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Photo-crosslinked acrylates degradation kinetics

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Abstract A series of crosslinked polyurethane acrylate solids with glass transition temperatures ranging from –49 to +65 °C was prepared by photopolymerization of specially formulated solvent-free resins. The kinetics of thermooxidative and thermal (in N_2) degradation of these crosslinked acrylate networks at temperatures ranging from 100 to 400 °C was studied as a function of crosslink density using thermogravimetry. The polyacrylate network degradation rate decreased with the increase of crosslink density, while apparent activation energy of degradation increased. Polyacrylate thermal stability increase with crosslinking was explained by decreased rate of oxygen and volatile products diffusion and/or slowing of depolymerization due to increased radical recombination rate, and decreased chain segments mobility in systems with higher crosslink density.

Keywords Activation energy · Crosslink density · Degradation · Glass transition · Kinetics · Polyacrylate · Polymer · Stability · Thermogravimetry

Introduction

Polymer degradation mechanism was extensively studied [1, 2, references therein]. Degradation in air includes reactions with oxygen leading eventually to formation of water and carbon dioxide (Schemes 1, 2) [1, 2]. Polymers with higher crosslink density are expected to be more stable due to reduced mobility of radicals, slower oxygen ingress, volatiles evaporation, and slower valency transfer, slower polymer segment mobility preventing radical escape from the cage [1, 3–6].

There is a disparity in the reported effect of crosslinking on polymer degradation rate [7–13]. It was reported, as expected, that crosslinking (or crystallization) decreases the rate of thermo-oxidation due to slower oxygen diffusion into polymer [1, 8], however, it was also reported, that lower chain mobility decreased thermal stability of the polymer [9]. No change in epoxy networks aging resistance with increased crosslinking was observed [10]. Thermal aging induced stress-relaxation time increase was reported to become larger with crosslink density increase [1, 11]. For vulcanized cis-1,4-polyisoprene increase of stability with degree of crosslinking was reported [12, 13]. The changes of stability were usually attributed to decrease in the rate of oxygen diffusion into highly crosslinked systems [1–7, 9, 14–17]. The method of crosslinking influenced the thermal degradation kinetics [18, 19]. The structure of crosslinking bridging bonds also influences crosslinking effect on degradation of polymers. Thus, sulfur vulcanized polyisoprene rubber was less stable than peroxide vulcanized rubber [12]. The rate of degradation was found to be proportional to the chain length between the crosslinks [13]. “To further complicate the problem of gaining comparative stability data, an enormous body of literature has been compiled from “off-the-shelf” polymers and routine thermal analysis data on materials of unknown structure” [7, p. 4].

Formal and statistical approaches to kinetics of polymer degradation were developed [1, 2, 4, 7, 14–17, 20, 21], and higher stability of crosslinked polymers was also attributed

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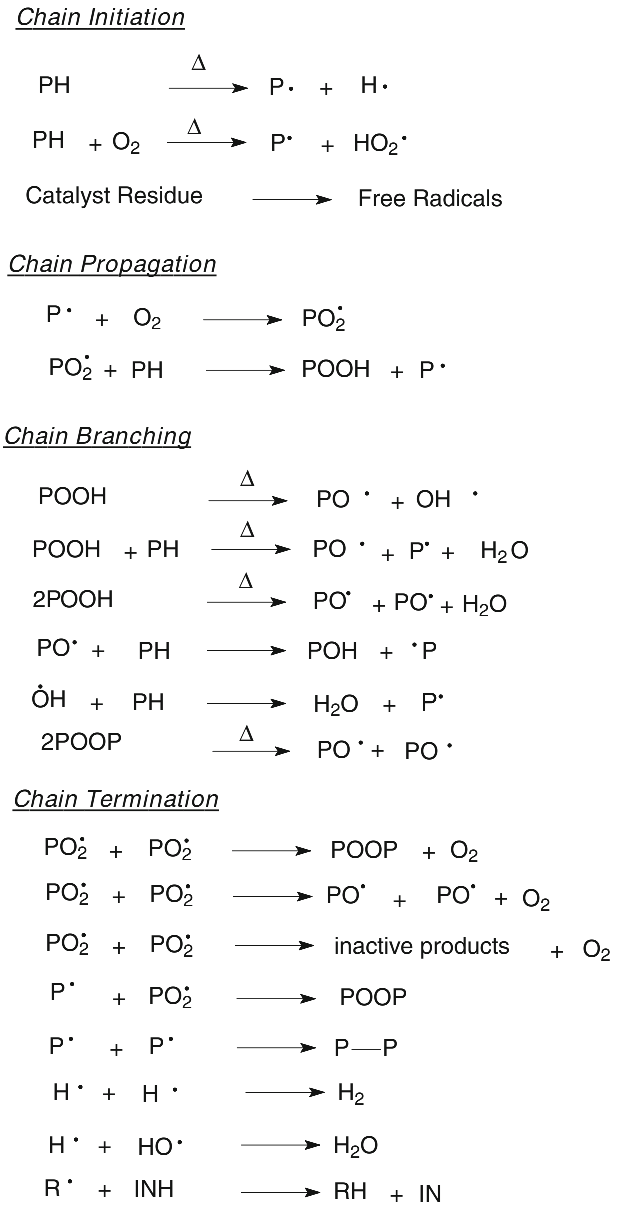
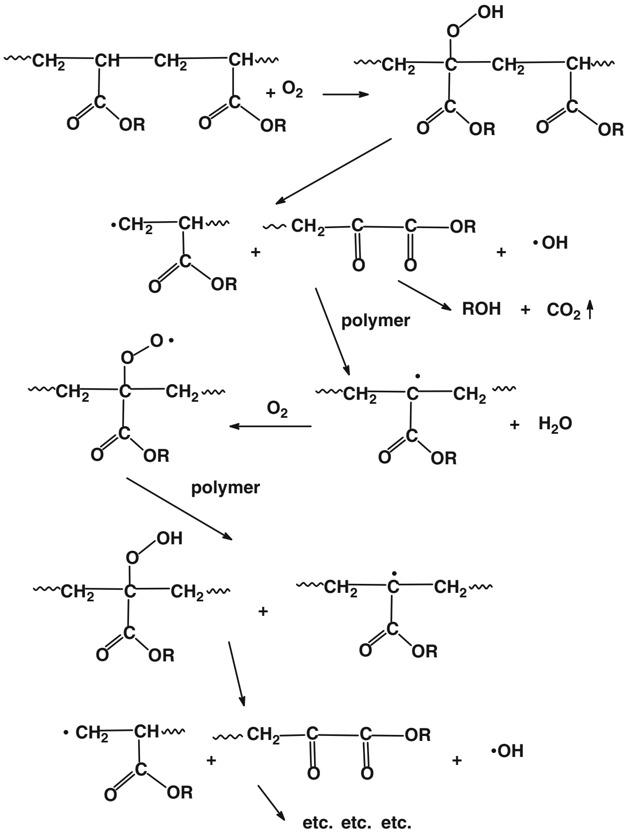


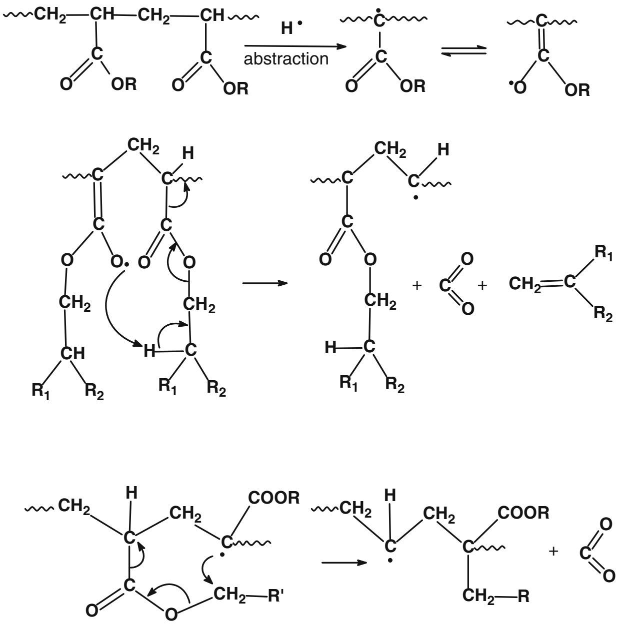
Scheme 1 Kinetic model of thermo-oxidative degradation of polymers [1, 2, 7, 34]

to the lower probability of bond scission due to thermal fluctuations [22], to the best of our knowledge, transition state theory approaches [23–29] were not applied to polymer degradation kinetics, precluding analysis of the degradation kinetics based on vibrational energy distribution.

The lack of consistent interpretation of the results was one of the reasons to revisit the effects of crosslinking on polymer stability. Derivation of mechanism of degradation based on thermogravimetric measurements was questioned, since only the kinetics of volatile products loss was monitored [30–33]. However, classic TG allows, albeit non-selective, direct monitoring of stability changes in polymer



Scheme 2 Volatile products formation mechanism in thermo-oxidative degradation of polyacrylates[7, 24, 70–72]



Scheme 3 Mechanism of acrylates decarboxylation in the absence of oxygen [7, 34–69]

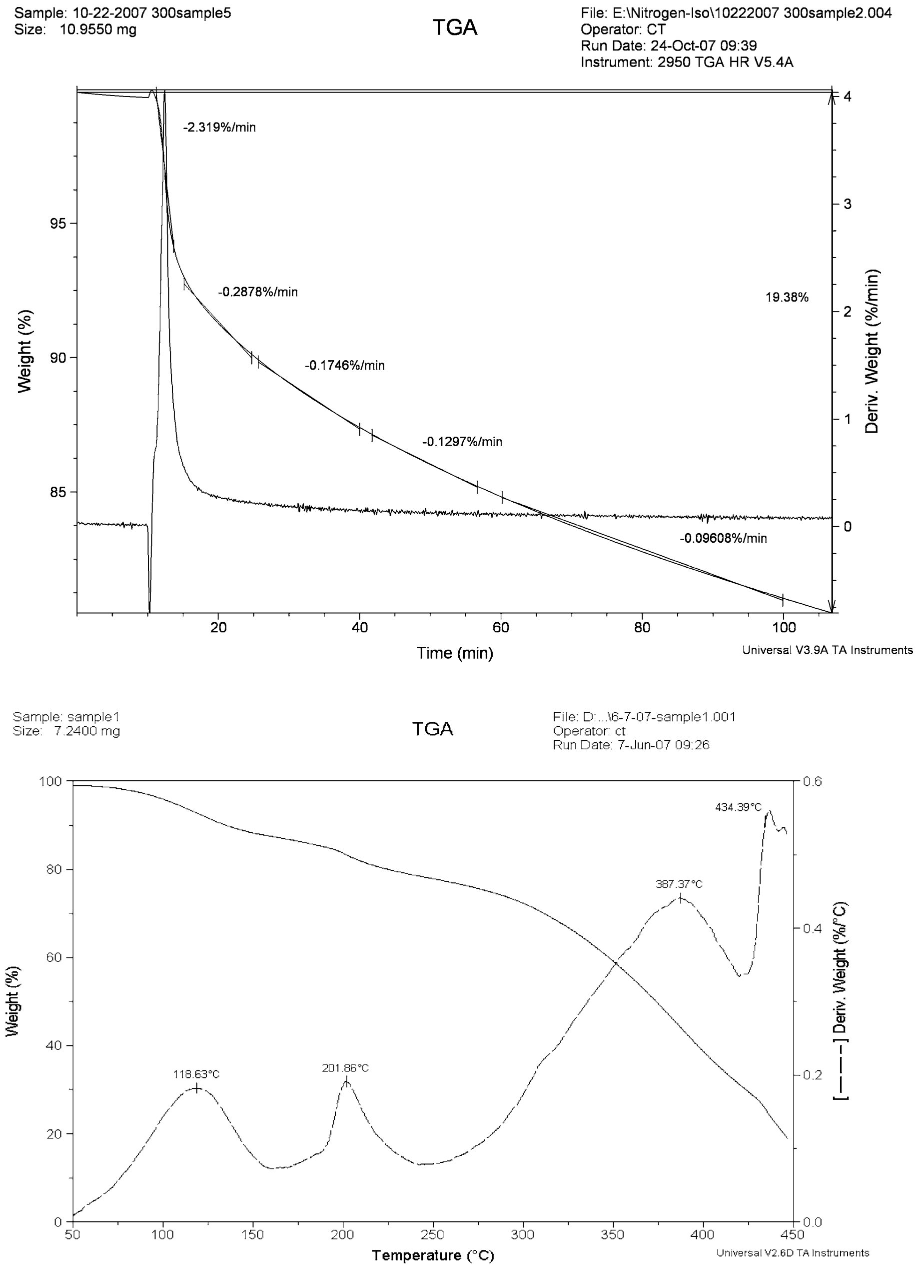


Fig. 1 A typical gravimetrically detected kinetics of thermal degradation of crosslinked polyurethane acrylate: O_2 flow = 60 cm^3 min^{-1}, left: isothermal 300 °C. The rate was determined as a best linear fit between two points. *Right* Temperature ramp at 10 °C min^{-1}. Polychronal weight loss kinetics is evident

systems. When polymer thermal degradation mechanism is established, such kinetic data can be successfully interpreted [1, 2, 7, 34–69].

To eliminate the uncertainties of "of-the-shelf polymer" analysis [7–19] a series of aliphatic urethane acrylate resins was formulated by us to produce, upon ultraviolet curing, polymeric films of known composition with well-defined glass transition temperatures (T_g) and crosslink densities. The choice of UV-curable acrylates was stipulated by high reproducibility of these polymers, absence of additives, good film formation. Most importantly, the mechanism of thermal and thermooxidative degradation of polyacrylates was extensively studied (Schemes 2, 3) [1, 2, 7, 34–69].

In the absence of oxygen, polyacrylates degrade through re-arrangements leading to decarboxylation, and formation of carbon dioxide, monomers and alcohols (Scheme 3) [7, 34–69]. In the presence of oxygen, formation of alcohol, decarboxylation and depolymerization take place as well, although through different reaction paths (Scheme 2) [7, 24, 70–72]. Initiation by oxygen usually accelerates the degradation rate. In the absence of oxygen, the rate of degradation will depend stronger on the segment mobility, proton and electron transfer rates and volatiles escape rate

(Schemes 2 and 3). It was suggested that volatiles loss rate may control the observed kinetics of polymer degradation [59, 60].

Reduction of free volume and rise in glass transition temperature with increase of crosslink density may change relative rates of diffusion of oxygen, and volatile products altering degradation kinetics [73–76]. Thus, we compared kinetics of degradation in the presence and absence of oxygen in the surrounding atmosphere.

Experimental

Instrumentation and processes

The resins were cured using a microwave discharge lamp equipped with a conveyor belt at 0.5 mJ cm^{-2} (Fusion UV Systems Inc.). UV dose was monitored prior to cure with Profiling Belt Radiometer, ILT 400, UVA (International Light Technology). The completeness of polymerization (>90% acrylate double bond conversion) was verified by acrylate double bond infrared absorption at 810 cm^{-1} (Nicolet 8700, Thermo Electron Corp.).

Dynamic mechanical analysis (DMA) (RSA3, TA Instruments) was conducted in a tensile mode at 1.0 Hz, using 5 to 6 mm wide, 100 to 200 µm thick film strips. The data were processed to yield glass transition temperatures and crosslink densities of the polyurethane acrylates, according to common practices based on a position of maximum of loss tangent, tan δ, [5, 6, 77–80].

TG was conducted in isothermal and temperature rump modes in oxygen or in dry nitrogen flow of 60 cm^3 min^{-1} using TGA 2950 system (TA Instruments). The film sample, ≈5 µg, was placed in an opened platinum pan. Isothermal conditions were achieved through equilibrating the sample at 30 °C for 10 min, razing the temperature to a desired value (100, 200, 300, or 400 °C), then maintaining this temperature for 90 min (Fig. 1). Temperature ramp experiments were conducted at 10 °C min^{-1} temperature increase rate from 30 to 450 °C (Fig. 3). In all of the

Table 1 Composition of resins forming photocrosslinked acrylate networks

Sample no.	Initiator[a], Irgacure 651 (%)	Initiator[a], Irgacure 184 (%)	Oligomer[a] difunctional CN966B85 (%)	Monomer[a] SR256 (%)	Monomer[a] difunctional SR238 (%)	Total difunctional acrylates (monomer and oligomer)[b] (%)
1	3	2	25	70	0	3.75
2	3	2	25	60	10	13.75
3	3	2	25	50	20	23.75
4	3	2	25	40	30	33.75
5	3	2	25	30	40	43.75
6	3	2	25	20	50	53.75
7	3	2	25	10	60	63.75
8	3	2	25	0	70	73.75

[a] Irgacure 651(Ciba), α, α,-dimethoxy-α-phenylacetophenone; Irgacure 184 (Ciba), 1-hydroxy-cyclohexyl-phenyl-ketone; SR256 (Sartomer), 2(2-ethoxyethoxy)ethyl acrylate; SR238 (Sartomer), 1,6-hexanediol di-acrylate; CN966B85 (Sartomer), urethane acrylate oligomer/monomer blend

[b] CN966B85 contains 15% SR238

Table 2 Glass transition temperatures and crosslink density of UV-cured acrylates

Sample No.	Total difunctional acrylates (cross linking) (%)	T_g (°C)	Rubbery plateau tensile storage modulus, E' (Pa)	Crosslink density ν_e (mol m^{-3})
1	3.75	−48.692	958809	116
2	13.75	−35.619	5207886	630
3	23.75	−20.602	12956066	1571
4	33.75	−4.7526	27467984	2969
5	43.75	16.416	55791517	5577
6	53.75	43.462	58717987	5875
7	63.75	52.891	93323115	9334
8	73.75	65.186	170000000	16975

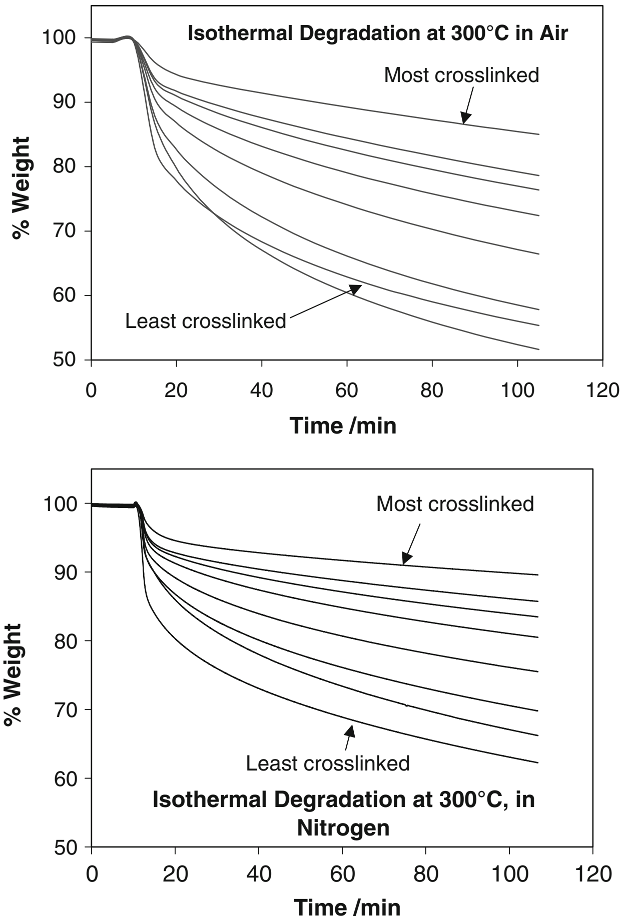


Fig. 2 Crosslink density effect on the kinetics of isothermal degradation of polyurethane acrylate films at 300 °C in ambient atmosphere and in nitrogen flow

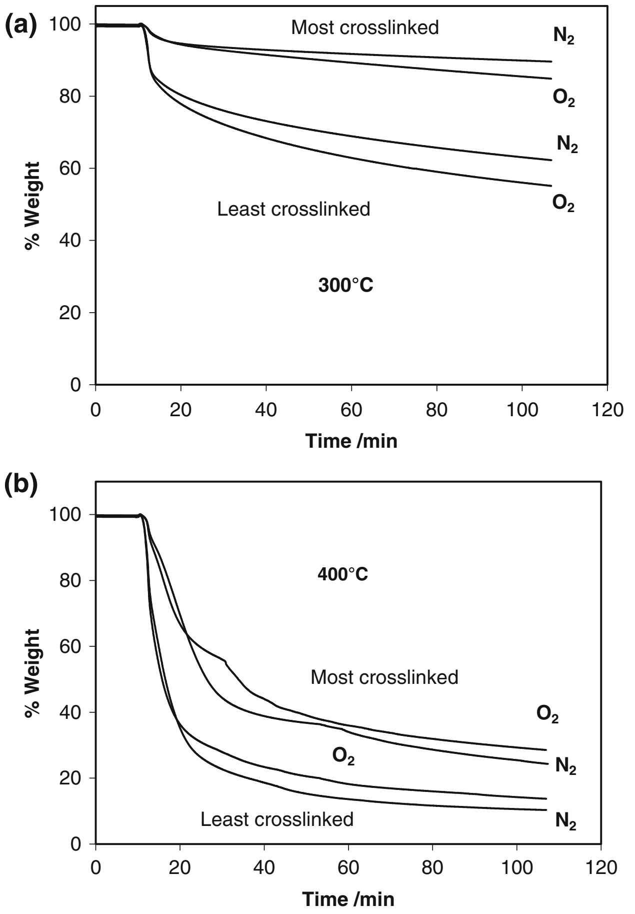


Fig. 3 Comparison of degradation kinetics in air and in nitrogen at 300 and 400 °C

experiments in nitrogen flow, N_2 was allowed to flow through the cell for 10 min after closing the cell and prior to the beginning of the heating cycle.

Materials

Oligomers and monomers were purchased from Sartomer Co., and initiators were from Ciba Specialty Chemicals Co. (Table 1). Commonly synthesized and commercially available oligomers are polyols or polyesters end-capped with acrylate either through ester, or through urethane bridge [81–84]. Number of urethane groups is usually twice the number of acrylate groups in oligomer [83]. Difunctional urethane acrylate oligomer, CN966B85, was selected since it yielded more flexible polymer solids [81–85]. The variation of glass transition temperature was accomplished by varying difunctional monomer concentration [83, 84]. The concentration of difunctional urethane acrylate oligomer was constant to reduce variability in degradation rates due to the presence of different numbers of urethane functional group. Use of difunctional oligomers ensured film formation upon cure.

Results and discussion

Glass transition temperatures of cured polyacrylates varied from −49 to +65 °C (Table 2). No loss of volatiles was observed below 200 °C. Thermal degradation of urethane and ester bridges above 250 °C is accompanied by depolymerization and volatile products formation [7]. Concentration of selected urethane di-acrylate oligomer blend with polyester main chain, CN966B85, was the same in all resin formulations to ensure invariant contribution of non-acrylate degradation to an observed thermally induced weight loss. The molecular weight of oligomer portion of the blend, CN966, was ≈5500 [85]. Thus, relative contribution of four urethane bridges per oligomer molecule to the thermally induced weight loss was low relative to that of ester groups. Mechanism of polyester degradation and forming volatiles are similar to polyacrylates degradation

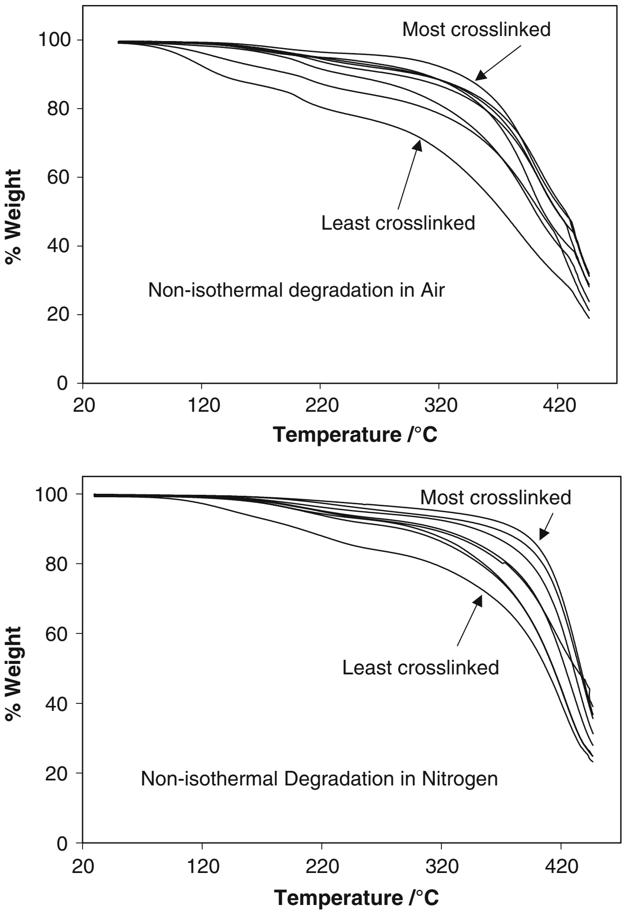


Fig. 4 Crosslink density effect on weight loss due to non-isothermal degradation of polyurethane acrylate films at ambient conditions (*top*) and in nitrogen (*bottom*). Heating rate = 10 °C min^{-1} from 300 to 450 °C

mechanism and degradation products [7]. Ester group contribution to thermally induced weight loss should also be relatively low considering that concentration of oligomer was ≈0.04 M. Regardless, the same mobility restrictions at higher degree of crosslinking should apply to ester and acrylate degradation [7].

The crosslink density of the UV-cured polyacrylates was calculated using an expression derived from Flory's rubber elasticity theory (Eq. 1, Table 2) [4–6, 86].

$$\nu_e = \frac{E'}{3RT} \tag{1}$$

where ν_e(mol m^{-3}) is a molar concentration of crosslinks, E' (Pa) is tensile storage modulus measured at the rubbery plateau, $R = 8.314$ J K^{-1} mol^{-1} is universal gas constant, and T (K) is absolute temperature.

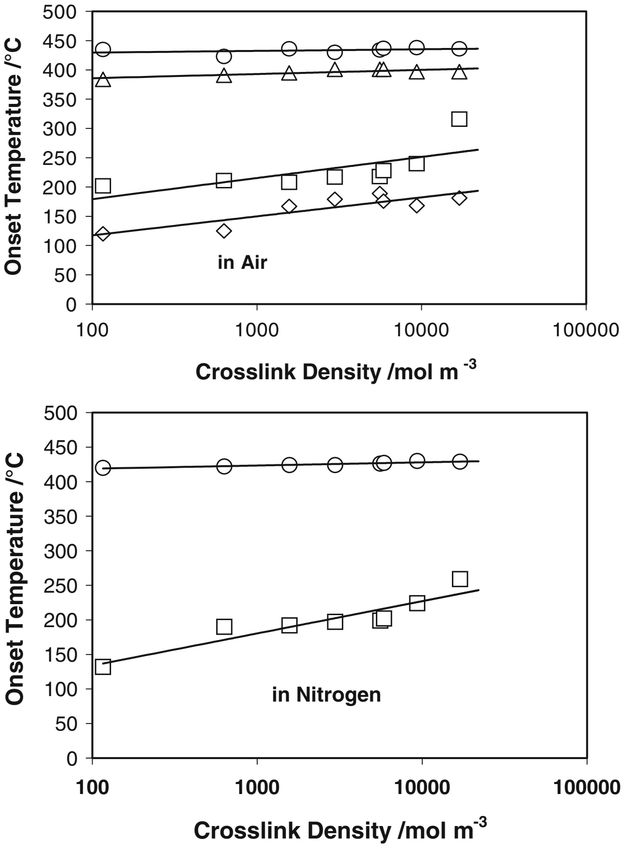


Fig. 5 Dependence of onset temperatures in non-isothermal degradation of photocrosslinked acrylates in nitrogen flow on crosslink density

The kinetics of isothermal degradation of photocrosslinked acrylates was monitored at three different temperatures (Figs. 1, 2 and 3) and under steadily increasing temperature (Figs. 1, 4) in air and in nitrogen flows. After 90 min lower overall weight loss was detected in almost all the cases in acrylate films with higher crosslink density in air and nitrogen flow.

Kinetics of polyacrylates degradation in air and in nitrogen differed substantially less than degradation kinetics of corresponding polymers with different crosslink densities (Fig. 3). At 400 °C, degradation in air was slower than that in nitrogen atmosphere, in spite of higher diffusion rate at this temperature (Fig. 3). Thermooxidative degradation initiation involves peroxides formation, consequent formation of initiating $\text{PO}^\bullet$ radicals, reactions with $\text{P}^\bullet$ radicals and so on (Schemes 1, 2 and 3) [1, 7, 34, 70–72], in addition to hydrogen abstraction and valency migration through cyclization (Schemes 2, 3) [1, 7, 34–69]. In the presence of oxygen, formation of alcohol, water and carbon dioxide was expected to be faster than in the nitrogen flow, due to autocatalysis (Scheme 1). Experimentally observed by us difference between weight loss in air and N_2 was practically crosslink independent. If oxygen uptake were rate limiting, difference in kinetics in inert environment and air would be higher, and would strongly dependent on crosslink density influencing diffusion-controlled reactions.

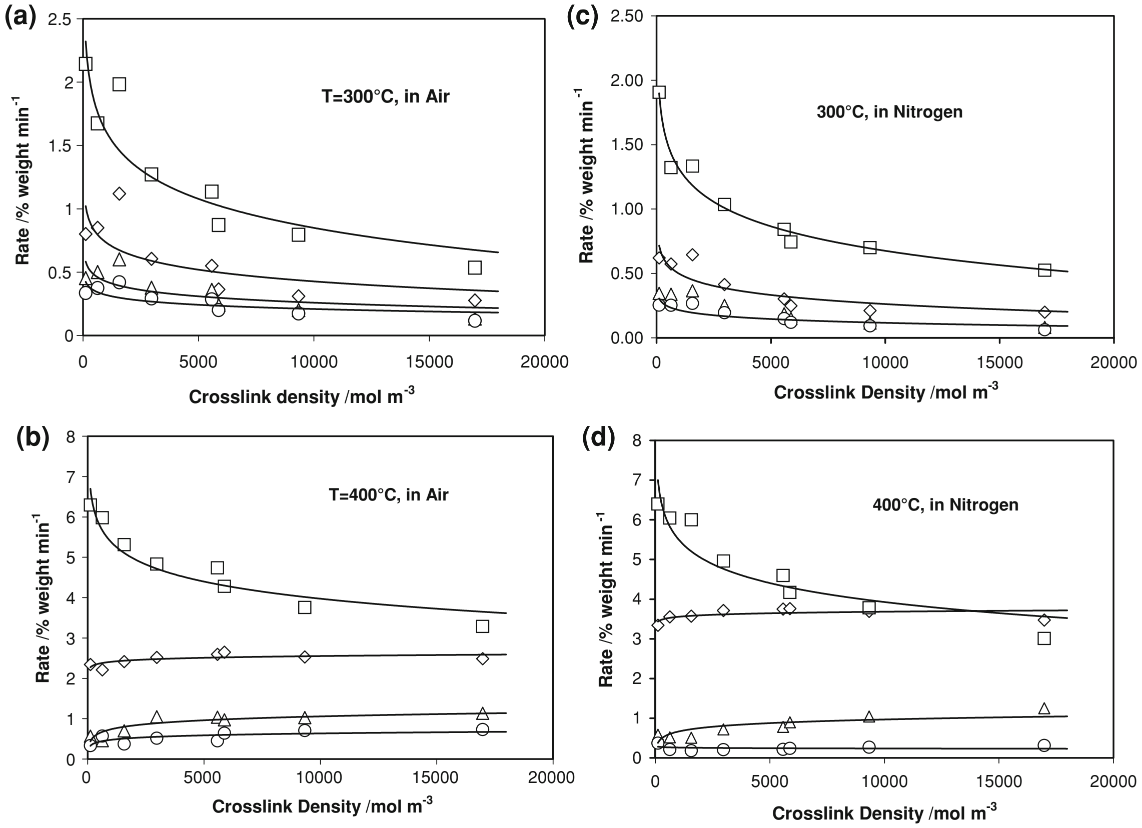


Fig. 6 Dependence of the thermal degradation rate of photocured urethane acrylate films on crosslink density. Rates were measured by the slope of the weight loss kinetic curves (Fig. 2) at different stages of degradation, as Δweight/Δtime at *square* 0 to 5 min, *diamond* 0–10 min, *triangle* 10–20 min, *circle* 20–30 min

The weight loss-detected degradation kinetics was polychronal, whether degradation was conducted isothermally or under temperature increase (Figs. 1, 2, 3 and 4) [1]. This may occur due to kinetic non-equivalence of reactive species in such non-uniform media as polymer solids [1]. Polychronal weight-loss kinetics observed by TG was also explained by multi-stage reaction producing monomer, aldehydes in early stages of degradation and alcohol and water in later stages [45–55, 61–63, 87], carbon dioxide, and methanol in the early and late stages of degradation of acrylates [37–44, 64, 88, 89]. In non-isothermal process conducted in airflow, up to six stages could be identified (Fig. 1). When non-isothermal degradation kinetics was monitored in nitrogen flow, at most, four stages were observed. The lower onset temperatures increased with crosslink density. Higher onset temperatures were independent on crosslink density or the atmosphere at which thermal degradation was conducted (Fig. 5). According to Emanuel and Buchachenko kinetic non-equivalency due to molecular motion is averaged at high temperature, leading to monochronal degradation kinetics [1]. It appears that such averaging occurred at all crosslink densities studied (Fig. 5).

Analysis of radical stability dependence on crosslink density of surrounding photopolymerized crosslinked acrylate networks found no correlation between crosslink density and oxygen effects [65]. This may occur because the diffusion rate of small molecules, like of oxygen and CO_2, in polymer matrix is substantially higher than the rates of other processes. Oxygen diffusivity in polymer matrix is $\geq 10^{-7}$ cm^2 s^{-1}, diffusivity of small molecules like alcohols, $\geq 10^{-9}$ cm^2 s^{-1}, while diffusivity of oligomers is $\leq 10^{-11}$ cm^2 s^{-1}, and these differences significantly influence kinetics of radical reactions in polymer matrix [90–99] and kinetics of thermal degradation [1, 2, 7, 34–69]. Oxygen diffusion rate, even slowed by higher crosslink density still would exceed the rates of other processes and thus, will not change differently the kinetics of degradation of polymers with different crosslinking. The formation mechanism of volatile products is similar with and without oxygen, since the same type of poly-radicals is formed (Schemes 1, 2, 3). If these stages of degradation are rate controlling, no or little difference between kinetics of degradation of in the presence of oxygen and in the inert environment should be observed. If volatile products evaporation step controls the

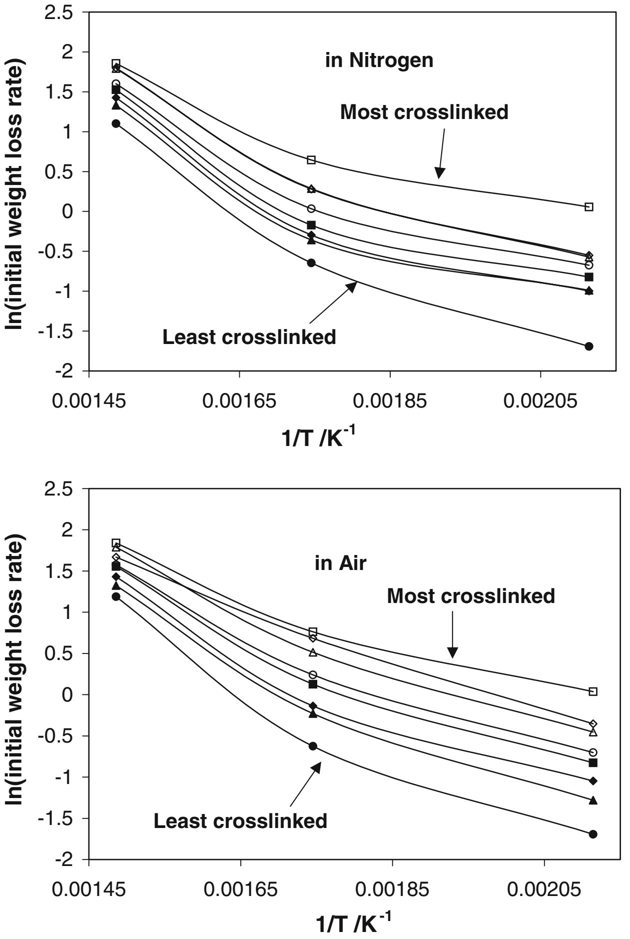


Fig. 7 Initial weight loss rate dependence on the inverse temperature (K)

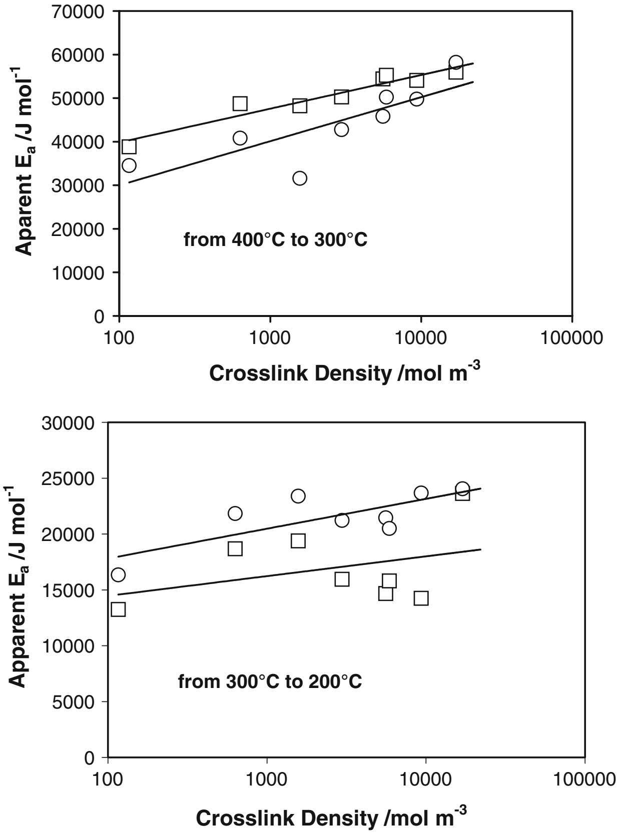


Fig. 8 Dependence of apparent activation energy of acrylates thermal degradation on crosslink density *square* in nitrogen flow; *circle* in air flow. Derived from the initial rates measured from 400 to 300 °C and from 300 to 200 °C

degradation kinetics, oxygen effect on weight loss kinetics would also be minimal.

According to work of Grassie [45–55], Cameron [37–44], Haken [56, 57] and others [100, 101], a majority of acrylate decomposition products are volatile. Haken in later work indicated formation of low volatility oligomer residue, but confirmed formation of substantial amounts of volatiles in higher molecular weight acrylates degradation: >40% was monomer in the early stages and carbon dioxide in the later stages of degradation [56, 57]. Since volatile products change over the degradation period, weight loss kinetics changes as well (Fig. 6). Lower weight loss rates we observed at advanced stages of degradation were in agreement with observations of Lomakin et al. [59, 60], Madorsky et al. [100], Fourie and McGill [101], and Zislina et al. [102]. At 400 °C rate of weight loss at advance degradation was increasing with crosslink density (Fig. 6). Zislina et al. attributed similar observation to the catalysis of degradation by the products [102], while others considered polymer-substrate interaction [101]. To differentiate rate-controlling step, we derived the apparent activation energies, E_a, of overall degradation using Arrhenius approach, applied to initial rates of the polyacrylate films weight loss (Figs. 7, 8) [23–29].

The polychronal degradation kinetics leads to multiple activation energies deduced at different temperature intervals as described by Emanuel and Buchachenko [1] (Fig. 7). The 200–300 °C Arrhenius slope yielded E_a ranging from 12.6 to 25 kJ mol^{-1}, while 300–400 °C slope yielded E_a in 33.5 to 58.6 kJ mol^{-1} (Fig. 8). Apparent activation energies in the presence of oxygen were generally lower than those in the nitrogen flow in the 300–400 °C temperature range and higher in temperature range 200–300 °C (Fig. 8). Apparent activation energies showed overall increase with increased crosslinked density. Similar values of E_a (from 23.4 to 79.9 kJ mol^{-1}) were reported for polyacrylates and polymethacrylates [8, 21, 103, 104]. Values >83.7 kJ mol^{-1} were reported elsewhere [60, 69, 105]. Majority of publications reported temperature dependent E_a [1, 8, 21, 69, 103, 104].

Lomakin et al. concluded that relatively low activation energies indicated degradation kinetics controlled by the rate of volatile product diffusion [56, 57, 60]. Oxygen diffusion control of thermooxidation was often suggested

[21]. However, almost no difference in rates of thermal degradation of polyacrylate samples of different thickness was found for thicknesses from 10 to 70 μ [59, 105].

Activation energy of small molecules diffusion depends on molecular interactions between the media and diffusing molecules [3, 23–29, 106]. These interactions should remain relatively invariant with crosslink density change. On the other hand, the rate of segment mobility controlling hydrogen transfer leading to polyacrylate decarboxylaion (Scheme 3) is strongly dependent on crosslink density [4–6]. Dependence of the degradation rate and E_a on crosslink density in chemically similar polymers indicated that segmental mobility leading to H-transfer through cyclic transition state is rate-controlling in polyacrylate thermal decomposition. The values of activation energies 12.6 to 83.7 kJ mol^{-1} also correspond to torsion of the side-chain segments in polymer [1, 4–6].

Conclusions

The kinetics of photocrosslinked urethane acrylates thermal degradation was monitored using TG by the loss of volatile products at temperatures 100–450 °C. The rate of early events of degradation, <5 min, decreased with the increased of crosslink density. At 400 °C and above, the rate of volatiles loss measured at the times closer to degradation completion, increased with crosslink density (Fig. 6). This may explain, why decreased stability at higher crosslinking was reported [9, 11].

Onset temperature of degradation and apparent activation energies of volatiles loss increased with increased crosslink density (Figs. 5, 8). The values of apparent activation energies, 3–15 kcal/mol may indicate that the torsion restriction in highly crosslinked acrylates was responsible for higher stability.

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