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Access to new polymeric-hindered amine stabilisers from oligomeric terpene resins

M.L. Binet, S. Commereuc*, P. Lajoie, J. Lacoste

Laboratoire de Photochimie Moléculaire et Macromoléculaire (UMR CNRS 6505),
Université Blaise Pascal et ENS Chimie de Clermont-Ferrand, F-63 177, Aubière Cedex, France

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Abstract

This paper reports on the use of terpene resins as precursors for synthesis of oligomeric stabilisers by photochemical grafting of acrylate monomer with suitable substituents as sterically hindered amine. Poly α and poly β pinenes react with singlet oxygen to produce macromolecular hydroperoxides. Then, the reactivity of 1,2,2,6,6-pentamethyl-4-piperidyl acrylate (PMPA) is sufficient to afford grafting by photochemical decomposition of ROOH at $\lambda > 300$ nm at 35°C. Hence, photo- and thermo-stability of the obtained polymeric hindered amine stabilisers are checked. Finaly, light and thermal stabilising efficiency of grafted terpenic resins are tested for different dienic polymers. From our results, all terpene additives prepared dramatically increase the lifetime (both in photo- and thermal-ageing) of parent polymers and dienic elastomers as polyisoprene and polyoctenamer which are well-known to be highly sensitive to oxidation.

Keywords: Terpene resins; Photo-oxidation; Thermo-oxidation; Grafting; Oligomeric hindered amine stabilisers

1. Introduction

The lifetime of polymeric materials closely depends on the efficiency of additives. It is generally admitted that an efficient additive should be soluble in the polymer to be stabilised. However, the explanation of the efficiency of a stabiliser is very complex and has to take into account of a lot of physico-chemical properties. During the last two decades remarkable progress has been achieved in understanding chemical principles and protective mechanism of stabilisers. Only a few published works deal with the physical aspects of polymer stabilisation [1–4]. A recent review claims that an efficient stabiliser should comply with the following basic requirements [1]:

- high solubility in the polymer (compatibility);
- minimal diffusion;
- high degree of homogeneity of active species in the polymer;
- sufficient mobility of the stabiliser.

The introduction of oligomeric stabilisers has been the main approach to reduce additive loss as a consequence of volatility and diffusion. However, Hrdlovic and Chmela [5,6] reported that the stabilisation efficiency decreased with increased molecular weight of the additive in case of hindered amine stabiliser (HAS) copolymers because of a lower compatibility and lower mobility of these stabilisers. In addition, diffusion of the stabiliser to the surface layers is important for protection of polymers, especially for UV ageing. Thus, Gugumus [7] showed that the best efficiency was achieved with additives having an average molecular weight of approximately 2700 g mol^{-1}. Hence, consideration of the results published specifically on the influence of average molecular weight led to considerable confusion [8]. In fact, it is difficult to separate the effect of each physical parameter from the others. So, Gugumus claimed that the performance also depends heavily on polymer, sample form and exposure conditions [8]. Unfortunately, no concrete data on the relationships between the different physical aspects of stabilisation were reported in the literature.

Polymer bound stabilisers have been suggested as a possible solution to overcome the problem of physical losses for a longer time [1,9]. The HAS grafted on elastomers have been proposed and tested [10–13]. However, high molecular weight of polyoctenamer and EPDM could induce a reduced mobility of the polymeric stabiliser and then could give inhomogeneities in distribution of piperidine moieties, leaving a great part of polymer matrix unprotected [1,9,14].

Hence, on the basis of previous works, we assume that oligomeric terpene resins consist in an interesting alternative

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* Corresponding author. Tel.: +33-4-73-407169; fax: +33-4-73-407700
E-mail address: sophie.commereuc@univ-bpclermont.fr (S. Commereuc).

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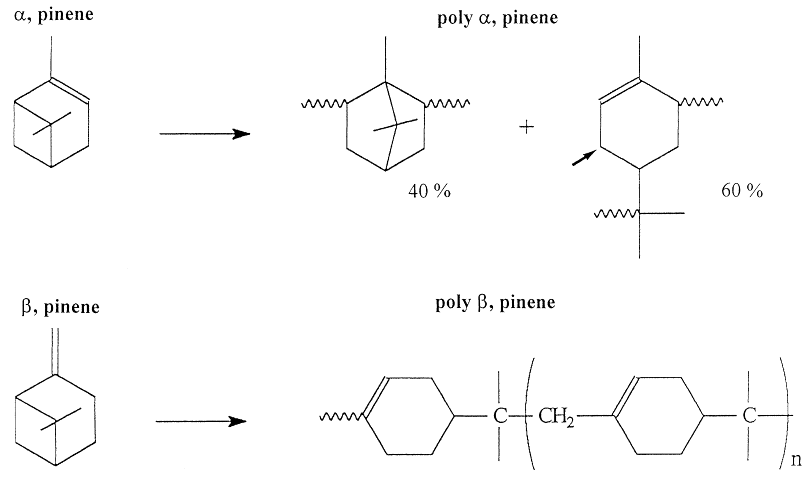


Scheme 1. Chemical structures of polypinenes.

way to access to new polymeric additives, after grafting of a suitable stabilising group as sterically hindered piperidine function. Indeed, terpene resins are low molecular weight hydrocarbon polymers (typically around 2000 g mol^{-1}) prepared by cationic polymerisation of natural products abundantly available from pine tree [15]. Polypinenes units contain unsaturated double bond and their chemical structures could be considered similar to that of dienic polymers as polybutadiene, polyisoprene, polynorbornene, etc. It is the reason why terpene resins have been used for many years in commercial applications such as adhesives, coatings and elastomeric sealants. The most commonly used resins are those based on α or β pinene. Poly α pinene and poly β pinene are excellent tackifiers of numerous elastomers as natural rubber, polyisoprene, polybutadiene, styrene-butadiene rubber, etc. [15–18].

Thus, good miscibility of terpenes resins with rubbers ensures good compatibility of grafted polyterpenes with these polymer matrixes. Such new stabilisers can be expected to have a good efficiency in the protection of elastomers because of the combination of a good compatibility with dienic polymers and sufficient molecular mobility (low M_n).

This paper reports on the grafting of HAS groups on polyterpenes in order to access to new oligomeric stabilisers. Grafting is performed by photochemical modification as it was already described for other dienic polymers [10,11,19,20]. Then, these new oligomeric additives are tested as light and thermal stabilisers for virgin polyterpenes and different elastomers as polyisoprene, polyoctenamer. Finally, their efficiency is compared to that of a commercial polymeric additive.

2. Experimental

2.1. Materials

Commercial polyterpenes resins were kindly supplied by Dèrivès Rèsiniques & Terpéniques (DRT, Dax-France) as Dercolite® A and Dercolite® S for the poly α pinene and the poly β pinene samples, respectively.

The chemical structures of both polypinenes used in this study are summarised in Scheme 1 based on ^{1}H NMR determination [15]. These compounds are low-molecular-weight oligomers and their molecular characteristics are shown in Table 1.

The dienic polymers used are polyisoprene, provided by Aldrich Corp., and polyoctenamer rubber, a member of the general series of polyalkenamers named Vestenamer®, produced by Creanova Company.

Preparation of the unsaturated monomer 1,2,2,6,6-pentamethyl-4-piperidyl acrylate (PMPA) is described in [21].

2.2. Sample preparation

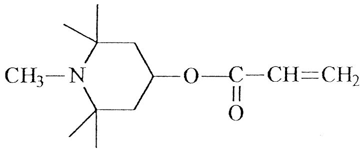
All polymeric materials (polyterpenes, polyisoprene and polyoctenamer) were twice precipitated from chloroform solution into methanol to remove any additives. Blends of polymeric additives and different dienic polymers were obtained by co-precipitation from a chloroform solution into methanol.

The films of polypinenes were cast onto KBr plates from a chloroform solution and then dried under vacuum at 30°C overnight. Coating films thicknesses were around 40 μm.

The films of elastomers (stabilised and not) were prepared by compression moulding between two polyester sheets during 1 min at 60°C under 100 bar. The thickness of the films was about 80 μm.

Table 1
Molecular characteristics of polypinenes from SEC measurements based on polystyrene calibration

	M_n	M_w	M_w/M_n
Poly α pinene	708	1251	1.8
Poly β pinene	1237	2913	2.3



Scheme 2. Chemical structure of 1,2,2,6,6-pentamethyl-4-piperidyl acrylate (PMPA).

2.3. Photo-hydroperoxidation and grafting

Hydroperoxidation was performed by irradiation at 365 nm at 35°C (125 W MAZDA mercury lamp with wood envelop) of a polyterpene solution in toluene ($27\,\mathrm{g\,l^{-1}}$) containing anthracene as sensitiser ($0.27\,\mathrm{mol\,l^{-1}}$). As it was previously described elsewhere [19], the reaction involved the production of singlet oxygen which reacts with the double bounds of terpene resins *(ene* reaction) leading to macromolecular allylic hydroperoxides. Hydroperoxide concentration was estimated by iodometric titration [22] based on the reduction of hydroperoxides by sodium iodide in excess in acidic medium according to the reaction

$$\mathrm{ROOH} + 2\mathrm{I}^- + 2\mathrm{H}^+ \rightarrow \mathrm{ROH} + \mathrm{I}_2 + \mathrm{H}_2\mathrm{O}$$

$$\mathrm{I}_2 + \mathrm{I}^- \rightarrow \mathrm{I}_3{}^-$$

The concentration of the triiodide subsequently formed is measured by UV spectrophotometry (Shimadzu UV 160) at 362 nm, using the commonly accepted extinction coefficient of $2.5 \times 10^4\,\mathrm{mol^{-1}\,l\,cm^{-1}}$.

It was previously reported that when the decomposition of ROOH is performed in the presence of unsaturated monomers, a free-radical polymerisation can be initiated and grafting occurs [20]. If suitable substituents as sterically hindered piperidine groups are located on the grafted molecules, the synthesis of new polymeric stabiliser can be achieved [10,11]. Hence, on the basis of previous works, grafting of HAS groups on hydroperoxidised polyterpens was carried out by irradiation at $\lambda > 300$ nm (medium pressure mercury arc, Mazda 400 W) at 35°C of the solution in presence of PMPA (see chemical structure in Scheme 2 and stoichiometric conditions in Table 2). Before irradiation, the solution was purged with argon for 5 min. The photochemical grafting principle is done in Scheme 3. According to the decomposition reaction of hydroperoxide, three possible initiations are reported to occur in the case of free radical polymerisation while alkyl radical is more reactive [10,22]. Thus, this latter could be considered as the more possible initiating species.

After grafting, residual ROOH were converted into alcohol by triphenylphosphine treatment [23]. The grafted polyterpenes were precipitated twice in methanol which is a good solvent for the monomer and the non-grafted oligomeric homopolymer [10,20].

Concentration of grafted species were determined from FTIR analysis (ester band at $1730\,\mathrm{cm^{-1}}$, $\varepsilon \approx 590\,\mathrm{mol^{-1}\,l\,cm^{-1}}$). The IR spectra were recorded on a Nicolet Impact 400 spectrometer (Omnic software).

2.4. Ageing tests

2.4.1. Photo-oxidation procedure

Polymer films were fixed on aluminium holders and then irradiated in a polychromatic set-up. A⟨⟨medium pressure⟩⟩ mercury source filtered by a borosilicate bulb (Mazda type MA 400) supplies radiation of wavelengths longer than 300 nm. This source was located along the focal axis of a cylinder with elliptical base. Samples turned around the other focal axis. The inside of the chamber is made of highly reflecting aluminium. Temperature of samples is controlled by a thermocouple connected with a temperature regulator device which controls a fan. All experiments were performed at 35°C. This device could be considered as a “low temperature” version of the commercial instrument SEPAP 12/24 (ATLAS material Testing Technology BV). Films were analysed after various exposure times.

2.4.2. Low-temperature thermo-oxidation procedure

Low-temperature thermo-oxidation experiments were carried out at 60°C in dark in an oven ventilated by natural convection.

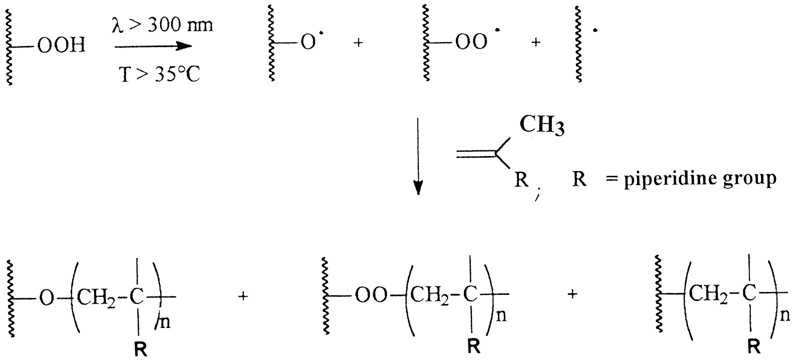
Chemical changes were detected by FTIR spectroscopy through the ageing tests (Nicolet Impact 400 spectrometer, Omnic software).

Table 2
Photo-grafting conditions and results

Sample name	f [a]	Grafting duration (min)	Residual ROOH (%)	Grafted HAS group (mmol/kg)	n [b]
Pβ120	2	60	84	120	2
PβEXC	10	60	72	294	4
Pβ300	2	30	–	–	–
	2	30	53	306	2
Pβ600	2	30	88	144	<2
	2	30	55	256	2
	2	30	47	569	3

[a] f is the intial stoichiometric ratio between acrylate monomer (PMPA) and initiator (ROOH) in toluene solution.

[b] n is the number of grafted PMPA molecule per decomposed ROOH.



Scheme 3. Photochemical grafting principle.

3. Results

3.1. HAS grafted polyterpenes synthesis

3.1.1. Hydroperoxidation in toluene solution

The course of hydroperoxides production and anthracene consumption is shown in Fig. 1 through hydroperoxidation of poly β pinene in toluene solution. The reason for the anthracene decay is its reaction with singlet oxygen producing 9,10-anthracene endoperoxide [11,19].

Any significant carbonyl absorption band could not be detected in FTIR spectra of hydroperoxidised polyterpenes in our experimental conditions. Indeed ROOH are assumed to be quite stable in toluene solution under irradiation at 365 nm [19]. Similar results are obtained for both poly α and poly β pinenes.

From our experimental results, the optimum duration of hydroperoxidation stage of polyterpenes in toluene solution under irradiation at 365 nm at 35°C is 6 h. Hence, the average hydroperoxide content is around 400 $\mathrm{mmol\,kg^{-1}}$ without any carbonyl formation which corresponds to fairly low modification yield since double bonds consumption is then around 5%.

3.1.2. Grafting in toluene solution

From our experimental results, summarised in Table 2, large excess of unsaturated monomer allows to drastically increase the grafting level (compare Pβ120 and PβEXC). Unfortunately, acrylates are known for their tendency to form long sequences by homopolymerisation (the number of grafted PMPA molecule per decomposed ROOH (*n* is twice higher for PβEXC). Hence, regarding to the average molecular weight of terpenic oligomer, grafting of PMPA in such experimental conditions results in something like a comblike copolymer instead of a single stabiliser molecule attachment to polymer [1].

Moreover, successive additions of PMPA every 30 min permit to limit the number of grafted acrylate unit per one ROOH group while increasing the yield of grafting (see Pβ300 and Pβ600). However, grafting of long sequences is readily favoured after 1 h of grafting reaction, so *n* increases whatever is the concentration of PMPA (see Pβ600).

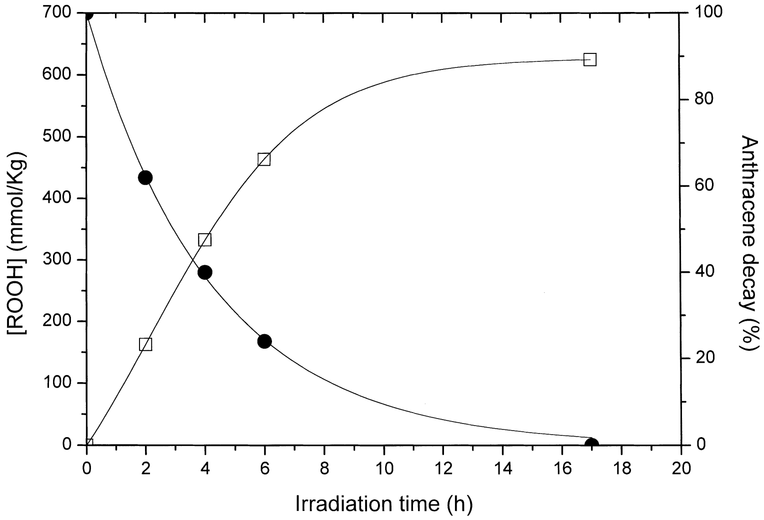


Fig. 1. Decrease of anthracene concentration (●) and production of hydroperoxides (□) in toluene solution during 365 nm irradiation of poly β pinene (27 $\mathrm{g\,l^{-1}}$).

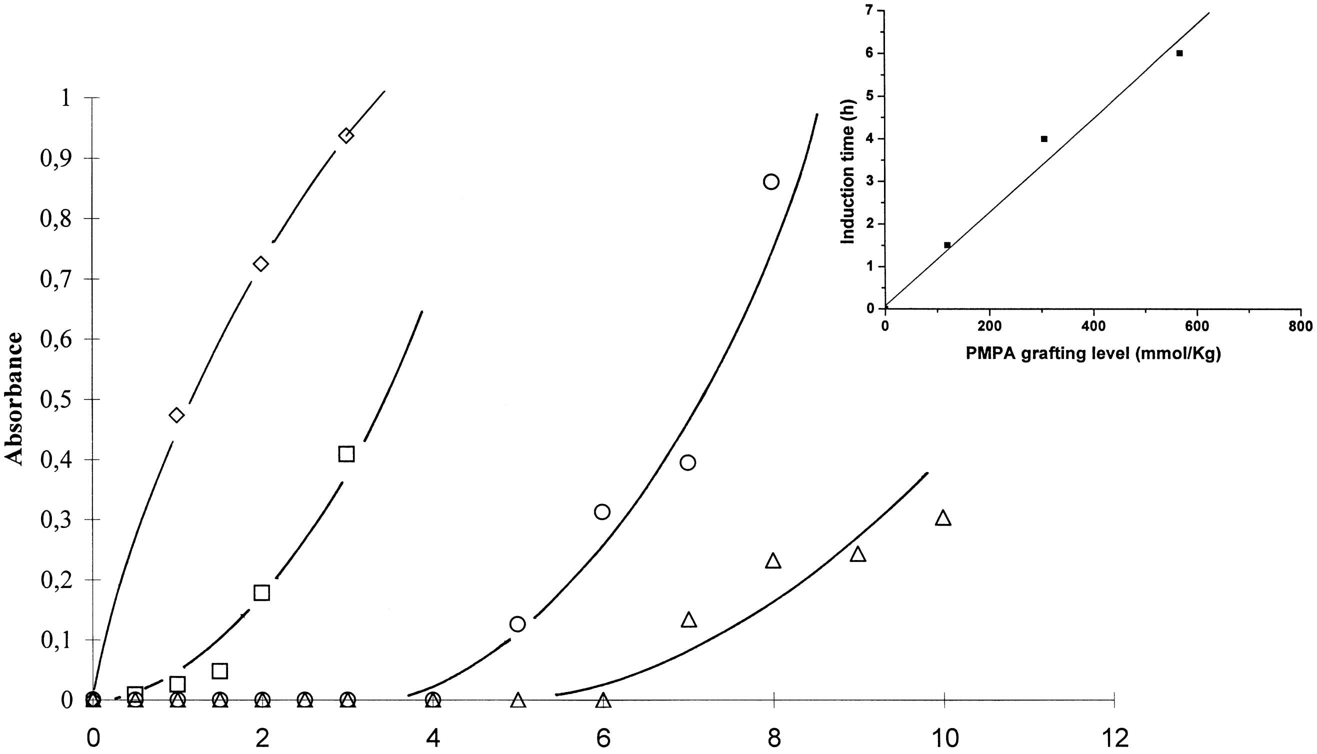


Fig. 2. Kinetic curves of carbonylated photo-products formation from photo-oxidation at $\lambda > 300$ nm at 35°C of grafted poly β pinene, named Pβx where x is the content of HAS moieties in mmol kg^{-1}. Films thickness 80 μm. Carbonyl absorbance at 1715 cm^{-1} for (◇) Pβ0: virgin poly β pinene, (□) Pβ120, (○) Pβ300, (△) Pβ600. Inset: correlation between HAS moieties content and induction time.

Thus, we assume that two additions of PMPA in solution each 30 min for 1 h consist in the best conditions for photochemical grafting of PMPA on poly α and poly β pinenes. Then a high grafting yield is obtained (around 45% of ROOH are consumed leading to the grafting of about 300 mmol kg^{-1} of HAS moieties on polyterpene backbone) while formation of long grafted sequences is quite minimised (only two piperidine groups is grafted per reacting ROOH).

3.2. Stability of these new polymeric hindered amine stabilisers

First, photochemical stability of polyterpenes bound HAS groups was checked. Fig. 2 shows that, in the experimental area, the sample with the lowest degree of grafting undergoes the highest degree of photodegradation, as it was easily expected. It should be important to point out that the induction period linearly increases with the piperidine moieties content. The inset in Fig. 2 plots the induction period as a function of the concentration of sterically hindered amine groups. A similar relationship has been already reported in case of polyolefins stabilised with low molecular weight HAS [8,24–26].

However, it should be stressed that all modified polypinenes show no oxidation after 5000 h of exposure to thermal-ageing at 60°C while carbonylated by-products are detected at the very beginning of exposure for virgin parent oligomers (see Fig. 3).

It is now clearly establish as it was expected that grafted polypinenes with PMPA show a fairly low sensitivity to oxidative degradation in comparison with the parent polymers. Hence, these conclusions suggest that these materials consist in interesting possible additives especially as

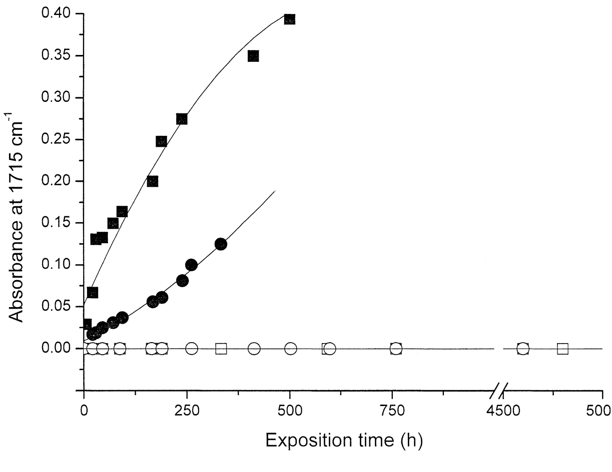


Fig. 3. Kinetic curves of carbonylated photo-products formation from thermooxidation at 60°C of grafted terpene resins, named Pβx and Pαx, for poly β pinene and poly α pinene, respectively, where x is the content of HAS moieties in mmol kg^{-1}. Films thickness 40 μm. Carbonyl absorbance at 1715 cm^{-1}: close symbols for virgin polypinenes (■) poly β pinene, (●) poly α pinene, open symbols for grafted terpenes (□) Pβ300, (○) Pα250.

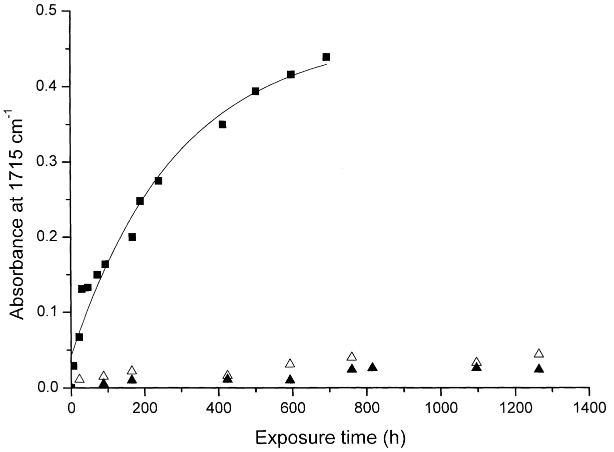


Fig. 4. Efficiency of poly β pinene grafted with PMPA on the thermal ageing of poly β pinene. Kinetic curves of carbonylated photo-products formation from thermooxidation at 60°C of poly β pinene, stabilised with grafted polypinene. Films thickness 40 μm. Carbonyl absorbance at $1715\,cm^{-1}$ for (■) control; and stabilised sample with (△) grafted poly β pinene Pβ300, (▲) grafted poly α pinene Pα250.

thermal stabilisers. Then, these new oligomeric grafted polypinenes were tested as thermal stabilisers of the parent polymers.

3.3. Efficiency as stabilisers of parent polymers

The pronounced efficiency of polyterpenes grafted with PMPA on the thermal-ageing of the parent polymer is reported on Fig. 4. The concentration of active species was $8.33 \times 10^{-3}\,mol\,kg^{-1}$. It corresponds with 3% w/w for Pβ300 and 4% w/w for Pα250. Carbonylated by-products are detected at very beginning of exposure for virgin poly β pinene while the thermooxidation rate is drastically reduced for stabilised films. Moreover, it is worthwhile to note that no significant difference is recorded between the two selected modified polyterpenes.

Thus, both poly α and poly β pinenes grafted with PMPA appear as very efficient stabilisers for terpene resins.

3.4. Efficiency as stabilisers of other dienic polymers

Now, according to our first experimental results, it is necessary to check the efficiency of these new stabilisers for different elastomers as polyisoprene and polyoctenamer in order to compare their ability to stabilise other dienic polymers with that of commercial polymeric additive.

Polyisoprene is especially very sensitive to oxidative degradation and its ageing has been widely studied [27–30]. Fig. 5 outlines the remarkable efficiency of poly β pinene grafted with PMPA on the thermo-oxidative degradation of polyisoprene. The induction period duration is multiply 100 times when polyisoprene is stabilised with 3% w/w of Pβ300 ($8.33 \times 10^{-3}\,mol\,kg^{-1}$).

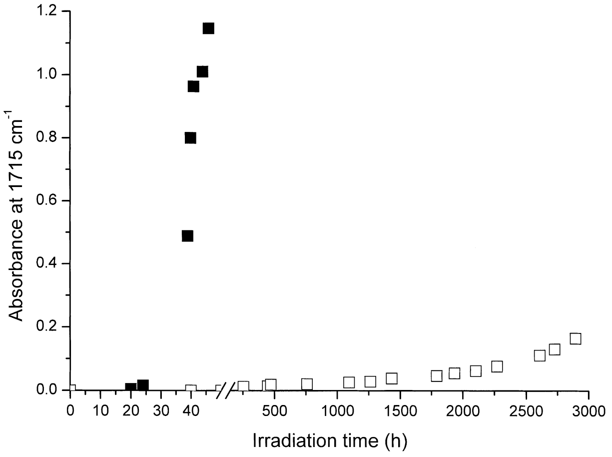


Fig. 5. Efficiency of poly β pinene grafted with PMPA on the thermal ageing of polyisoprene. Kinetic curves of carbonylated by-products formation from thermooxidation of polyisoprene at 60°C. Films thickness 70 μm. Carbonyl absorbance at $1715\,cm^{-1}$ for (■) virgin polyisoprene (control), (□) polyisoprene stabilised with 3% w/w of Pβ300.

Grafted oligomeric polypinenes with HAS moieties were tested as light stabilisers of polyoctenamer. As it was described above, the induction time of carbonyl development upon photo-oxidation of Vestenamer films is directly proportional to piperidine concentration when the polymer matrix is stabilised with PMPA grafted polyterpenes (not shown).

Elsewhere, Fig. 6 compares their efficiency to that of a commercial polymeric HAS (Tinuvin 622 provided by Ciba–Geigy). The concentration of active species is similar in all cases ($8.33 \times 10^{-3}\,mol\,kg^{-1}$). A quite similar stabilising efficiency is reached both with grafted poly β pinene (Pβ600) and commercial additive.

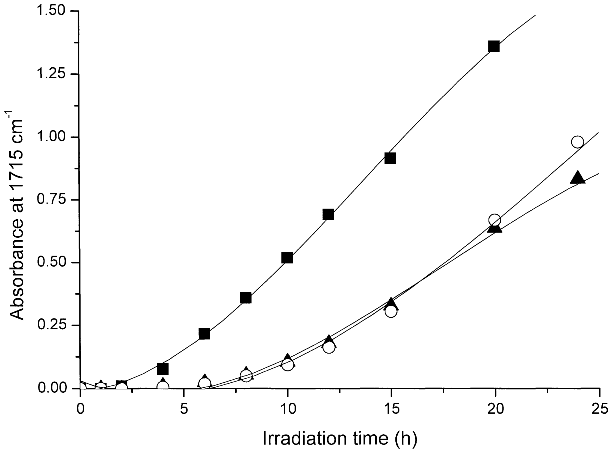


Fig. 6. Efficiency of poly β pinene grafted with PMPA on the photo-oxidation of polyoctenamer. Kinetic curves of carbonylated by-products formation from photo-oxidation at $\lambda > 300\,nm$ at 35°C. Films thickness 100 μm. Carbonyl absorbance at $1715\,cm^{-1}$ for (■) virgin polyoctenamer (control) and polyoctenamer stabilised with (▲) 1.6% w/w of Pβ600, (○) 0.2% w/w of Tinuvin 622.

4. Conclusion

The use of terpene resins as precursors for the synthesis of oligomeric stabilisers seems to be successful. As it was already described before for elastomers, the grafting of hindered amine piperidine groups can be performed by using macromolecular hydroperoxides as intermediates obtained in mild conditions ($\lambda = 365$ nm, 35°C). The reactivity of PMPA is sufficient to afford grafting by photochemical decomposition at $\lambda > 300$ nm at 35°C.

Then, HAS grafted poly α and poly β pinenes consist in interesting possible additives for dienic polymers. All terpene additives prepared dramatically increase the lifetime (both in photo- and thermal-ageing) of parent polymers and elastomers as polyisoprene and polyoctenamer which are well-known to be highly sensitive to oxidation.

Elsewhere, poly α and poly β pinenes are mainly used in adhesives and as tackifiers. But, numerous others uses are described in sheet carbon and copying paper, paints and varnishes, plasticisers. It is worthwhile to note that natural terpene resins are nontoxic, nonphytotoxic, nonsensitising to the skin and inert to diluted acids, alkalis and salts. So, because of their properties they can be approved for food contact application. Hence, systems formed by polyolefin (as iPP, HDPE, etc.) and polypinene resins are recently proposed to produce miscible blends suitable for the production of films for food packaging [31]. Thus, further investigations are now needed to check the interest of such new oligomeric HAS from polyterpenes in case of other systems than dienic polymers as polypropylene-terpene resins blends.

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