3
		Ac ₂ O (1.2)	6	5 mol% nBu ₄ NCl
OLE-ox	1.2 C=C/chain	(C ₂ H ₅ CO) ₂ O (1.2)	18	5 mol% nBu ₄ NCl
		(C ₃ H ₇ CO) ₂ O (1.2)	18	5 mol% nBu ₄ NCl
		(C ₄ H ₉ CO) ₂ O (1.2)	18	5 mol% nBu ₄ NCl
LIN-ox	1.5 C=C/chain	Ac ₂ O(2)	6	5 mol% nBu ₄ NCl



Fig. 5. (a) Storage modulus (G') profile of plastisol as a function of temperature and (b) Loss modulus (G'') profile of plastisol as a function of temperature.



Fig. 6. Infuence of lateral chain length on storage modulus (G) profile of plastisol as a function of temperature.

4. Conclusion

In conclusion, we have found that solid bases such as cheap and easily available hydrotalcites are suitable catalysts for ring opening of epoxides with acetic anhydride. Moreover, these solid bases are easy to separate, non-toxic and show a good stability versus temperature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.11.020.

References

- L.I. Nass, C.A. Heiberger, Encyclopedia of PVC, vol. 2, second edition, Marcel Dekker Inc., New York, 1987, p. 202.
- [2] L.G. Krauskopf, A. Godwin, in: C.E. Wilkes, J.W. Summers, C.A. Daniels (Eds.), PVC Handbook, Hanser Gardner, 2005, p. 173.
- [3] S.E. Djilai, T. Bouchami, F. Krid, N. Boudiaf, D. Messadi, Eur. Polym. J. 26 (2000) 1981.
- 4] A. Marcilla, S. Garcia, J.C. Garcia-Queseda, Polym. Test. 27 (2008) 221.
- [5] http://www.biohub.fr/.
- [6] B. Nielsen, F.V. Sparso, J.K. Kristiansen, WO 01/14466 A1 (2001).
- [7] R. Hinault, H. Lê Chien, J. Barbier, WO 06/075071 (2006).
- [8] P. Bondioli, in: D. Gunstone, R.J. Hamilton (Eds.), Oleochemical Manufacture and Applications, Sheffield Academic Press, 2001, p. 74.
- [9] H. Schuster, L.A. Rios, P.P. Weckes, W.F. Hoelderich, Appl. Catal. A 348 (2008) 266.
- [10] P.S. Lathi, B. Mattiasson, Appl. Catal. B 69 (2007) 207.
- [11] J. Hancsok, M. Bubalik, M. Törö, J. Baladincz, Eur. J. Lipid Sci. Technol. 108 (2006) 644.
- [12] H. Wagner, R. Luther, T. Mang, Appl. Catal. A 221 (2001) 429.
- [13] J.A. Melero, J. Iglesias, G. Morales, Green Chem. 11 (2009) 1285.
- [14] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, Energy Fuels 22 (2008) 207.
- [15] F.R. Ma, M.A. Hanna, Bioresour. Technol. 70 (1999) 1.
- [16] M. Guidotti, R. Psaro, M. Sgobba, N. Ravasio, in: G. Centi, R.A. van Santen (Eds.), Catalysis for Renewables, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, p. 257.
- [17] G. Fogassy, C. Pinel, G. Gelbard, Catal. Commun. 10 (2009) 557.
- [18] B. Veldurthy, J.M. Clacens, F. Figueras, Adv. Synth. Catal. 347 (2005) 767.
- [19] B. Veldurthy, F. Figueras, Chem. Commun. (2004) 734.
- [20] D.P. Debecker, E.M. Gaigneaux, G. Busca, Chem. Eur. J. 15 (2009) 3920.
- [21] B.F. Sels, D.E. DeVos, P.A. Jacobs, Catal. Rev. 43 (2001) 443.
- [22] A. Vaccari, Appl. Clay Sci. 14 (1999) 161.
- [23] J. Palomeque, J.M. Clacens, F. Figueras, J. Catal. 211 (2002) 103.
- [24] B. Rangarajan, A. Havey, E.A. Grulke, P.D. Culnan, J. Am. Oil Chem. Soc. 72 (1995)
- 1161.
- [25] A. Campanella, M.A. Baltanas, J. Am. Oil Chem. Soc. 76 (2002) 373.

- [26] M.T. Benaniba, N. Belhaneche-Bensemra, G. Gelbard, Energy Ed. Sci. Technol. 21 (2008) 71.
- [27] F. Figueras, in: A. Gil, S.A. Korii, R. Trujilane, M.A. Vicente (Eds.), Pillared Clays and Related Catalysts, Springer, 2010, p. 422.
 [28] D. Tichit, M.H. Lhouty, A. Guida, B.H. Chiche, F. Figueras, A. Auroux, D. Bartalini,
- E. Garrone, J. Catal. 151 (1995) 50.
- [29] R.S. Varma, Tetrahedron 58 (2002) 1235.
- [30] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
- [31] L.G. Krauskopf, J. Vinyl Additive Tech. 9 (2003) 159.
- [32] O. Fenollar, D. Garcia, L. Sanchez, J. Lopez, R. Balart, Eur. Polym. J. 45 (2007) 2674.
- [33] S.Y. Kwak, J. Appl. Polym. Sci. 39 (1995) 3507.
 [34] H. Boudhani, C. Laine, R. Fulchiron, P. Cassagnau, Rheol. Acta 46 (2007) 825.
- [35] N. Nakajima, D.W. Ward, J. Appl. Polym. Sci. 28 (1983) 807.
 [36] A. Marcilla, J.C. Garcia, M. Beltran, Eur. Polym. J. 33 (1997) 753.
- [37] H. Boudhani, R. Fulchiron, P. Cassagnau, Rheol. Acta 48 (2009) 135.