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Thermooxidation and photooxidation of some resins used in melting adhesive composites

L. Popa[a], M. Giurginca[b], T. Zaharescu[c,*]

[a] Anticorosiv SA, Bucharest 74584, Romania
[b] University POLYTECHNICA, Bucharest 78126, Romania
[c] ICPE-CA, Advanced Research Institute on Electrical Engineering, Splaiul Unirii 313, Sector 3, P.O. Box 87, Bucharest 74204, Romania

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Abstract

Thermal oxidation and photodegradation of alkyl, alkyl–aromatic and synthetic resins were investigated. The ageing temperatures were selected in the range 150–200 °C. The progress in chemical degradation depicted by changes in characteristic absorption bands was monitored by spectral techniques. Differential scanning calorimetry investigation and chemical determination of hydroperoxide content were also performed. Based on the experimental data the main kinetic characteristics of the degradation processes were calculated. A discussion on the mechanistic aspects concerning thermal and photochemical ageing of the resins studied is also presented.

Keywords: Resins; Thermal degradation; Photooxidation; Spectroscopy

1. Introduction

Numerous applications of melting adhesive compositions may be extended to new areas according to detailed studies on the effects induced by various formulations on physical and chemical characteristics [1]. In most of the circumstances the improved performances of adhesives are correlated with satisfactory features, like dispersion of additives, easy processability and efficient adhesion of long life commodities.

Structural changes induced by the action of energy transfer to adhesives during thermal and photooxidation affect material behavior and the accumulation of different intermediates can be pointed out [2–7]. The lack of detailed information concerning the evolution of different chemical structures of adhesives makes difficult the understanding of mechanistic aspects of degradation for this class of materials.

2. Experimental details

The present investigations were carried out on various types of resins with different consistencies: aliphatic, aromatic, aromatic–aliphatic, pentaerythritolester and glycerolester of resin acid, hydrogenated resin ester. Their structures are shown in Fig. 1. Various manufacturers provided these materials. They were tested without any previous purification because one goal of the present work was a study carried out under industrial conditions. However, the separation of possible impurities would influence the behavior of the final products by the presence of small amounts of retained solvent. Their main characteristics are listed in Table 1.

Thermal degradation was performed at temperatures between 150 and 200 °C in an air-circulating oven (Caloris, Romania). Photodegradation was achieved by exposure of specimens to ultraviolet (UV) light (250–365 nm) for 96 h. Several temperatures of irradiation environments were selected over the range between 22 and 70 °C to achieve a low error in the evaluation of the activation energies.

Modifications occurred during thermal and photodegradation were assessed using miscellaneous procedures:

- infrared (IR) spectral analysis (FT-IR spectrophotometer, Avatar 320, USA);
- ultraviolet spectral analysis (UV-Vis NIR 570, JASCO, Japan);
- differential thermal analysis (DSC-FP900, Mettler, USA);
- titration of hydroxyperoxides by iodometry method.

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* Corresponding author. Tel.: +40-1-3467235; fax: +40-1-3467283.
E-mail addresses: traian_z@hotmail.com, traian_zaharescu@yahoo.com (T. Zaharescu).

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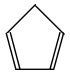
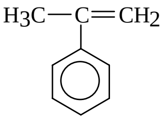
Table 1
Some main characteristics of tested resins

Resin type	Trade name	Melting point (°C)	Garner color	Acidity index (mg KOH/g)
Aliphatic	Piccotac 95C[a]	96	3	–
Aliphatic–aromatic	Novares TK/10H[b]	100–110	4–5	0.1
Aromatic monomer[c]	Kristalex F 85[d]	99	<1	–
Glycerin esterified	Permalyn 5095[a]	86	3	6
Glycerin esterified and finally hydrogenated	Foral 85[a]	81	<1	–

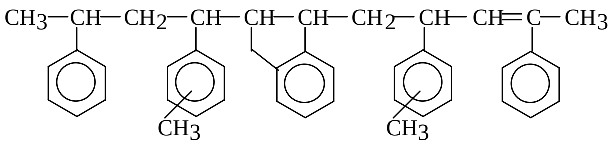
[a] Hercules (The Netherlands).
[b] Ruetgers UFT AG (Germany).
[c] Monomer symbolizes styrene unit.
[d] Exxon Chemicals (USA).



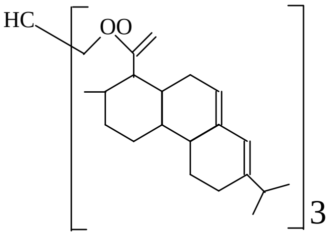
Aliphatic type (C5)



Aromatic type (C9)



Aliphatic/aromatic type (C5/C9)



Esterified type

Fig. 1. Monomer types of the resins studied.

3. Results and discussion

The effects induced by of accelerated thermal and photodegradation on different molecular configurations of hot melt adhesives is always related to the split of weak bonds. The evaluation of the physical and chemical characteristics allows the interpretation of specific reactions in which free radicals are involved.

3.1. Photooxidative degradation

The main specific bands mentioned below were selected for description of time changes in degradation product concentrations:

- for alkyl resin: $\nu_1 = 3430\,\text{cm}^{-1}$ and $\nu_2 = 970\,\text{cm}^{-1}$;
- for alkyl-aromatic resin: $\nu_1 = 3437\,\text{cm}^{-1}$ and $\nu_2 = 1730\,\text{cm}^{-1}$;
- for esterified resin: $\nu_1 = 880\,\text{cm}^{-1}$ and $\nu_2 = 815\,\text{cm}^{-1}$;
- for esterified and hydrogenated resin: $\nu_1 = 880\,\text{cm}^{-1}$ and $\nu_2 = 815\,\text{cm}^{-1}$;
- for aromatic resin: $\nu_1 = 960\,\text{cm}^{-1}$, $\nu_2 = 3450\,\text{cm}^{-1}$ and $\nu_3 = 700\,\text{cm}^{-1}$.

Fig. 2 presents the modifications promoted by photons in organic substrates. Some initial statements can be mentioned:

(a) In the case of alkyl resin increase in the intensities of 970 and 3430 cm^{-1} bands revealed; the first band initial existing is ascribed to C=C *trans* units; the second one is growing while resin is photooxidized (Fig. 2a). The pre-existing band at 1730 cm^{-1} exhibits low intensity and provides minor changes placed at the experimental error limits. In this case, any modification of it does not allow quantitative kinetic treatment.
(b) Monotone increases in new formed bands at 1720 and 3427 cm^{-1} prove the development of an oxidation state of the alkyl-aromatic resin (Fig. 2b).
(c) Aromatic-monomer styrene resin exhibits a light change in the absorbance at 3450 cm^{-1}. At the same time, the band at 700 cm^{-1} ascribed to νCH_{ar} vibration remains unchanged. The absorbance of 960 cm^{-1} band presents smooth decrease.
(d) Esterified resin shows diminution in the absorbance of 815 and 880 cm^{-1} bands (Fig. 2c). These decreases occurred simultaneously but the degradation rate obtained by spectral measurements at 880 cm^{-1} takes place 25% faster than similar process at 815 cm^{-1} band. Both bands describe unsaturation: $\nu = 880\,\text{cm}^{-1}$ is ascribed to end-vinyl ($R_2C{=}CH_2$), while $\nu = 815$–$820\,\text{cm}^{-1}$ is attributed to trisubstituted vinyl units ($R_1R_2C{=}CHR_3$).

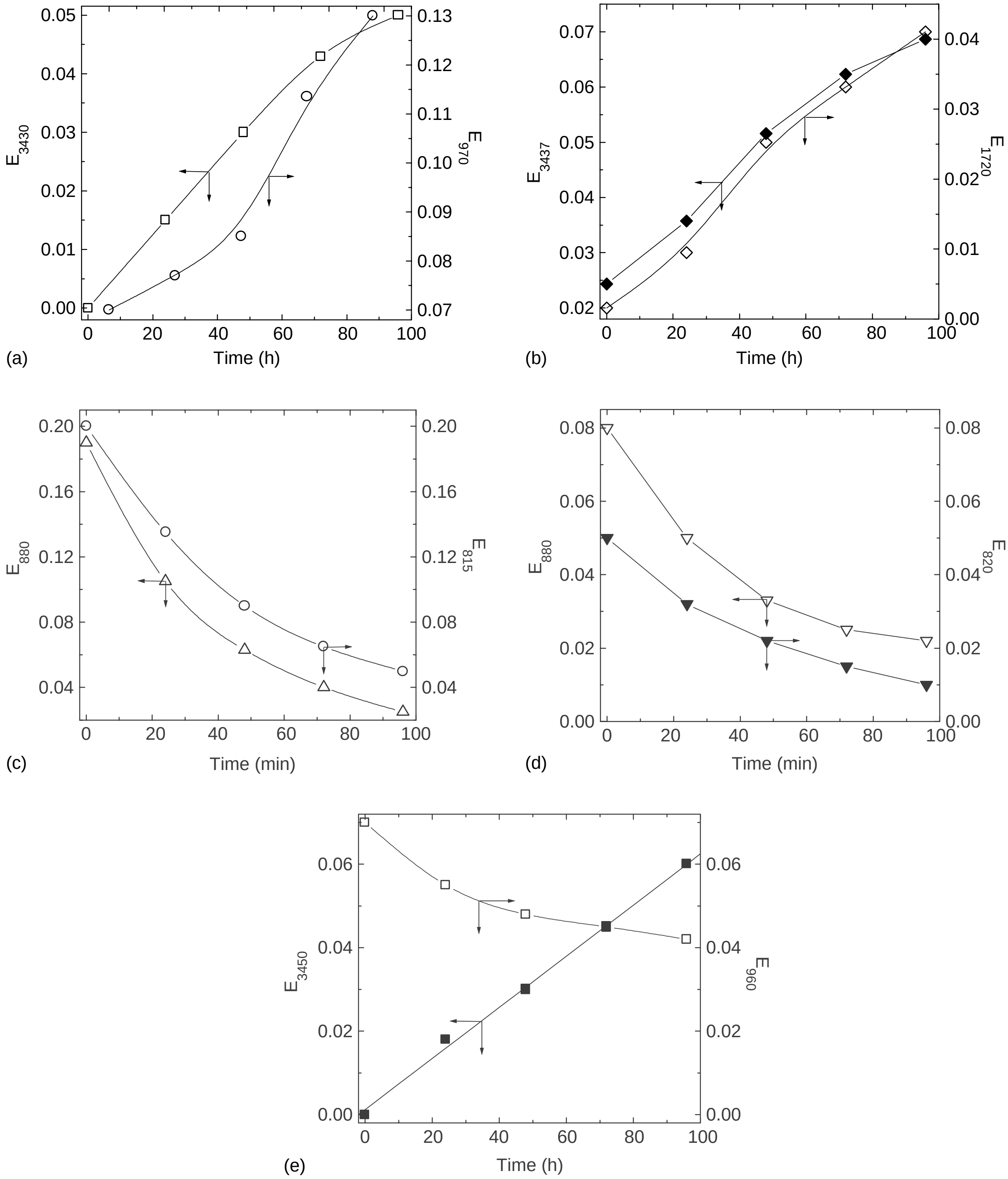


Fig. 2. Changes in various extinction values during photooxidation of the resins studied: (a) alkyl resin; (b) aromatic resin; (c) esterified resin; (d) esterified and hydrogenated resin; (e) monomer aromatic resin.

(e) Esterified and hydrogenated resin displays the same bands as esterified resin (Fig. 2d) whose absorbencies, especially at 880 cm^{-1}, are lowering as degradation temperature rises. Fig. 2d shows that the higher concentration of double bonds exists in esterified and hydrogenated resin than is measured in esterified resin.

(f) Monomer aromatic resin presents two contradictory evolutions. The band at 3450 cm^{-1} that characterizes the accumulation of hydroperoxides reveals a linear time dependency while the extinction values for 960 cm^{-1} band decreases gently (Fig. 2e).

The dependencies of extinction on ageing time allow to determine global activation energies involved in photooxidation (Table 2). From the present data this degradation process occurs as a first order reaction. It may be noticed that

Table 2
Activation energy of photooxidation process

Resin	Activation energy calculated from spectral data (kJ mol^{-1})			
	3450 cm^{-1}	1720 cm^{-1}	970 cm^{-1}	815 cm^{-1}
Alkyl type	76.7	–	99.1	–
Alkyl–aromatic type	90.6	91.2	–	–
Esterified	125.2	–	–	90.1
Esterified and hydrogenated	70.9	–	–	75.4
Monomer styrene	153.4	–	92.6	–

monomer styrene resin shows noteworthy resistance by exposure to UV radiation.

3.2. Thermal degradation

The thermal degradation of resins was accomplished over large temperature range (150–200 °C) simulating industrial conditions under these materials are usually used. The dependencies of extinction on degradation time were obtained for the same bands, as there were concerned for photodegradation assessment. The reaction order was found to be 2 that is different from the value obtained for UV degradation. The global activation energies required by resins in thermal deterioration are listed in Table 3.

Calorimetric investigations point out the correlation between resin structure and thermal behavior of studied compounds. In Fig. 3a, melting process and phase transition occur at the early heating stage (60–80 °C) followed by thermal degradation of esterified resin may be noticed. A different behavior exhibited by the alkyl-aromatic resin (C5/C9 type) is presented in Fig. 3b, where thermal melting and phase modification take place between 80 and 85 °C. The degradation starts in the temperature range 210–230 °C; it goes on till the temperature of 385 °C is achieved.

Table 4 shows the content of hydroperoxides determined after heating/cooling cycles for various periods. The diminish in ROOH amounts corresponds to the depletion of this compounds. But, in the case of esterified resin the spread in values of hydroperoxide content may denote the simultaneous formation and depletion of these intermediates followed by generation of new oxygenated radicals.

Table 3
Activation energy of thermooxidation process

Resin	Activation energy calculated from spectral data (kJ mol^{-1})		
	3450 cm^{-1}	1720 cm^{-1}	970 cm^{-1}
Alkyl type	98.5	–	84.7
Alkyl-aromatic type	–	229.0	–
Esterified	200.0	107.2[a]	–
Esterified and hydrogenated	220.0	115.0[a]	–

[a] Spectral measurements performed at 1610 cm^{-1}.

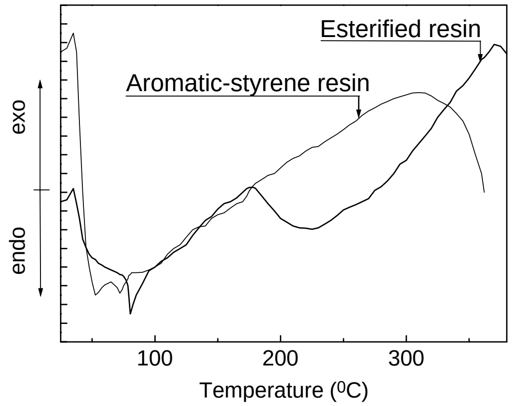


Fig. 3. Differential scanning calorimetry curves for (a) aromatic-styrene monomer and (b) esterified resin.

3.3. Mechanism of oxidative degradation

Oxidation of resins at different temperatures follows the classical chain mechanism of the oxidative degradation of hydrocarbons [8].

(1) Initiation

$$RH \rightarrow R^{\bullet} + H^{\bullet}$$

(2a) Propagation

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$2\,ROOH \rightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$$

(2b) Branching

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$$

(3) Termination

$$2R^{\bullet} \rightarrow R - R$$

$$ROO^{\bullet} + R^{\bullet} \rightarrow ROOR$$

$$2ROO^{\bullet} \rightarrow ROOOOR$$

$$ROOOOR \rightarrow R'OH + R''R'''C{=}O + O_2$$

Table 4
Amounts of hydroperoxides formed during thermooxidation of resins

Resin	Hydroperoxide content (mM g^{-1}) after heating for			
	1 h	2 h	3 h	5 h
Alkyl	0.0083	0.0035	0.0010	0.0002
Alkyl–aromatic	0.0053	0.034	0.0030	0.0020
Esterified	0.0038	0.040	0.0034	0.0029

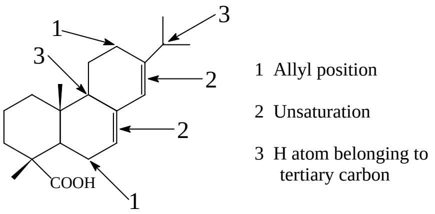


Fig. 4. Reactive sites on resin structures.

The branching stage (2b) is achieved at high temperatures or under the action of UV radiation. At room temperatures peroxyl, hydroperoxyl radicals, and other oxygenated intermediates appear during propagation stage (2a). They will go on the autocatalytic degradation by reactions gathered in the sequence (2a).

An additional effect of degradation is the coloring of specimens due to the generation of carbonyl products mentioned in the third stage of termination. Fig. 4 presents the most possible reactive sites where the attack of oxygen will create oxidation precursors. It means that there are several possibilities (allyl positions, double bonds and hydrogen atoms belonging to tertiary carbon atoms) through which resins of studied types are degraded. The reactivity of this kind of structures has been proved on resin derivatives that may be act as oxidation initiators in elastomer matrix at certain concentration [9].

4. Conclusions

The instability of resins usually incorporated in hot melt formulations with industrial applications was studied under accelerated degradation. Our data demonstrate the existence of hydroperoxides as oxidation intermediates. They will determine material properties like color and viscosity. A modification in the adhesive structure results in large differences in thermal stability characterized by dissimilar values of the activation energies.

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