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# Synthesis of Polyolefin Based Materials with Improved Thermo-Oxidative Stability

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**Summary:** Polyolefin based materials with chemically bonded phenol compounds have been synthesized. Two unsaturated polyolefins: an ethylene/propylene/5,7-dimethyl-1,6-octadiene terpolymer and an ethylene/5,7-dimethyl-1,6-octadiene copolymer, were used as starting materials. The functionalisation method involves a two-step procedure that consists in the hydrochlorination of the substituted pending double bonds, followed by grafting of the phenol compound. This procedure was found to be more effective for the terpolymer than for the corresponding copolymer. The reasons for this are discussed. A thermogravimetric study, in air atmosphere shows that, poly(ethylene-co-5,7-dimethyl-1,6-octadiene) grafted with 2-*tert*-butyl-4-methylphenol present improved thermo-oxidative stability when compared to a polyethylene reference.

**Keywords:** antioxidants; EPDM; functionalisation of polymers; non-conjugated dienes; polyolefins

## Introduction

Unsaturated polyolefin-based materials, obtained from the polymerisation of olefins with non-conjugated dienes, can be modified by chemical reaction providing a successful route for the synthesis of side-functional polyolefins (PO). By incorporation of polar functional groups it is possible to improve ultimate properties of PO such as adhesion and compatibility with other polymers. Several examples of modification processes of the pending double bonds of unsaturated polyolefins are described in literature and may include: hydroboration followed by oxidation to hydroxyl groups,[1-4] epoxidation,[3-8] bromination,[5] hydroxylation,[9] sulfonation,[10] oxidation to aldehyde and carboxylic acid functions[6,11] and hydrosilylation.[12, 13]

Alternatively the unsaturations introduced in PE main chain may be used for chemical

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binding of stabilizers in order to inhibit some degradation mechanisms of PE, detrimental to polymer performance. Aromatic functional compounds, such as hindered phenols, are efficient hydrogen donors and can act as radical scavengers preventing thermo-oxidative degradation. Phenolic additives are the most widely used admixed stabilizers for olefin-based polymers. Chemically bound phenols as stabilizers may offer important advantages over admixed additives since they cannot be lost by migration or volatilisation and therefore will guarantee a longer protection of the materials.

In previous works we synthesized olefin-based co- and ter-polymers, using a linear asymmetrically substituted diene, the 5,7-dimethylocta-1,6-diene (5,7-DMO), as comonomer.[14-18] This diene, obtained from terpene fractions, possesses in addition to its vinyl unsaturation a tri-substituted double bond that limits side reactions, like crosslinking or cyclisation, which may occur during copolymerisation. Moreover high amounts of 5,7-DMO can be incorporated in the polymer chains, by careful selection of the metallocene geometry catalyst.

We report now on a two step procedure for the grafting of phenol compounds on these 5,7-DMO based co-and terpolymers, which involves: (1) hydrochlorination of the pendant double bond followed by (2) the grafting of the aromatic compound. The thermal-oxidative stability of an ethylene/5,7-DMO copolymer grafted with 2-tert-butyl-4-methylphenol is also examined.

## Experimental

Hydrochlorination reaction: An ethylene/propylene/5,7-DMO terpolymer (8 mol-% of diene units; $\overline{M}_n$ =60 000 g.mol$^{-1}$, $\overline{M}_w/\overline{M}_n$ =2,) prepared with Et(Ind)$_2$ZrCl$_2$/MAO and an ethylene/5,7-DMO copolymer, (3.5 mol-% diene units, $\overline{M}_n$ =38 000 g.mol$^{-1}$, $\overline{M}_w/\overline{M}_n$ =2.7) prepared with [($\eta^5$-C$_5$Me$_4$)SiMe$_2$(NtBu)]TiCl$_2$/MAO were dissolved respectively in n-heptane at room temperature and in toluene at 60°C. A ten times molar excess of Et$_3$SiH and SnCl$_4$, relatively to unsaturations was added. The reaction time was 20 min for the terpolymer and 1 hour for the copolymer. During the reaction a white precipitate was formed. At the end this precipitate was filtered and the polymer was precipitated with methanol and vacuum dried.

Grafting of the phenol compounds: Both hydrochlorinated 5,7-DMO-based-terpolymer and

-copolymer were dissolved in n-heptane, at 60 °C. Previously distilled phenol and $BF_3OEt_2$ were added to the hydrochlorinated terpolymer and the mixture was stirred for 16 h. 2-tert-butyl-4-methylphenol and $BF_3OEt_2$ were added to the hydrochlorinated copolymer and reacted for 20 h. At the end, the mixture was washed with water and concentrated by distilling the solvent. Both polymers were precipitated with ethanol and vacuum dried.

Characterisation of the polymers: $^1H$ and $^{13}C$- NMR spectra were recorded on Bruker AC200 and AC250 spectrometers, in different solvents (1,1,2,2-tetrachloroethane-$d_2$, benzene-$d_6$ and dichloromethane-$d_2$). The molar masses of the terpolymers were evaluated by SEC (Varian 5500, UV and refraction index double detection) in THF, at room temperature on the basis of polystyrene standards. Infrared spectra were collected on polymer-KBr pellets with a Perkin Elmer 1600 FT-IR spectrophotometer. Thermogravimetric tests were performed with a Setaram LabSys TG-DTA thermobalance, under an air flux at a rate of 10 K.min$^{-1}$ between 50 and 700 °C.

## Results

### Hydrochlorination of ethylene/propylene/5,7-DMO terpolymers

The introduction of chloride functions onto polymer chains is an interesting preliminary step for further functionalisation chemistry. Based on data reported by Kennedy, hydrochlorination of unsaturated polyolefins was first attempted in the presence of

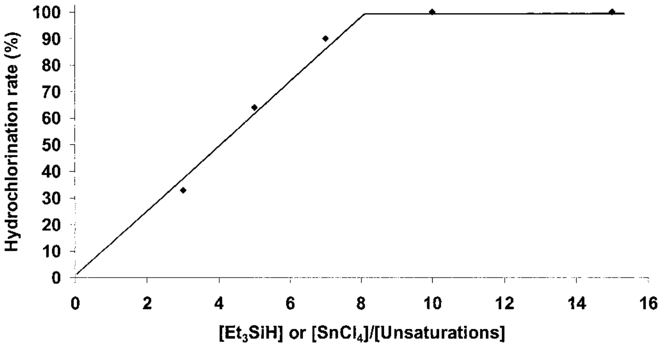


Figure 1. Hydrochlorination rate of a poly(ethylene-co-propylene-co-5,7-DMO) in function of the molar ratio $[SnCl_4]$/[unsaturation]; Solvent hexane; T=25 °C; $[SnCl_4]/[Et_3SiH]=1$; [unsaturation]= 3.10$^{-2}$ mol.L$^{-1}$.

$Et_3SiH/SnCl_4$ mixture.[19] The experimental conditions were optimised in order to improve the efficiency of the reaction.

It was found that hydrochlorination rate is controlled by the amounts of $Et_3SiH$ and $SnCl_4$ introduced in the reaction mixture. Complete hydrochlorination of the pending double bonds needs, at room temperature, about 10 equivalents (with respect to the unsaturations) of $SnCl_4$ and $Et_3SiH$. It should be noted that this reaction, complete or partial, proceeds with neither formation of gel nor evolution of the initial molar mass of the terpolymer. Under selected conditions the hydrochlorination reaction results in the total disappearance of the ethylenic proton, as shown in the $^1H$-NMR spectrum (Figure 2).

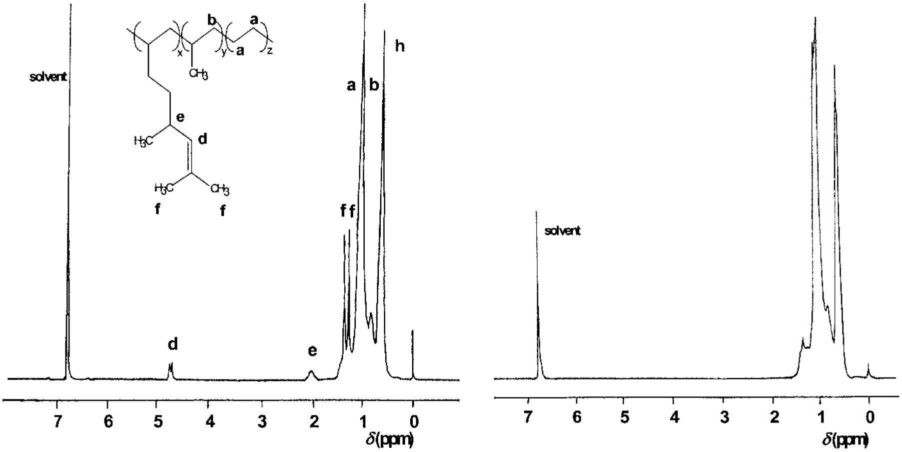


Figure 2. 1H-NMR spectra in deuterated benzene of a poly(ethylene-co-propylene-co-5,7-DMO) (a) and the same polymer after reaction with $Et_3SiH/SnCl_4$ (b). Conditions: reaction time 20 min; solvent n-heptane; T = 25 °C; $[SnCl_4]/[Et_3SiH]=1$; $[SnCl_4]/[\text{unsaturation}]= 10$.

The analysis of the $^{13}C$-NMR spin echo spectrum before and after hydrochlorination (Figure 3) supports the formation of tertiary chlorine groups. Two new peaks are observed; one at 72 ppm, characteristic of the quaternary carbon bonded to chlorine, and other at 52 ppm, corresponding to the secondary carbon in $\alpha$ position relatively to the quaternary carbon. This data shows that hydrochlorination reaction of the pending double bonds of the terpolymer is quantitative and regio-selective (Scheme 1).

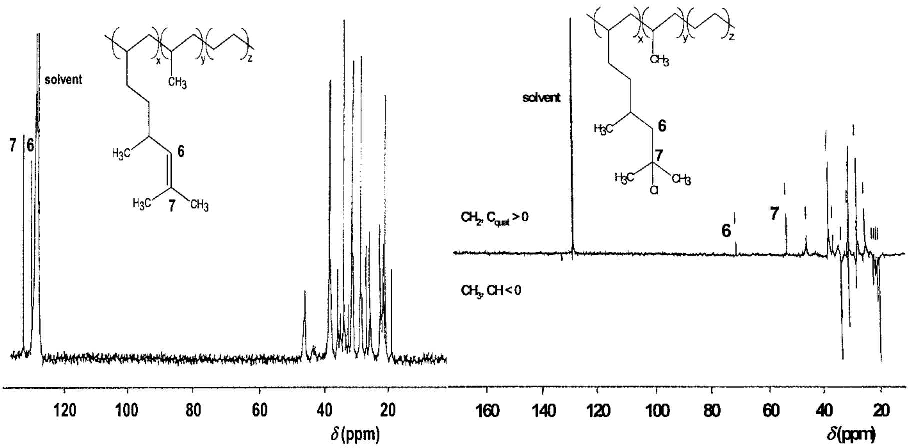
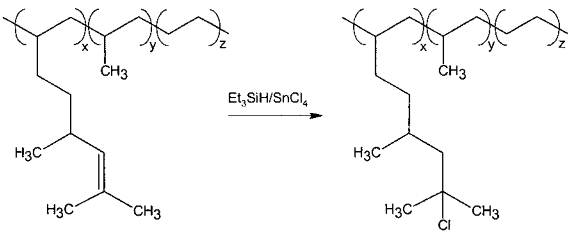


Figure 3. $^{13}$C-NMR spectrum of a poly(ethylene-co-propylene-co-5,7-DMO) (a) and the corresponding spin echo spectrum of the same polymer after addition of $Et_3SiH/SnCl_4$ (b). Same reaction conditions as in Figure 1.



Scheme 1. Hydrochlorination of an ethylene/propylene/5,7 DMO terpolymer.

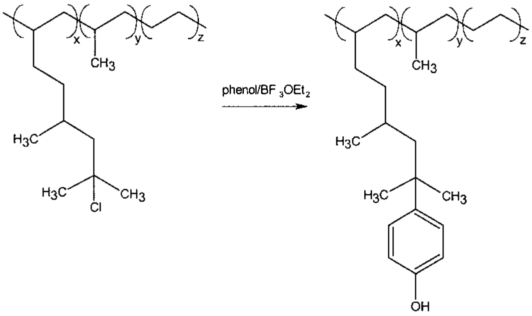
## Hydrochlorination of ethylene/5,7-DMO copolymers

Based on the results presented above the hydrochlorination of ethylene/5,7-DMO copolymers was also performed with a 10 times excess of $SnCl_4/Et_3SiH$. To increase polymer solubility reaction was carried out at 60 °C and toluene was used as solvent. The reaction time was increased to 1 h. FT-IR results show that the characteristic band of the substituted 5,7-/DMO double bond, at 842 cm$^{-1}$, is absent in the reaction product. In the modified polymer new bands characteristic of the C-Cl bond are observed at 653 and 577 cm$^{-1}$. The $^{1}$H-NMR spectrum shows however the presence of residual unsaturations at 4.8 ppm. The $^{13}$C-NMR spectrum of the modified polymer confirms the presence of chlorine: new peaks were observed at 52.7 and 72.4 ppm. This spectrum also reveals some other peaks that could be related to side reactions.

In summary, whereas a clean and complete hydrochlorination was achieved for ethylene/propylene/5,7-DMO terpolymers, for the corresponding ethylene copolymers the hydrochlorination is only partial (70 % yield). This fact can be related to the low solubility of the ethylene/5,7-DMO copolymers when compared to EPDM's, and to the use of high reaction temperatures (60 °C), that may favour side reactions.

## Grafting of phenol on hydrochlorinated ethylene/propylene/5,7-DMO terpolymers

Friedel-Crafts type reactions allow substitution, in the presence of Lewis acids, of tertiary chlorine functions by aromatic derivatives. Kennedy et al. using boron trifluoride diethyl etherate ($BF_3OEt_2$) as Lewis acid, synthesized a bisphenol-terminated polyisobutene, starting from a α-ω-tert-chloropolyisobutene.[20] Based on this data we have performed the phenol grafting reaction in similar conditions: at 55 °C, in presence of an excess of phenol, using the same Lewis acid and n-heptane as solvent (Scheme 2).



Scheme 2. Grafting of phenol on a hydrochlorinated ethylene/propylene/5,7 DMO terpolymer.

The $^1$H-NMR spectrum of the modified polymer is shown in Figure 4. The aromatic ring protons of phenol are observed at 6.6 ppm and 7.2 ppm; a broad signal representative of the hydroxyl group proton is also detected at 4.8 ppm. In the chosen conditions, the phenol-grafting rate, calculated from the 1H NMR spectrum, is higher than 75 % with respect to

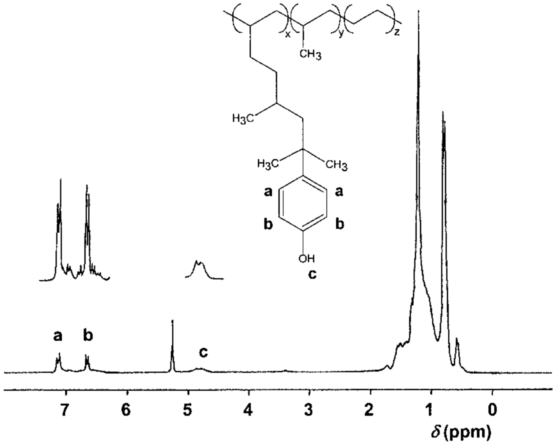


Figure 4. $^1$H-NMR spectrum in $CD_2Cl_2$ of poly(ethylene-co-propylene-co-5,7-DMO) with grafted phenol groups.

hydrochlorinated groups.

Grafting of phenol groups was confirmed by SEC, using UV and refraction index double detection. In fact, the hydrochlorinated 5,7-DMO based EPDM does not have a detectable response in UV but, the SEC chromatogram after phenol grafting shows a strong UV response.

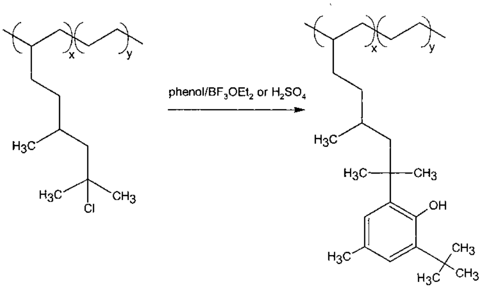
Additional phenol grafting tests were carried out in different conditions (Table 1). A 10 equivalents excess of phenol in relation to tertiary chlorine functions is necessary to avoid chain-coupling reactions.

Table 1. Grafting of phenol on 5,7-DMO-based EPDM. Solvent: *n*-heptane; reaction time: 16 h; [functions] = $2.5 \times 10^{-2}$ M; [$BF_3OEt_2$] = 0.2 M.

| Functions on the terpolymer | [phenol]/[functions] | *T* (°C) | Grafting rate (%) | Notes |
|---|---|---|---|---|
| Chlorine | 3 | 55 | / | Chain coupling |
| Chlorine | 7 | 55 | / | Chain coupling |
| Chlorine | 10 | 55 | 75 | Unimodal SEC peak |
| Chlorine | 15 | 65 | 78 | Unimodal SEC peak |

## Grafting of 2-tert-butyl-4-methylphenol on hydrochlorinated ethylene/5,7-DMO copolymers

The addition of 2-tert-butyl-4-methylphenol to hydrochlorinated ethylene/5,7-DMO copolymers was investigated (Scheme 3).



Scheme 3. Grafting of 2-tert-butyl-4-methylphenol on a hydrochlorinated ethylene/5,7 DMO copolymer.

In agreement with the strategy described for the phenol grafting on hydrochlorinated EPDM, the hydrochlorinated ethylene/5,7 DMO copolymer was reacted for 20 h at 60 °C with 2-tert-butyl-4-methylphenol in the presence of $BF_3OEt_2$. Despite its lower ability to dissolve ethylene/5,7-DMO copolymers, n-heptane was used as a solvent since toluene could compete strongly with phenol, for grafting onto the polymer structure. The $^1$H-NMR spectrum of the reaction product shows new peaks in the aromatic region, at 6.4, 6.7 and 6.9 ppm, and the presence of non-reacted double bonds. In the $^{13}$C-NMR spectrum, the peaks at 52.7 and 72.4 ppm of the hydrochlorinated group are still present although significantly reduced in intensity, confirming the partial substitution reaction. In conclusion, 2-tert-butyl-4-methylphenol grafting takes place, although it does not completely remove chlorine groups from the chains.

In order to evaluate the effect of grafted 2-tert-butyl-4-methylphenol onto the copolymer thermo oxidative stability, a thermogravimetric study, in air atmosphere, was performed.

The thermogravimetric curve of the modified copolymer is compared to that of a polyethylene reference (Figure 5). The phenol-grafted copolymer starts main degradation process (in terms of weight loss) at a temperature near 400 °C, which is almost 50 °C higher than the one observed for homopolyethylene. However a slow degradation process is visible in the range 300 - 400 °C, which can be attributed in part to the elimination of HCl[21] from remaining hydrochlorinated units in the modified ethylene/5,7 DMO copolymer. The presence of chlorine residues in the phenol-grafted copolymers may be detrimental for future applications. An alternative route, that guarantees the total absence of these residues, consists of the direct introduction of phenol groups on the pendant unsaturations of 5,7-DMO based copolymers. Comparison data of direct route vs. indirect route will be published elsewhere.

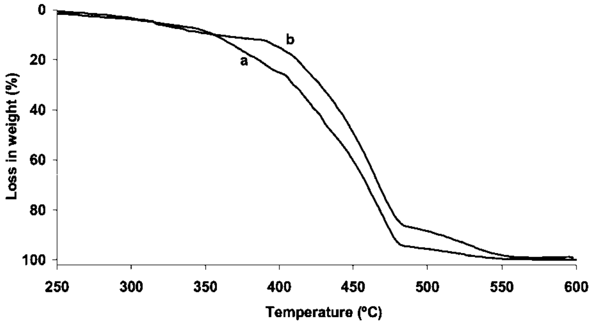


Figure 5. Thermogravimetric curves of: homopolyethylene (a) and ethylene/5,7 DMO copolymer modified with 2-*tert*-butyl-4-methylphenol (b).

The higher stability of the grafted copolymers may be explained considering that thermo-oxidative degradation is mostly due to the formation of peroxy radicals by free radical reactions. In presence of efficient hydrogen donors, such as hindered phenol compounds, these radicals react and form hydroperoxides, preventing therefore the abstraction of hydrogen from the polymer backbone. The fact that in our case the phenol group is covalently bonded to the polymer allows us to expect an increased durability and efficiency of the polymer protection.

## Conclusion

Phenolic compounds were chemically bonded to unsaturated polyolefin-based polymers in order to reduce thermal oxidative degradation of these polymeric materials that leads to a loss of physical and optical properties of the polymer.

The synthesis of poly(ethylene-co-propylene-co-5,7-DMO) grafted with phenol and of poly(ethylene-co-5,7-DMO) grafted with 2-*tert*-butyl-4-methylphenol was performed using a two-step procedure involving: hydrochlorination of pending double bond followed by phenol grafting. This route was found to be very effective for the ethylene/propylene/5,7-DMO terpolymer and lead to a phenol-grafting rate higher than 75 %. However the used procedure revealed to be much less efficient when applied to ethylene/5,7-DMO copolymers. This behaviour might be related to: (i) the smaller diene contents and higher crystallinity of 5,7-DMO copolymers when compared to the corresponding terpolymers (resulting in much lower solubility of copolymers); (ii) the higher reaction temperature used for hydrochlorination of the copolymers, which may lead to an increase of side reactions; (iii) and finally the bulkiness of the hindered phenol used, which in one way should be more effective in preventing thermo-oxidative degradation, but may reduce in some extent the efficiency of the grafting reaction.

Compared to polyethylene, the ethylene/5,7-DMO copolymer grafted with 2-*tert*-butyl-4-methylphenol exhibits higher thermal oxidative stability. Long-term durability is also expected since this covalently bonded phenol group will not migrate as happens in stabilization of polyolefins by compounding.

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