



Synthesis and characterization of unsaturated polyester resins cured by frontal polymerization

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(Received: November 20, 2003; published: January 3, 2004)

Abstract: Various crosslinking agents have been used to frontally cure the unsaturated polyester derived by the reaction of maleic anhydride and 1,2-propanediol. The effect of composition of the curing mixture on the front velocity and its maximum temperature, as well as on the thermal properties of the obtained materials, is described.

Introduction

The air pollution resulting from the use of low-boiling toxic components in polymeric materials is often a dramatic problem to face. Legislation tends to prevent volatile organic compound (VOC) emissions by limiting the presence of these products in reaction mixtures. Although styrene (St) is considered an important air pollutant, it is widely used in many commercial applications such as the preparation of unsaturated polyester (UPE)/St resins [1].

In a recent work, we have reported the first successful preparation of a UPE/St resin cured by frontal polymerization (FP) [2]. In the present paper, we present the FP of new UPE systems in which St is substituted by various less VOCs.

Indeed, because of their relatively low toxicity and volatility, acrylates [3] and diurethane diacrylates [4] are among the preferred alternative curing agents in place of St. In addition, they are often able to enhance mechanical properties of the resulting materials. Herein, we will describe the possibility of exploiting the FP technique in the easy and fast preparation of UPE resins (UPERs) cured by several relatively low volatile compounds belonging to the above chemical classes.

FP is a technique that uses the exothermicity of a polymerization reaction to promote the formation of a travelling hot front able to self-sustain and convert the monomer close to the reaction zone into polymer. Initially investigated by Chechilo *et al.* [5], FP was lately extensively studied by Pojman *et al.* who polymerized acrylic monomers [6-8] and epoxy resins [9].

In recent years, Mariani *et al.* have extended the use of the FP technique to other polymerizing systems, specifically dicyclopentadiene [10], polyurethanes [11,12],

interpenetrating polymer networks [13] and a UPE/St resin [2]. Several applications of FP have been proposed: White *et al.* investigated the curing of epoxy-based materials [14], Pojman *et al.* prepared thermochromic composites [15] and polymer-dispersed liquid crystal (PDLC) materials [16], Morbidelli *et al.* obtained homogenous polymer blends [17] and copolymers [18], Washington and Steinbock synthesized hydrogels [19], Mariani *et al.* prepared PDLC films [20] and applied FP to the consolidation of porous materials [21].

In this work, we report on the synthesis and characterization of several UPERs obtained by the UPE shown in Fig. 1 (hereinafter UPE) which was cured by 2-hydroxyethyl acrylate (HEA) or mixtures constituted of acrylic acid 2-[6-(2-acryloyloxyethoxycarbonylamino)hexylcarbonyloxy]ethyl ester (DUDA, Fig. 2) and St or HEA.

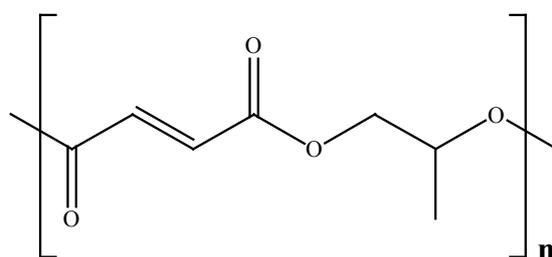


Fig. 1. The UPE used in the present work

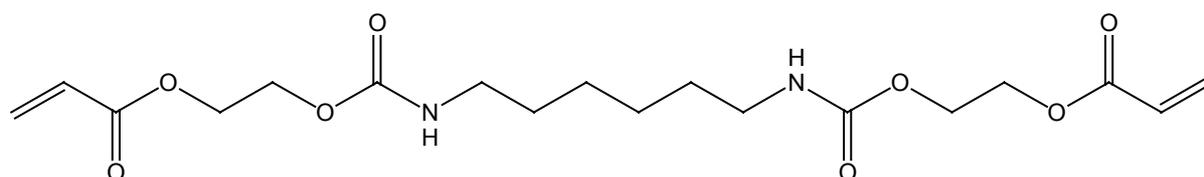


Fig. 2. The diurethane diacrylate (DUDA) used as a curing agent in the present work

Experimental part

HEA, St and benzoyl peroxide (BPO) were purchased from Aldrich and used as received. Aliquat[®] persulfate (APS), UPE and DUDA were prepared as reported in the literature [22,2,23].

Technical equipment: K-type thermocouple connected to a digital thermometer reader Delta Ohm model DO 9416. DSC measurements were obtained with a Mettler DSC 30 in a temperature range between -100 and +200°C, with a heating rate of 10°C/min, under nitrogen atmosphere. Two consecutive scans were collected for each sample; first scans were used for estimation of monomer conversion; thermal properties (T_g data) were measured on the second scan.

Throughout the discussion section, abbreviations will be used. Each is composed of some characters and refers to samples: the character before the hyphen indicates the technique with which the sample was synthesized (F for frontal polymerization; B for batch polymerization). The characters after the hyphen refer to the crosslinking agent(s) (H for HEA; SD for mixtures composed of St and DUDA; HD for mixtures composed of HEA and DUDA). The number is used to distinguish different samples.

Reproducibility of T_{\max} (as defined in Fig. 3) data was $\pm 5^{\circ}\text{C}$ and that of front velocity, V_f , was ± 0.05 cm/min. Error bars in the following plots indicate these variation ranges.

The composition of samples discussed in the text is given in Tab. 1. In this table, the weight content of UPE refers to the total amount of UPE + crosslinking agent(s).

In the following, [APS] and [BPO] are expressed in mol-% with reference to 100 mol of crosslinking agent(s).

Tab. 1. Composition of samples with acronyms used in the text

Sample	UPE ^a in wt.-%	HEA/HD ^b in wt.-%	DUDA/HD ^c in wt.-%	St/SD ^d in wt.-%	DUDA/SD ^e in wt.-%	Initiator in mol-%
F-H1	70	100	0	-	-	3.0 ^f
B-H1						
F-H2	30	100	0	-	-	3.0 ^f
F-SD1	70	-	-	16	84	2.0 ^g
B-SD1						
F-SD2	70	-	-	33	67	2.0 ^g
B-SD2						
F-HD1	70	84	16	-	-	3.0 ^f
B-HD1						
F-HD2	70	67	33	-	-	3.0 ^f
B-HD2						
F-HD3	70	50	50	-	-	3.0 ^f

^a Weight content of UPE referred to the total amount of reaction mixture.

^b Weight content of HEA referred to the total amount of crosslinking agent HD.

^c Weight content of DUDA referred to the total amount of crosslinking agent HD.

^d Weight content of St referred to the total amount of crosslinking agent SD.

^e Weight content of DUDA referred to the total amount of crosslinking agent SD.

^f APS. ^g BPO.

FP runs

In a typical run, a non-adiabatic glass test tube (inner diameter: 16 mm) was loaded with an appropriate quantity of UPE homogeneously mixed with a suitable amount of curing agent(s) (HEA, or mixtures of DUDA and St (hereafter SD), or mixtures of DUDA and HEA (hereafter HD)) and a radical initiator (BPO or APS). The total amount of mixtures was always 7.0 g (Tab. 1).

A K-type thermocouple was placed into the above mixtures and located at c. 2 cm from the bottom of the tube. Temperature was monitored with a digital thermocouple reader (sampling rate: 1 Hz). FP reactions were ignited by heating the external wall of the tube in correspondence to the upper surface of the mixture until the formation of the travelling front started.

After the end of the experiments, test tubes were cooled to room temperature. Afterwards, the crosslinked polymers were ground, extracted in a Soxhlet with diethyl ether to remove the unreacted products and dried in vacuum. Yields were quantitative.

Batch polymerization runs

Control samples having the same composition as their FP counterparts were synthesized by standard batch methods in the same above reactors placed in a thermostatic oil bath set at 80°C for 1 h. Product work-up was as described above. Yields were quantitative.

Results and discussion

Use of HEA as the crosslinking agent

HEA was chosen as a substitute of St for its properties of high reactivity, high solubility, low volatility and low toxicity. Initially, the reaction conditions under which *pure* FP can be performed have been determined. The term 'pure' refers to FP as the unique polymerization mode occurring at a given time. In particular, it indicates that no spontaneous polymerization (SP) occurs simultaneously.

APS was used as the radical initiator, this compound being able to give radicals without forming gaseous species responsible for bubble formation in the resulting material. In a first set of experiments its amount was kept constant and equal to 3.0 mol-%.

Pure FP occurs only when $20 \leq \text{HEA} \leq 100$ wt.-% (with reference to the total amount of HEA + UPE). When $\text{HEA} < 20$ wt.-%, FP does not take place. This fact is attributable to a non-sufficient amount of released heat for FP to self-sustain. A temperature profile recorded during a typical FP experiment is shown in Fig. 3.

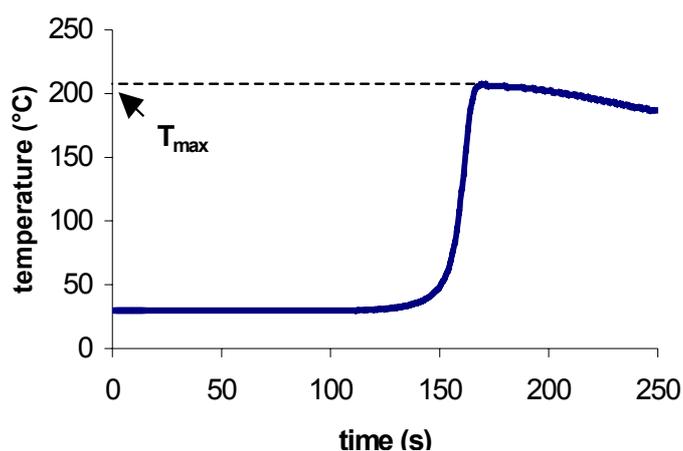


Fig. 3. A temperature profile recorded during a typical FP run (F-H2)

T_{\max} is the maximum temperature reached by the propagating front. The flat part of the curve, referring to regions not yet reached by the front, confirms that no SP was simultaneously occurring. Indeed, if this was not the case, due to the exothermicity of the latter, a temperature increase should be recorded.

In Fig. 4, T_{\max} as a function of UPE weight content is reported ($[\text{APS}] = 3.0 \text{ mol-}\%$). As can be seen, the larger the amount of UPE, the lower T_{\max} . In particular, when $\text{UPE} > 80 \text{ wt-}\%$, FP does not self-sustain or does not start at all. This fact and the finding that the highest temperature of 228°C refers to the FP of neat HEA suggest that the whole reaction is *driven* by that of the latter monomer. Indeed, if the amount of HEA is not sufficiently large, the quantity of heat released does not permit FP to sustain itself.

Similar considerations can be made by looking at the dependence of V_f on the UPE content (Fig. 5). Indeed, also this parameter looks strongly influenced by the heat released during HEA polymerization, thus resulting in a dramatic V_f decrease from 15.5 cm/min (neat HEA) down to 0.25 cm/min (at $\text{UPE} = 80 \text{ wt-}\%$).

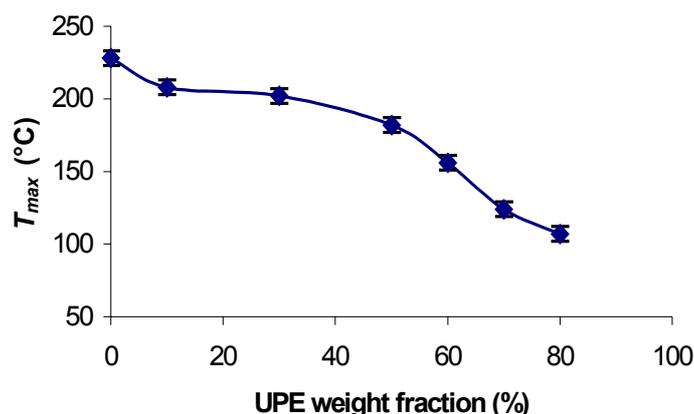


Fig. 4. T_{\max} as a function of the amount of UPE in the UPE/HEA system ($[\text{APS}] = 3.0 \text{ mol-}\%$)

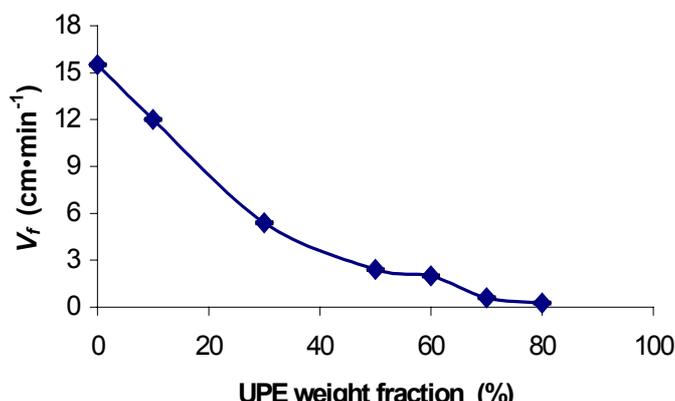


Fig. 5. V_f as a function of the amount of UPE in the UPE/HEA system ($[\text{APS}] = 3.0 \text{ mol-}\%$)

In a second set of experiments, the effect of APS concentration on T_{\max} and V_f was investigated by keeping constant the HEA content ($30 \text{ wt-}\%$). T_{\max} was found to be strongly dependent on $[\text{APS}]$, which was allowed to range from 1.0 to $10 \text{ mol-}\%$ (Fig. 6). The former is the minimum value of APS necessary for FP to occur. Also in this case, the corresponding V_f plot shows a quite similar trend (Fig. 7).

V_f rises as APS increases, ranging from 0.3 cm/min (at $[\text{APS}] = 1.0 \text{ mol-}\%$) to 0.7 cm/min (at $[\text{APS}] = 5.0 \text{ mol-}\%$). This plateau value is kept also for $[\text{APS}] = 10 \text{ mol-}\%$.

The T_g values of two samples having the same composition prepared by FP and batch reaction (F-H1 and B-H1, respectively) are collected in Tab. 2 together with those of the other samples discussed in the following. The data indicate a substantial independence of T_g from the polymerization technique used (34°C for B-H1 and 35°C for F-H1).

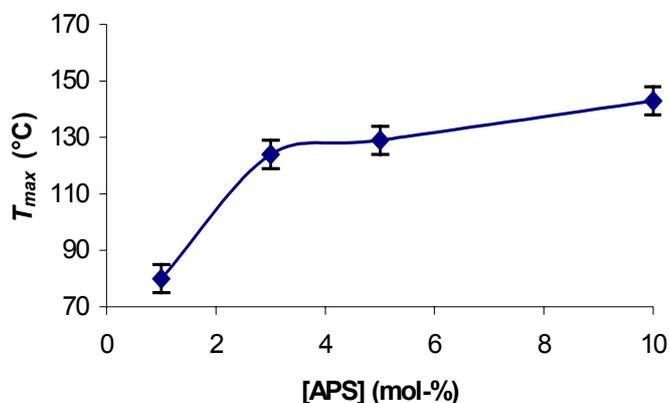


Fig. 6. T_{max} as a function of initiator concentration in the UPE/HEA system (HEA = 30 wt.-%)

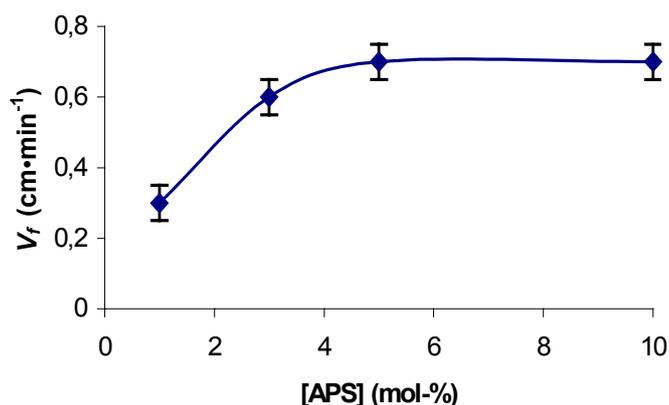


Fig. 7. V_f as a function of initiator concentration in the UPE/HEA system (HEA = 30 wt.-%)

Tab. 2. T_g values (in °C) of some samples prepared in the present work

F-H1	B-H1	F-SD1	B-SD1	F-SD2	B-SD2	F-HD1	B-HD1	F-HD2	B-HD2
+35	+34	+52	+48	+45	+53	+29	+36	+32	+39

DSC traces (1st and 2nd scans) of the F-H and B-H samples investigated do not evidence the presence of exothermic peaks due to unreacted functionalities in the polymerized mixtures. This fact and gravimetric analysis infer that both polymerization techniques allow reaching complete conversion. As an example, the DSC thermograms related to the 1st scan performed on samples F-H1 and B-H1 are reported in Fig. 8.

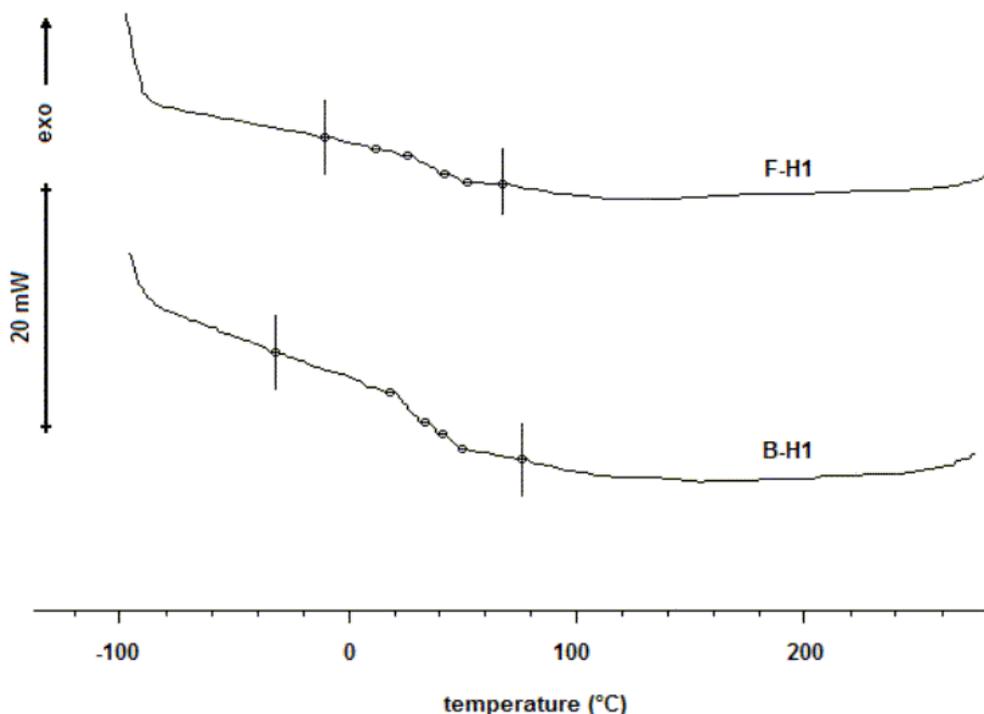


Fig. 8. DSC thermograms of samples F-H1 and B-H1 (1st scan)

Use of St and DUDA mixtures as crosslinking agents

UPE/St resins are very common. However, in some cases St can be partially replaced by a diurethane diacrylate such as DUDA (Fig. 2). This class of monomers is easily obtained by reaction between a diisocyanate and a hydroxyacrylate. According to ref. [23], we have synthesized DUDA starting from hexamethylene diisocyanate and HEA. In this part of the present work, this compound has been used in the frontal curing of UPE together with various amounts of St.

On the basis of what was previously studied by us [2], and taking into account the common commercial formulations, we have investigated the frontal curing of UPE with 30 wt.-% of crosslinking agents (SD). SD was a mixture of St and DUDA in various relative ratios. BPO was employed as the radical initiator because of its use in practical applications. Its concentration was kept constant and equal to 2.0 mol-%.

The effect of the amount of DUDA on T_{\max} and V_f is reported in Tab. 3. It can be seen that FP takes place only when the content of DUDA in SD is smaller than 50 wt.-%. Accordingly, the larger the amount of DUDA, the lower T_{\max} . At variance, no significant V_f variations have been found in the aforementioned range ($V_f = 0.5 - 0.6$ cm/min).

Tab. 3. V_f and T_{\max} as functions of the DUDA/SD ratio

Sample	DUDA/SD in wt.-%	V_f in cm/min	T_{\max} in °C	Polymerization mode
F-SD1	16	0.5	171	FP
F-SD2	33	0.6	153	FP
F-SD3	50	-	-	no FP

Subsequently, the DUDA/SD ratio was kept constant (= 33 wt.-%) and the amount of BPO was allowed to vary in the range $1.0 \leq [\text{BPO}] \leq 5.0$ mol-% in which pure FP took place. Indeed, it was found that when $[\text{BPO}] > 5.0$ mol-%, simultaneous SP was present, while when $[\text{BPO}] < 1.0$ mol-%, FP did not occur.

V_f and T_{\max} as functions of $[\text{BPO}]$ are reported in Figs. 9 and 10, respectively. In the considered FP range, both these parameters are characterized by a sharp variation: from 0.2 cm/min and 88°C (at $[\text{BPO}] = 1.0$ mol-%) to plateau values located at 0.5 cm/min and $\approx 155^\circ\text{C}$ (at $3.0 \leq [\text{BPO}] \leq 5.0$ mol-%).

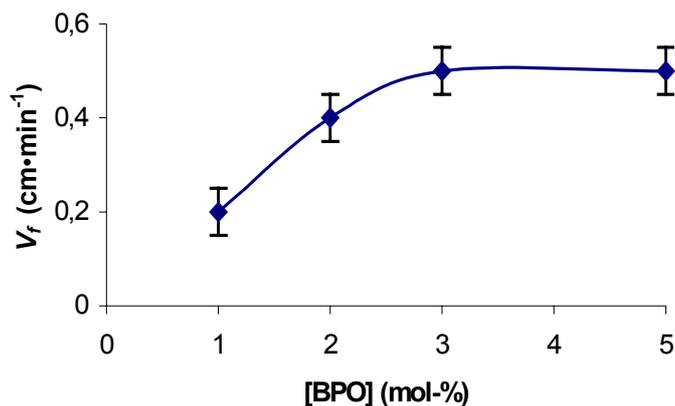


Fig. 9. V_f as a function of $[\text{BPO}]$ in the UPE/SD system (DUDA/SD = 33 wt.-%)

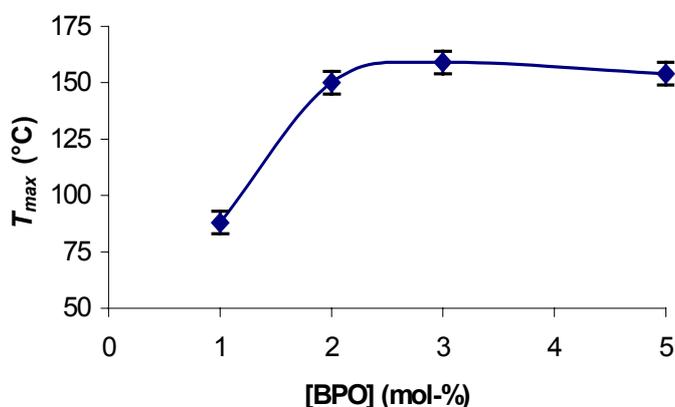


Fig. 10. T_{\max} as a function of $[\text{BPO}]$ in the UPE/SD system (DUDA/SD = 33 wt.-%)

As previously discussed for the UPE/HEA systems, also the DSC analyses performed on UPE/SD products (obtained by either frontal or batch reactions) do not evidence any exothermicity. Therefore, complete monomer conversion was reached by both polymerization techniques. As an example, the DSC thermograms related to the first scan of samples F-SD1 and B-SD1 are reported in Fig. 11.

By contrast, we had found the presence of exothermic peaks in DSC traces of a similar system crosslinked in a batch process with styrene only [2]. Hence, the introduction of the diurethane diacrylate in the curing mixture allows reaching higher conversions during the batch polymerization reaction.

Moreover, as reported in Tab. 2, also in this case FP and batch processes lead to cured structures having similar thermal behaviour. By comparing the data in Tab. 2, it can be inferred that T_g values of F-SD and B-SD samples are higher than those of

the F-H and B-H series. This behaviour can be attributed to the larger mobility that HEA imparts to the final material with respect to the mixture SD.

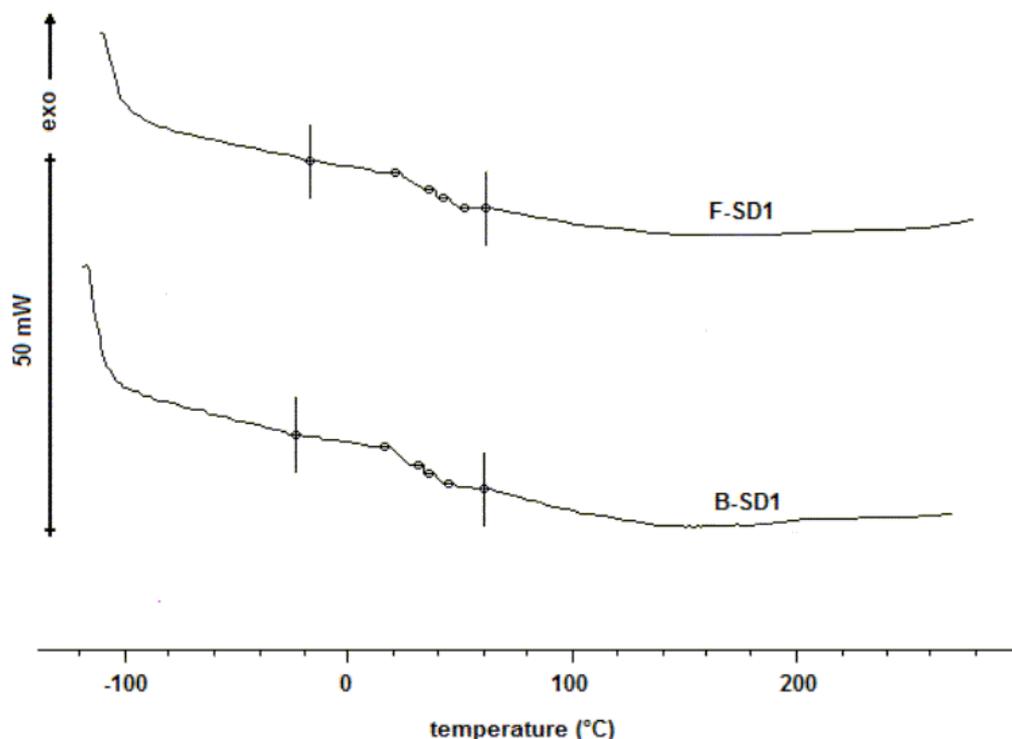


Fig. 11. DSC thermograms of samples F-SD1 and B-SD1 (1st scan)

Use of HEA and DUDA mixtures as crosslinking agents

To take a complete survey, another study was performed using various mixtures of HEA and DUDA as crosslinking agents (HD). Also in this case, the UPE/HD weight ratio was kept constant and equal to 70/30. In all these experiments, APS was used as the radical initiator.

The dependence of T_{\max} and V_f on the HEA content is given in Tab. 4 for constant [APS] (3.0 mol-%). Similarly to what was found in the UPE/SD system, also in this case FP takes place only when the amount of DUDA in the curing mixture is < 50 wt.-%. However, this was due to the fact that, at larger DUDA contents, phase separation occurs.

Tab. 4. V_f and T_{\max} as functions of the HEA/HD ratio ([APS] = 3.0 mol-%)

Sample	HEA/HD in wt.-%	V_f in cm/min	T_{\max} in °C
F-H1	100	0.6	124
F-HD1	84	0.8	119
F-HD2	67	0.6	129
F-HD3	50	0.6	147

The composition of the crosslinking mixture does not have significant effects on maximum temperature when HEA/HD \geq 67 wt.-%. For smaller HEA contents, this figure rose to 147°C (HEA = 50 wt.-%). In the same range V_f kept almost constant at c. 0.6 cm/min with a maximum of 0.8 cm/min when the amount of HEA in HD was equal to 84 wt.-%.

A last series of experiments was performed to obtain information on the dependence of T_{max} and V_f on APS concentration (Tab. 5). Pure FP was observed in the range $1.0 \leq [APS] \leq 10$ mol.-%. Again, for $[APS] < 1.0$ mol.-% no FP took place due to the small amount of heat released in the curing reaction. However, FP did not occur also when $[APS] > 10$ mol.-%. This finding is consistent with the gradual decrease of T_{max} as $[APS]$ increases (from 126°C at $[APS] = 1.0$ mol.-%, to 111°C at $[APS] = 10$ mol.-%). However, it is not consistent with what was reported above for the other systems studied in the present work. At variance, the corresponding V_f trend shows an evident increase from 0.4 to 0.9 cm/min when $[APS]$ rises from 1.0 to 10 mol.-%, respectively.

Tab. 5. V_f and T_{max} as functions of APS concentration (HEA/HD = 70 wt.-%; UPE/HD = 70/30 w/w)

Sample	[APS] in mol.-%	V_f in cm/min	T_{max} in °C
F-HD4	1.0	0.4	126
F-HD5	5.0	0.8	120
F-HD6	10	0.9	111

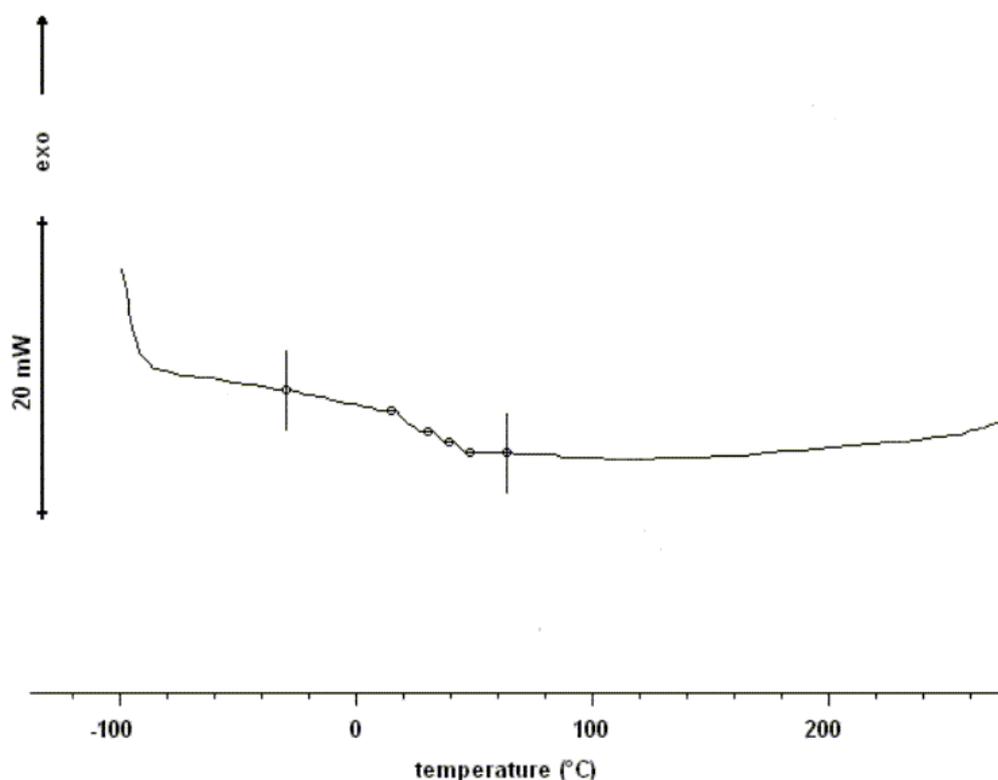


Fig. 12. DSC thermogram of sample F-HD1 (1st scan)

A possible explanation of this apparent anomaly can be given by taking into account the diluting effect of APS, which is characterized by high molecular weight (c. 753) and, therefore, is used in relatively large weight amounts. Its contribution could be that of dispersing heat, thus decreasing T_{\max} when its concentration rises. However, [APS] increase corresponds to a larger number of growing macromolecules per time unit, with the effect of increasing V_f .

As reported for the other systems previously discussed, DSC thermograms do not exhibit any exothermicity regardless of the type of polymerization used for product preparation. As an example, a DSC trace referring to sample F-HD1 is reported in Fig. 12.

Therefore, also in this case products prepared by FP substantially behave like those obtained through batch polymerization, as also confirmed by their T_g values (Tab. 2). Furthermore, no effect of the composition of the HD curing mixture can be pointed out. However, the replacement of St with HEA changes the T_g values of the obtained product (see Tab. 2), which decrease and become very similar to those determined for UPE/HEA systems, according to the increased mobility of the polymer network.

Conclusions

A new series of UPERs cured with different crosslinking agents was successfully prepared by FP. At variance to what was previously found by us for the corresponding UPE/St resin [2], the thermal properties of all the products prepared in the present work have not been found to be influenced by the type of polymerization process adopted for their preparation. Indeed, while in that previous work batch polymerizations were characterized by lower conversion degrees than FP ones, in the present study no differences have been found in this respect. However, T_g values are dependent on the crosslinking agent composition (HEA, SD, HD).

Finally, FP confirms to be a reliable polymerization method useful in an increasing number of practical applications having the advantage of being faster than the conventional technique (a few minutes, depending on V_f and reactor length, instead of 1 h) and that does not need continuous energy supply apart from that necessary for the ignition.

Acknowledgement: We wish to thank Berta Azpericueta for her kind assistance in the preparation of the manuscript. Funds provided by the University of Sassari and Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali (INSTM) are gratefully acknowledged.

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