Article

Poly(2-alkyl/aryl-2-oxazoline)-Imidazole Complexes as Thermal Latent Curing Agents for Epoxy Resins

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ABSTRACT: One-component epoxy resins (OCERs) with improved stability (shelf life) and controlled curing temperatures were prepared using epoxy resins and polyoxazoline-imidazole (POZ-Im) based thermal latent curing agents (TLCs). POZ homopolymers with molar masses of 1000, 2000, and 5000 g/mol were obtained via cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline, 2-propyl-2-oxazoline, 2-pentyl-2-oxazoline, and 2-phenyl-2-oxazoline. TLCs were prepared by physically entrapping imidazole, the curing agent, in the POZ matrix at the homopolymer/Im (HP/Im) ratios of 1:1 and 5:1 and characterized by FTIR and TGA. TLCs were then mixed with bisphenol A diglycidyl ether (DGEBA) to obtain OCERs with Im concentrations of 1, 3, and 5 wt %. Dynamic DSC tests were performed to determine the effect of the pendant group and molar mass of POZ, the POZ/Im ratio, and Im concentration on the curing behavior of the OCERs, whereas isothermal DSC tests were carried out to examine their thermal stability and optimal curing temperatures. Optical microscopy was performed to study the compatibility of the TLCs with DGEBA. This study showed that the dispersion quality of TLCs is highly associated with the compatibility of POZs and DGEBA, which affected the release of Im, thus left limit temperatures of curing. In addition, higher left limit temperatures were obtained when the POZ/Im ratio increased. Isothermal DSC results conformed to the improved stability and better thermal latency of the samples with a POZ/Im ratio of 5:1. Moreover, the higher left limit temperatures were obtained with the lowest molar mass of POZ due to the better interaction between the −OH end group of POZ and Im. The shelf life of PEOZ 1K-Im 5:1 1% OCER was predicted at −20, 0, and 20 °C, with an estimated 15.3 days at 20 °C using isothermal DSC and rheology at 50, 60, and 70 °C. Overall, this research contributes to the development of OCERs by introducing POZ-Im complexes as novel TLCs. The findings shed light on the importance of compatibility in achieving optimal dispersion and release of Im and the role of the POZ/Im ratio and POZ molar mass in controlling left limit temperatures, ultimately influencing the curing behavior of OCERs.
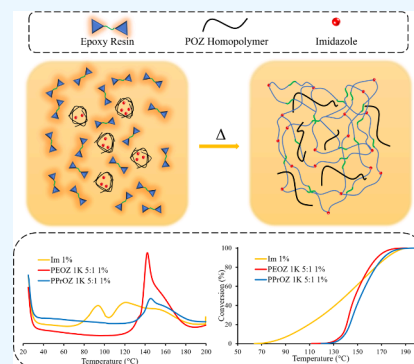
INTRODUCTION

Epoxy resins are the most versatile members of thermoset materials that undergo curing reactions to generate a highly cross-linked structure with several favorable performance characteristics such as excellent resistance to chemicals, moisture, and corrosion, outstanding mechanical strength, and great thermal and adhesive properties.[1−3] Thus, they have been used in many application fields such as coatings,[4−7] adhesives,[8−10] electronic device encapsulants,[11−13] and composites.[14,15] Additionally, they have advantages in terms of formulation diversity for numerous applications.[16] A variety of curing agents such as phenols, acid anhydrides, carboxylic acids, amines, and imidazoles are utilized for epoxy curing to obtain cross-linked thermoset polymers.[17] The epoxy curing reactions occur via three routes depending on the type of curing agent: step-growth polymerization, chain-growth polymerization, or a combination of both.[18] For instance, primary and secondary amines initiate the step-growth polymerization while tertiary amines such as imidazole (Im)

start the chain-growth polymerization.[19] Arimitsu et al. reported that imidazoles have received attention, since their catalytic amount is sufficient to initiate the chain-growth polymerization of epoxy resins. On the other hand, since imidazoles gradually undergo curing reactions and generate cross-linked networks due to their high reactivity with epoxy resins at low temperatures, it is difficult to utilize them in one-component epoxy resins (OCERs).[17]
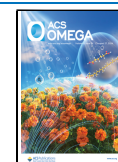
In contrast to two-component resins, OCERs are readily used as a combination of a resin and a latent curing agent. The latent curing agents can be activated by heat, light, moisture, or pressure.[20] OCERs with thermal latent curing agents (TLCs)

are highly desirable since they are more stable at ambient temperature (have enhanced shelf life) compared to two-component epoxy resins and initiate curing only at elevated temperatures.[21] Moreover, OCERs with TLCs are more homogeneous and provide energy efficiency and money-saving by eliminating the need for cold chain storage and shipping.[22] In particular, extending the shelf life and controlling the curing temperature are principal concerns while selecting the TLCs in OCERs. Hence, epoxy resins can be stored over a very long period and curing can be initiated at the desired time.[23] TLCs work via two mechanisms. The first mechanism is based on the use of TLCs having crystalline structures that do not dissolve in epoxy resins at low temperatures but get activated upon melting at elevated temperatures.[24] DICY is one of the good examples of this type of curing agent since it is not soluble in epoxy resin at ambient temperature; whereas, it starts to melt and get activated when the temperature reaches between 160 and 180 °C. DICY has a shelf life of 6 to 12 months. The second mechanism is based on the use of a precursor compound, such as a complex or conjugate form of a curing agent. Chen et al. reported the physical entrapment of Im in a polyethylene glycol (PEG) matrix using a solvent evaporation method. They found that PEG1000-Im had better latency and curing performance as TLC compared to those of other PEGs with different molar masses. The cured resins had T_g values around 150 °C, which was an indication of full conversion of DGEBA.[25]

Recently, TLCs have been developed by encapsulating curing agents with polymers instead of using high-temperature curing agents such as DICY. The encapsulation is widely used due to its feasibility and effectiveness.[26] Chen et al. validated that the polymer structure and properties significantly affect the curing performance of the entrapped TLCs in polymer matrices. Moreover, polymer molar mass, functional groups of the polymer, and the miscibility/compatibility of the TLCs with the resin affect the curing behavior of TLCs.[27] Two methods are used to obtain the encapsulated latent curing agents, including TLCs. The first method is based on the chemical bonding of curing agents and polymers to form polymer matrix capsules, which are inactive until the time when the curing agent is required for the curing process. The second route is the physical entrapment and encapsulation of curing agents in polymers. In this method, curing agents are released from the polymer capsule and activate to initiate the curing process when the temperature increases above the melting point of the polymer. Polyethylene glycol, poly-caprolactone, polystyrene, poly(vinyl alcohol), and acid-hexadecyl acrylate copolymer are mostly used for the entrapment of curing agents in polymers.[28−31] Entrapment of curing agents can be accomplished through several processes, including solvent evaporation, spray drying, and freeze-drying. Shin and co-workers used solvent evaporation or spray-drying methods to achieve the Im encapsulation in the polycaprolactone matrix with the target that the polycaprolactone melts at elevated temperatures resulting in the reaction of released Im with the epoxy resin.[31] The TLCs prepared by physical entrapment/encapsulation of curing agents in polymer matrices still require improvements both in their preparation and in tailoring their curing temperatures, shelf life, and compatibility with different resins. The current investigations focus on the development of OCERs that can be stored at room temperature and have a longer shelf life and mild curing temperatures.

In this paper, we prepared tunable poly(2-oxazoline) homopolymer-Im (HP-Im) complexes as TLCs for OCERs to improve the processability and energy efficiency, thus lowering the cost of thermal curing of epoxy resins. In particular, formerly synthesized poly(2-oxazoline) homopolymers with three different molar masses and Im were used to prepare the TLCs. Im was physically entrapped in the homopolymer by a solvent evaporation method. The prepared TLCs were mixed with DGEBA to obtain OCERs and the curing behavior of the OCERs was investigated. The effect of POZ pendant group and molar mass, POZ/Im ratios, and Im concentration in epoxy resin on the curing behavior of obtained OCERs was studied using DSC. The curing behavior was examined in terms of the curing enthalpy, left limit temperatures of curing, and conversion.

■ EXPERIMENTAL SECTION

Materials. The monomers (2-ethyl-2-oxazoline (EOZ), 2-propyl-2-oxazoline (PrOZ), 2-pentyl-2-oxazoline (PeOZ), and 2-phenyl-2-oxazoline (PhOZ)) were synthesized following procedures reported by our group.[32] The synthesis and characterization procedures, reported by our group as well,[33] of the POZ homopolymers having different molar masses are available in Supporting Information (SI). Bisphenol A diglycidyl ether (DGEBA, molar mass: 340.41 g·mol⁻¹) was purchased from Sigma-Aldrich. Dichloromethane (DCM) and sodium sulfate (Na₂SO₄) were purchased from Merck. Unless stated otherwise, no further purification was performed on the chemicals. Deionized water was acquired from a Merck Direct-Q-3 UV.

Instruments. Dynamic differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo HP DSC 2+ instrument. The samples were weighed in the amounts of 13−20 mg on the DSC pans. The dynamic DSC thermograms were obtained from the first heating run in the range of 25 to 200 °C with a heating rate of 2, 5, and 10 °C/min under a nitrogen atmosphere. Thermogravimetric Analysis (TGA) measurements were performed on a Mettler Toledo TGA/ DSC 3+ in the range of 25 to 1000 °C. Samples of 10−20 mg were heated at 10 °C/min under a nitrogen atmosphere with a flow rate of 100 mL/min. Fourier-Transform Infrared (FTIR) spectra were obtained with a ThermoScientific Nicolet iS50 FTIR spectrometer using an attenuated total reflectance (ATR) accessory. The transmission mode was used, and the resolution was 16 cm⁻¹. The dispersion quality of the TLCs and Im in the DGEBA resin was examined with a Nikon Eclipse LV100ND optical microscope. Time sweep rheology analyses were performed with an Anton-Paar MCR 302 Rheometer using a gap of 1 mm, a shear strain of 0.1%, and a frequency of 1 Hz. The transmittance spectrum was recorded at room temperature on a Perkin Elmar Lambda 950 UV−vis−NIR spectrometer. Dynamic mechanical analysis (DMA) was carried out to investigate the mechanical and thermal properties of a cured sample with a Mettler Toledo DMA-1 equipped with the single cantilever holder, which leaves a free sample length of 17−17.5 mm. The measuring frequency was 1.0 Hz and the oscillation amplitude was 15 μm. The temperature range was between 0 and 200° C with a heating rate of 3 K/min.

Entrapment of Imidazole in Polyoxazoline Homopolymer (POZ HP) Matrix. Poly(2-ethyl-2-oxazoline) (PEOZ), poly(2-propyl-2-oxazoline) (PPrOZ), poly(2-phenyl-2-oxazoline) (PPhOZ), and poly(2-pentyl-2-oxazoline) (PPeOZ)
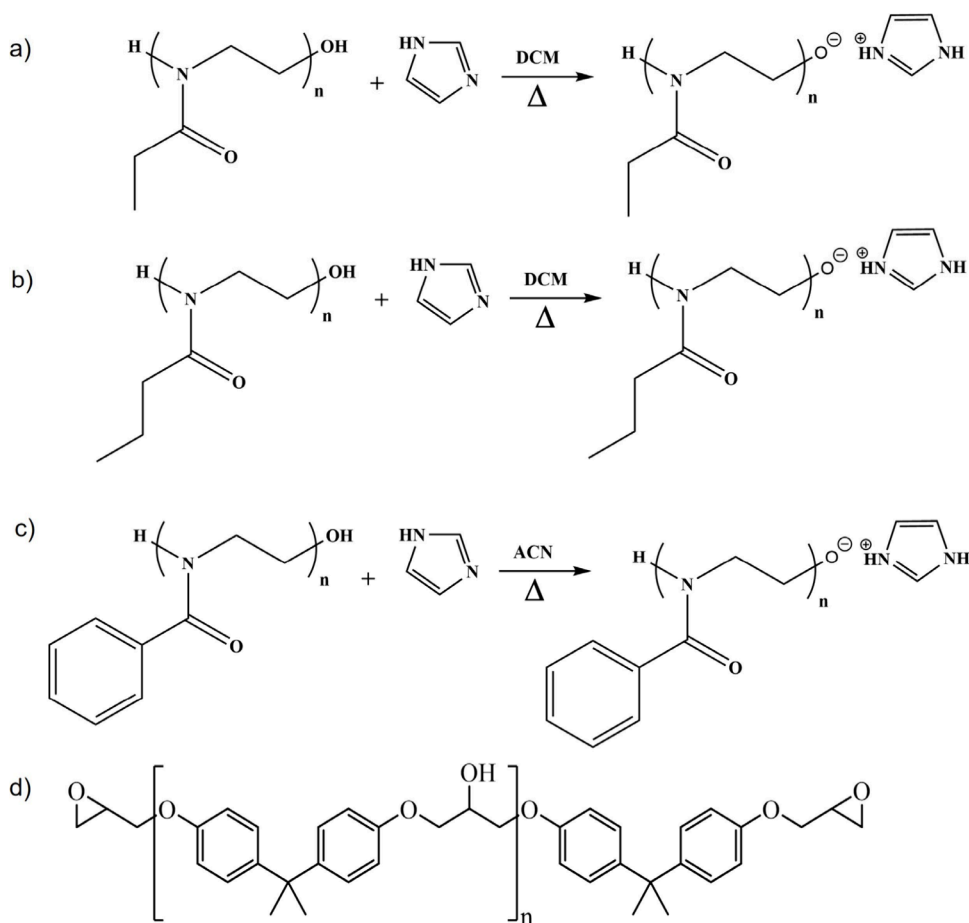
Figure 1. Complex formation between POZ homopolymers and Im (a) PEOZ-Im, (b) PPrOZ-Im, and (c) PPhOZ-Im, and (d) the structure of the DGEBA resin.
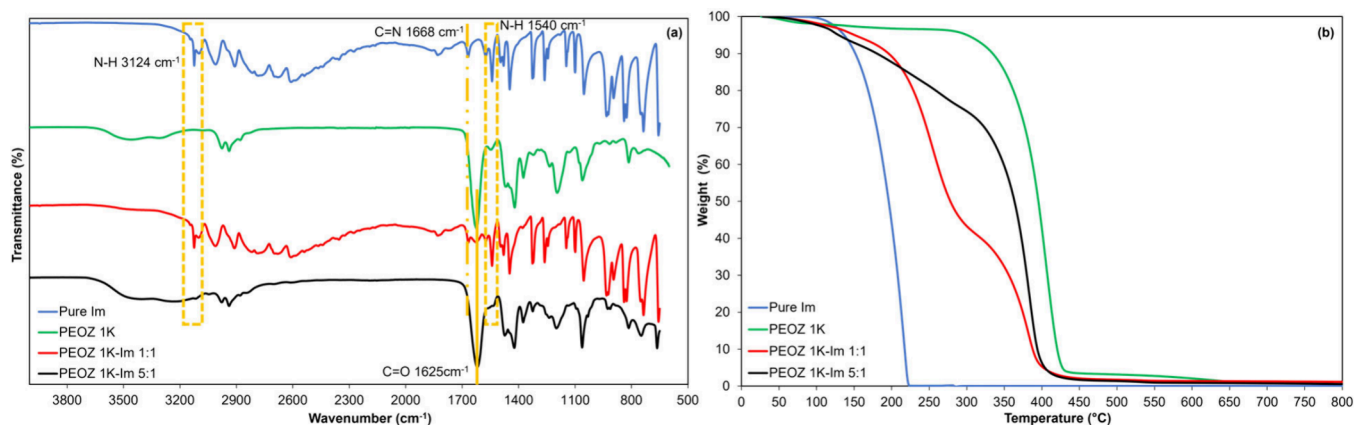

Figure 2. FTIR spectra of Im, PEOZ 1K, and their complexes (PEOZ 1K: Im 1:1 and PEOZ 1K: Im 5:1) (a). TGA thermograms of pure Im, PEOZ 1K, and PEOZ 1K/Im 1:1 and PEOZ 1K/Im 5:1 complexes (heating rate: 10 °C/min) (b).

homopolymers with molar masses of 1000, 2000, and 5000 g/mol were used with Im to prepare POZ HP-Im TLCs. The synthesis procedures and characterization data for the homopolymers are available in the SI (see SI, Parts 1, 2, and 3). HP/Im ratios of 1:1 and 5:1 were used, and the concentrations of Im in DGEBA (Im: E) were set to 1, 3, and 5 wt %. PEOZ, PPrOZ, and PPeOZ homopolymers and Im were dissolved in DCM to prepare a 10 wt/v% solution having a final HP/Im ratio of 1:1 and 5:1. The solutions were heated to reflux (40 °C) in an oil bath and kept stirring for 2 h.

A rotary evaporator was used to remove the DCM under reduced pressure. The prepared HP-Im TLCs were further dried at 25 °C under 1 mbar vacuum pressure overnight. After being dried, the obtained solid TLCs were ground to a fine powder form. The fine powder of HP-Im TLC was mixed with DGEBA resin to give Im concentrations of 1, 3, and 5 wt %. The mixture was prepared by slow manual mixing using a spatula under ambient conditions. On the other hand, for PPhOZ homopolymers, HP and Im were dissolved in acetonitrile (ACN) and the solution was heated to reflux (82

°C). The remaining preparation steps were the same as the steps followed for the other homopolymers (Figure 1).

Curing Procedure of PEOZ 1K-Im 5:1 1% OCER. The prepared TLC of PEOZ 1K-Im 5:1 was cooled to subzero temperature and then ground with a mortar and pestle. The ground powder was mixed with DGEBA resin at 1% ratio using a homogenizer at 1000 rpm for 10 min in the ice bath. The sample was degassed for half an hour. Then, the corresponding cast sample was poured into a Teflon mold. The curing of PEOZ 1K-Im 5:1 1% was performed at 80 °C for 30 min and then at 120 °C for 3 h. To achieve full curing, the sample was held at 160 °C for 8 h. Eventually, the corresponding cast sample was cut and polished to the DMA specimen.

■ RESULTS AND DISCUSSION

Confirmation of Complex Formation Between POZ Homopolymers and Imidazole. The complex formation of POZ homopolymers and Im was confirmed by FTIR and TGA analysis. As a representative of all POZ HP-Im complexes, the results for PEOZ 1K/Im complexes in 1:1 and 5:1 ratios are provided in the following section. Since other POZ HP-Im complexes behaved the same way as PEOZ/Im complexes, their FTIR and TGA data are not shown. Figure 2a shows the FTIR spectra of Im, PEOZ 1K, and PEOZ-1K/Im 1:1 and PEOZ/Im 5:1 complexes. In the FTIR spectrum of Im, the sharp C═N peak of Im was observed at 1668 cm^{-1}, while the peaks related to the N−H bending and stretching of Im were seen at 1540 and 3124 cm^{-1}, respectively. In the FTIR spectrum of PEOZ 1K, amide peaks were observed at 1625 cm^{-1}. In the FTIR spectrum of the PEOZ 1K-Im complex, the sharp C═N peak of Im and the broad C═O peak of PEOZ 1K merged. Furthermore, other peaks of Im and PEOZ 1K were noted in the FTIR spectra of the obtained complexes. Similar FTIR spectra were observed for the other POZ-Im complexes.

TGA thermograms shown in Figure 2b demonstrate the thermal stability and degradation temperature of pure Im, PEOZ-1K, and PEOZ 1K-Im complexes in 1:1 and 5:1 ratios. The single-step decomposition of Im was at 178−222 °C ($T_{d,onset}$) with a residue of less than 0.1%, conforming to the high purity of Im. TGA thermograms showed that PEOZ 1K-Im 1:1 and PEOZ 1K-Im 5:1 followed multistep decompositions since each component of the complex had a different decomposition temperature. The degradation steps for PEOZ 1K-Im 1:1 were observed at 206−357 °C ($T_{d,onset}$, 55.3 wt %) and 357−800 °C ($T_{d,onset}$, 39.0 wt %). Thus, the % weight loss values of the two degradation steps validated the 1:1 ratio of HP/Im. The weight loss (2.57%) observed up to 130 °C stemmed from the evaporation of the water absorbed by the complex. The total degradation was completed with a 0.96% residue. In the case of PEOZ 1K-Im 5:1, the first decomposition was observed at 121−357 °C ($T_{d,onset}$) and corresponded to a 24.3% weight loss. The second decomposition step was performed at 357−800 °C ($T_{d,onset}$) with a 72.5% weight loss. The moisture absorbed by the complex was 3.0 wt % (up to 120 °C). The ratios obtained from the TGA thermograms confirmed the 5:1 HP: Im ratio. The total decomposition of PEOZ 1K-Im 5:1 was completed with a 0.1% residue. Similar TGA thermograms were observed for the other POZ-Im complexes.

Dynamic DSC Results and Parameters Affecting Curing Behavior of OCERs. *Dynamic DSC Results of OCERs Containing POZ-Im TLCs and Epoxy Resin-Im*

Mixtures. Dynamic DSC analyses were performed to assess the thermal latency behavior of OCERs containing POZ-Im TLCs. Dynamic DSC results of the OCERs were compared with those of the epoxy resin-Im mixtures. Table 1 shows

Table 1. Dynamic DSC Results of Curing of Epoxy Resin-Im Mixtures[a]

curing agent	molar mass (g/mol)	Im/E (wt %)	enthalpy (J/g)	left limit temp (°C)	right limit temp (°C)
Im	68.077	1%	55.91	63.88	192.31
		3%	104.22	63.30	192.43
		5%	199.99	68.07	191.81

[a]Heating rate: 10 °C/min.

dynamic DSC results of epoxy resin-Im mixtures. The data in Table 1 showed that epoxy resin-Im mixtures had different enthalpy values depending on the Im concentrations in DGEBA, namely, 1, 3, and 5 wt %, with the highest enthalpy reached when 5 wt % Im was used. The left-limit and right-limit temperatures of curing were at 63−68 and 192 °C, respectively, and differed slightly with the change in Im concentration.

The dynamic DSC data for the DGEBA-Im mixtures in Table 1 was compared to the dynamic DSC data for the OCERs in Tables 2 and 3 to evaluate thermal latency behavior of these systems. The results presented in Table 2 and Table 3 were separated based on the POZ: Im ratio. Table 2 shows the data for the OCERs containing the POZ: Im 1:1 TLCs, whereas Table 3 shows the data for the OCERs containing POZ: Im 5:1 TLCs. The dynamic DSC results were analyzed systematically considering the effect of four important parameters, namely, POZ/Im ratio (1:1 and 5:1), Im concentration (1, 3, and 5 wt %), POZ structure (pendant group type: ethyl, propyl, pentyl, and phenyl), and POZ molar mass (1K, 2K, and 5K), on the thermal latency behavior of the prepared OCERs. These parameters are discussed below in the order of importance of their effect on thermal latency.

Effect of POZ/Im Ratio on Curing Behavior of Prepared OCERs. Tables 2 and 3 show the data for the OCERs containing the POZ/Im 1:1 TLCs and POZ/Im 5:1 TLCs, respectively. This section discusses the results in terms of the POZ/Im ratio. The effect of other parameters is discussed in the relevant sections below based on the data presented in Tables 1−3. When the data was analyzed for two POZ/Im ratios of 1:1 and 5:1 by keeping all other parameters the same, it was observed that an increase in the POZ/Im ratio from 1:1 to 5:1 resulted in an upward shift in left-limit temperatures of curing meaning that as the amount of POZ increased with respect to Im, there was a latency in curing. This behavior was observed at all Im concentrations with all polymer types and molar masses. For instance, when the left-limit temperatures of PEOZ 1K-Im 1:1 1% in Table 2 were compared with that of PEOZ 1K-Im 5:1 1% in Table 3, it was observed that there was a shift from 94.09 to 111.55 °C. When the polymer type, polymer molar mass, and Im concentration were changed, for example in the case of PPrOZ 5K-Im 3%, the left-limit temperatures of curing changed the same way as the previous example, from 70.98 to 87.17 °C. The analysis of all results showed that left-limit temperatures of curing shifted to higher values at temperature ranges of 7−29 °C for PEOZ, 9−47 °C for PPrOZ, 10−29 °C for PPeOZ, and 13−37 °C for PPhOZ

Table 2. Dynamic DSC Results of the OCERs Containing POZ/Im 1:1 TLCs

TLC	molar mass	Im/E (wt %)	Im-normalized enthalpy (J/g)	left limit temp (°C)	right limit temp (°C)
PEOZ-Im	1K	1%	145.97	94.09	196.03
		3%	400.46	85.80	194.64
		5%	445.12	78.79	185.87
	2K	1%	373.66	64.04	199.79
		3%	468.25	63.45	194.30
		5%	310.83	60.02	196.82
	5K	1%	194.54	84.49	194.92
		3%	307.08	60.17	154.65
		5%	362.80	57.86	190.70
PPrOZ-Im	1K	1%	329.70	72.46	196.45
		3%	449.18	82.99	196.19
		5%	474.58	70.12	179.71
	2K	1%	482.18	67.71	195.34
		3%	409.77	68.22	198.86
		5%	518.44	61.39	199.67
	5K	1%	213.90	77.90	198.66
		3%	479.59	70.98	194.45
		5%	423.04	50.89	198.99
PPeOZ-Im	1K	1%	286.61	69.50	193.27
		3%	505.81	60.14	200.34
		5%	634.67	54.46	196.38
	2K	1%	107.91	87.98	192.74
		3%	507.34	72.14	200.01
		5%	586.91	60.81	200.01
	5K	1%	276.51	76.52	192.41
		3%	475.32	61.02	200.08
		5%	674.39	56.89	198.53
PPhOZ-Im	1K	1%	268.11	57.10	197.96
		3%	218.05	66.02	199.84
		5%	435.81	58.62	198.98
	2K	1%	93.44	62.06	199.75
		3%	432.65	45.28	199.81
		5%	375.84	57.32	192.83
	5K	1%	183.70	66.21	191.53
		3%	447.16	57.03	198.88
		5%	417.54	60.56	199.77

Table 3. Dynamic DSC Results of the OCERs Containing POZ/Im 5:1 TLCs

TLC	molar mass (g/mol)	Im/E (wt %)	Im-normalized enthalpy (J/g)	left limit (°C)	right limit (°C)
PEOZ-Im	1K	1%	63.31	111.55	191.22
		3%	176.85	99.49	191.64
		5%	349.72	85.64	176.62
	2K	1%	45.08	93.48	195.13
		3%	73.53	101.69	184.52
		5%	143.62	95.33	176.58
	5K	1%	27.89	100.71	184.46
		3%	92.88	99.43	187.43
		5%	142.29	97.49	187.85
PPrOZ-Im	1K	1%	26.46	119.73	197.85
		3%	263.38	88.63	197.95
		5%	426.07	90.38	199.80
	2K	1%	62.28	77.61	193.18
		3%	142.40	66.27	199.86
		5%	279.20	61.20	199.82
	5K	1%	71.09	102.07	189.90
		3%	221.40	87.17	194.56
		5%	432.64	82.77	191.84
PPeOZ-Im	1K	1%	127.64	100.95	190.48
		3%	527.82	72.92	198.81
		5%	547.10	72.73	196.09
	2K	1%	124.00	98.13	195.02
		3%	349.70	83.67	199.18
		5%	544.63	74.67	198.92
	5K	1%	111.08	93.28	189.80
		3%	136.64	93.16	196.36
		5%	259.89	90.10	199.88
PPhOZ-Im	1K	1%	118.44	88.40	195.11
		3%	277.24	75.19	199.90
		5%	356.98	73.64	199.95
	2K	1%	36.50	89.37	182.72
		3%	215.49	81.48	199.87
		5%	289.48	78.96	199.54
	5K	1%	107.39	78.90	198.86
		3%	143.43	69.70	189.81
		5%	293.33	69.58	196.26

polymers in comparison to the left-limit temperatures of curing of DGEBA-Im mixtures.

Figure 3 shows the DSC thermograms and conversion curves of DGEBA-Im 1%, POZ HP 1K-Im 1:1 1% (a1, a2), and POZ HP 1K-Im 5:1 1% (b1, b2). The observations provided for Tables 1−3 are more clearly seen in these thermograms and conversion curves.

Effect of Imidazole Concentration on Curing Behavior of Prepared OCERs. Dynamic DSC results of the OCERs containing POZ-Im TLCs at 1, 3, and 5 wt % Im concentrations (shown in Tables 2 and 3) indicated that as the Im concentration increased, the left-limit temperature (the lowest temperature at which an exothermic heat flow is greater than the limit of detection of the DSC instrument[34]) values decreased irrespective of the HP: Im ratio, polymer type, and polymer molar mass. To illustrate this with examples, dynamic DSC results of PEOZ 1K-Im 1:1 at 1, 3, and 5 wt % Im concentrations were examined (Table 2). The left-limit temperatures were found to be 94.09, 85.80, and 78.79 °C, respectively. Additionally, left-limit temperatures for PPrOZ 5K-Im 5:1 at 1, 3, and 5 wt % Im concentrations were found to

be 102.07, 87.17, and 82.77 °C, respectively. As a general trend, the higher left limit temperatures of both POZ:Im of 1:1 and 5:1 samples were obtained at 1 wt % Im concentration. As Im concentration increases from 1 to 5 wt % the amount of free Im increases, which results in an increase in enthalpy of curing and a decrease in the left limit temperature of curing.

Effect of POZ Pendant Group on Curing Behavior of Prepared OCERs. Dynamic DSC results of the OCERs containing POZ: Im 1:1 TLCs and POZ: Im 5:1 TLCs at 1, 3, and 5 wt % Im concentrations were also examined to investigate the effects of pendant group type of homopolymers on the curing behavior of OCERs. When the data was analyzed for all POZ: Im ratios of 1:1 and 5:1 at the same Im concentration (shown in Figure 4 and Tables 2 and 3), it was observed that the miscibility of the polymer matrix with DGEBA significantly affects the curing behavior of the OCERs with the TLCs. The higher miscibility causes a decreasing trend in the left-limit temperature values. The samples with 2-phenyl and 2-pentyl pendant groups have lower left limit temperatures of curing compared to the samples with 2-ethyl and 2-propyl pendant groups. This behavior may be associated
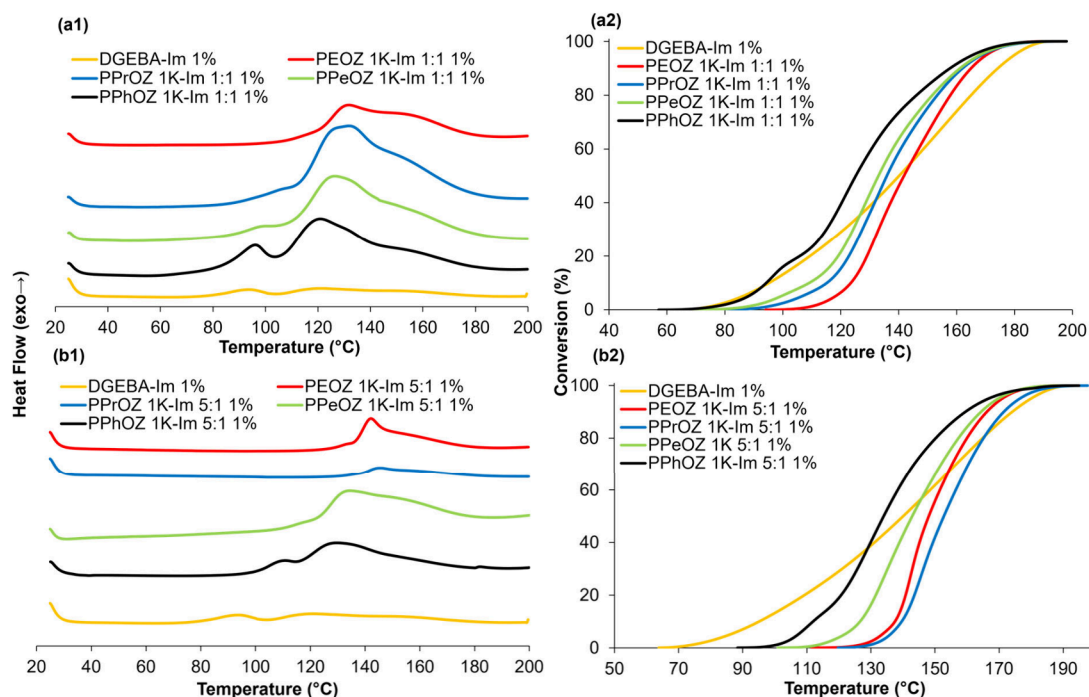
Figure 3. DSC thermograms and conversion curves of POZ HP 1K-Im 1:1 1% (a1, a2) and POZ HP 1K-Im 5:1 1% (b1, b2) (heating rate: 10 °C/min).
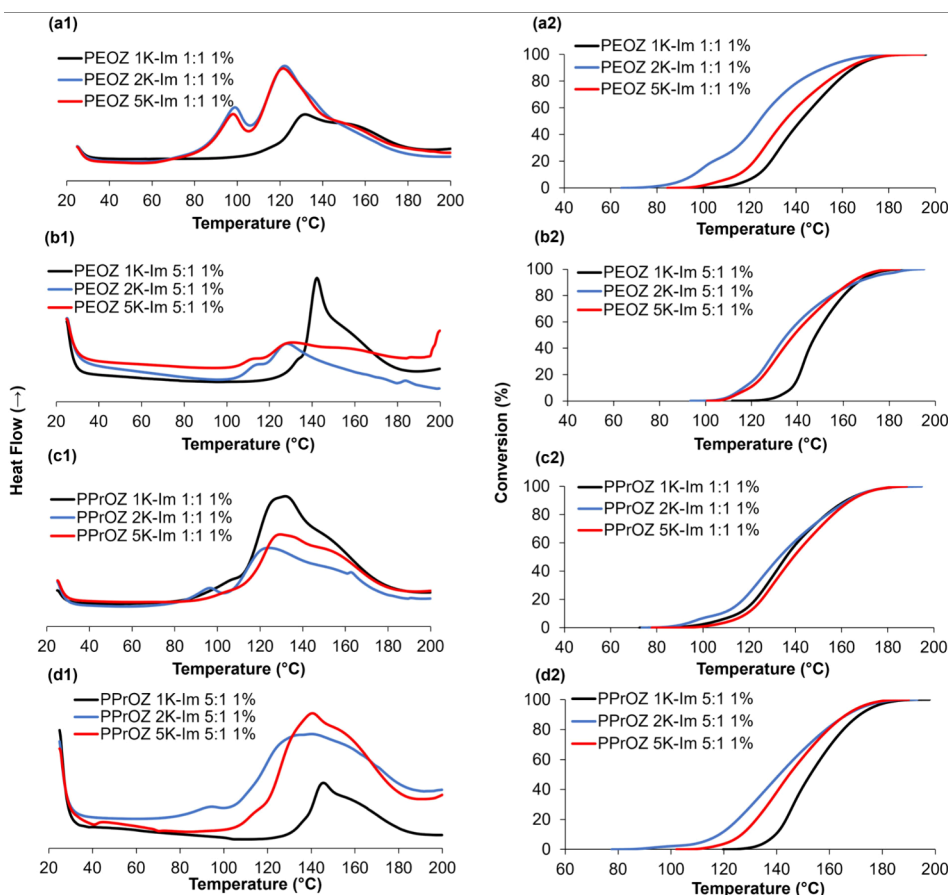

Figure 4. DSC thermograms and conversion curves for DGEBA-PEOZ-1K-Im ((a1, a2), (b1, b2)) and DGEBA-PPrOZ 1K-Im OCERs ((c1, c2), (d1, d2)) (heating rate: 10 °C/min).

with the miscibility of these polymers with DGEBA resulting in an accelerated release of Im from the HP-Im complex, which

can be related to the interactions of the 2-phenyl and 2-pentyl group with the aromatic groups of DGEBA. For the polymers
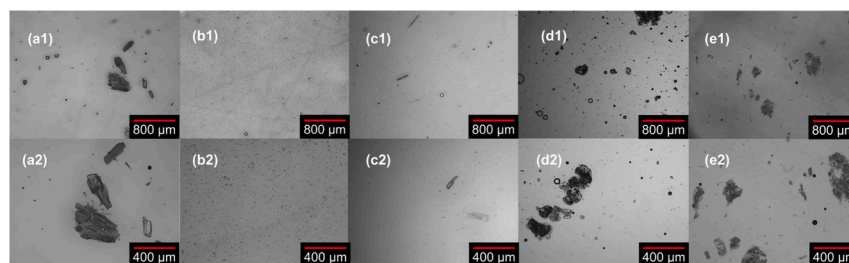
Figure 5. Optical microscopy images of (a) DGEBA-Im 1%, (b) PEOZ 1K-Im 1:1 1%, (c) PPrOZ 1K-Im 1:1 1%, (d) PPeOZ 1K-Im 1:1 1%, and (e) PPhOZ 1K-Im 1:1 1%.

with aliphatic pendant groups such as 2-ethyl, 2-propyl, and 2-pentyl, the homopolymers with 2-pentyl groups have higher miscibility with the resin. Thus, the left limit temperature values are in the following order for the pendant groups: 2-phenyl< 2-pentyl <2-propyl <2-ethyl. For instance, left limit temperatures of the PEOZ-Im 1:1 1% (94.09 °C), PPrOZ-Im 1:1 1% (72.46 °C), PPeOZ-Im 1:1 1% (69.50 °C), and PPhOZ-Im 1:1 1% (57.10 °C) indicated that PPhOZ exhibited a faster release of Im compared to PPeOZ, PPrOZ, and PEOZ, respectively. This trend was observed for all OCERs. In addition, better miscibility between PEOZ and PPrOZ polymers and Im can be assumed since these homopolymers and Im have hydrophilic characteristics. However, since other homopolymers, PPeOZ and PPhOZ are hydrophobic, immiscibility between these polymers and Im were observed. Due to the compatibility between different homopolymers and Im, the dispersion quality of Im in POZ differs. Im is well dispersed in PEOZ and PPrOZ while not in others. Therefore, PEOZ-Im and PPrOZ-Im TLCs can be dispersed well in DGEBA and the immiscibility of Im with DGEBA can provide latency, whereas Im in other polymers behaves like virgin Im, thus, their left limit temperatures of curing are lower. Miscibility/immiscibility behavior of the TLCs are examined in detail in the Optical Microscopy Images section.

Effect of POZ Molar Mass on Curing Behavior of Prepared OCERs. To examine the effect of the molar mass of POZ homopolymers on the curing behavior of OCERs, dynamic DSC analyses were performed. DSC thermograms and conversion curves are shown in SI, Figures S2−S12. Since the samples of different molar masses were prepared with the same weight of the polymer, homopolymers with a molar mass of 1K were expected to provide a higher molar content of −OH end groups. Thus, the lower molar mass leads to a higher interaction between the −OH and Im making the release of Im slower and the left limit temperatures to shift to higher temperatures. For instance, OCERs containing PEOZ 1K, 2K, and 5K polymers at 1:1 HP/Im ratio and 1% Im concentration had left limit temperatures of 94.09, 64.04, and 84.49 °C, respectively. This general trend shows that 1K samples have higher left limit temperatures compared to those of other molar mass polymers at the same Im ratio. On the other hand, for 5K polymers, the polymer matrix with longer backbones provides the opportunity for the entrapment of Im in the polymer matrix regardless of the protonation. Homopolymers with 2K molar mass exhibit unsatisfactory behavior in terms of shifting the left limit temperatures of curing to higher values. This behavior is also valid for most of the PPrOZ, PPeOZ and PPhOZ-based TLCs.

Considering the obtained data, it was concluded that PEOZ 1K-Im 1:1 1%, PEOZ 1K-Im 5:1 1%, PPrOZ 1K-Im 1:1 1%

and PPrOZ 1K-Im 5:1 1% OCERs provide more latency compared to the other OCERs. Thus, four promising candidates among 72 HP-Im complexes were selected, and related results are shown in Figure 4.

Further investigations, including the miscibility studies of prepared TLCs with DGEBA and their long-term stability at different temperatures, were carried out using these four candidates. Although the left limit temperature values of the 5:1 samples have higher values among the two selected data sets, the 1:1 samples were also chosen to make a reliable comparison between the prepared systems. In addition, the enthalpy values of 5:1 samples are lower than those of 1:1 samples at the same Im concentration owing to the lower amount of free Im in the HP-Im complex leading to the insufficient introduction of Im to the curing reaction and lower enthalpy values.

Optical Microscope Images. Optical microscopy imaging was conducted to investigate the behavior of the DGEBA-Im 1% and the POZ 1K based OCERs. Figure 5(a1),(a2) shows that hydrophilic Im fragments stay as bulky pieces inside the hydrophobic DGEBA resin when no polymer is involved. This results in a heterogeneous mixture of DGEBA and Im with Im being localized in numerous spots. The same trend can also be seen in PPeOZ 1K 1:1 1% and PPhOZ 1K 1:1 1% OCERs where big chunks of polymer-Im complexes are scattered throughout DGEBA. This trend arises from the better affinity of these polymers for DGEBA due to their high hydrophobicity and impedes the microencapsulation between polymer and Im resulting in polymer-Im complexes staying as big fragments. Heterogeneity of these samples has resulted in localized curing and decreased enthalpy of curing. The heterogeneous distribution seen in PPeOZ 1K-Im 1:1 1% and PPhOZ 1K-Im 1:1 1% OCERs is replaced with well-dispersed microcapsules in PEOZ 1K-Im 1:1 1% and PPrOZ 1K-Im 1:1 1% OCERs without aggregates. The entrapment of Im in the polymer matrix has led to the formation of microcapsules with PEOZ 1K-Im 1:1 1% OCERs as PEOZ is the most hydrophilic polymer among the studied polymers. The average diameter of the microcapsules was measured by ImageJ software to be 4.26 μm for the PEOZ 1K-Im 1:1 1% sample. This micro-encapsulation shows itself in the curing studies as a higher left limit temperature of curing and a higher curing enthalpy, meaning that it provides latency in the curing reaction and fine distribution of the curing agent in the epoxy resin.

Also, to study the effect of the HP: Im on the microencapsulation, a comparison of four chosen OCERs was performed, which is shown in Figure 6. The images for PEOZ 1K-Im 5:1 1% and PPrOZ 1K-Im 5:1 1% (Figure 6(b1), (b2)) show a higher density of microcapsules in comparison with their 1:1 counterparts. This, in turn, increases the left
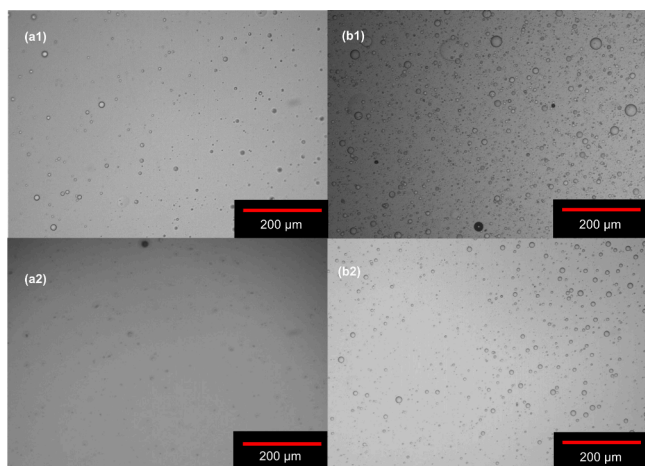
Figure 6. Optical microscopy images of (a1) PEOZ 1K-Im 1:1 1%, (a2) PPrOZ 1K-Im1:1 1%, (b1) PEOZ 1K-Im 5:1 1%, and (b2) PPrOZ 1K-Im 5:1 1%.

limit temperatures of curing but decreases Im-normalized enthalpy, which may be due to the slower release of Im as a consequence of higher amounts of polymer. The observed curing latency in OCERs containing PEOZ- and PPrOZ-based TLCs can be attributed to the efficient microencapsulation of Im. Since inefficient microencapsulation of Im in PPhOZ- and PPeOZ-based OCERs is observed, these TLCs fall short of providing any significant latency in return.

Isothermal DSC Results. To investigate the stability of the TLC systems, isothermal DSC tests were carried out for DGEBA-Im 1% and the four chosen OCERs. The isothermal DSC tests were carried out at 70, 90, and 110 °C based on the left limit temperatures of curing of the chosen OCERs. The curves for DGEBA-Im 1% and the chosen OCERs are shown in Figure 7.

After the isothermal DSC test, the dynamic DSC tests were performed from 25 to 250 °C at a heating rate of 10 °C/min to determine the residual enthalpy of curing. The enthalpy values both for the isothermal DSC step and the following dynamic DSC step are shown in Table 4. Examining the results for all temperatures, OCERs with chosen TLCs provide latency in comparison to the DGEBA-Im 1% sample. This latency can be seen as a shift in the characteristic double-peak of Im curing to the right for all of the OCERs. The biggest shift belongs to the PEOZ 1K-Im 5:1 1% sample at all temperatures with PPrOZ 1K-Im 5:1 1%, PEOZ 1K-Im 1:1 1% and PPrOZ 1K-Im 1:1 1% having smaller shifts, respectively. It is also worth noting that at lower temperatures, the peaks expand over longer time intervals. This expansion is also more distinct in the PEOZ 1K-Im 5:1 1% sample.

The enthalpy values show an increasing trend for DGEBA-Im samples as the temperature is increased from 70 to 110 °C and the opposite is true for residual enthalpies. However, for OCERs there is an increase in enthalpy from 70 to 90 °C and a subsequent decrease from 90 to 110 °C. This again may be due to the kinetics of Im release in DGEBA. At high temperatures, Im seems to be cured before full diffusion into DGEBA and subsequent local curing makes diffusion harder for unreacted Im resulting in decreased enthalpy of curing. A decreasing trend is also observed for residual enthalpies of TLC systems the same as DGEBA-Im samples. Higher enthalpy values are seen in PPrOZ 1K-Im 1:1 1% and PEOZ 1K-Im 1:1 1%

samples at all temperatures in comparison to DGEBA-Im. Taking the optical microscope images into account, this is due to a homogeneous distribution of Im throughout DGEBA realized by the polymers. However, they do not provide high stability at lower temperatures, as opposed to 5:1 samples. PEOZ 1K-Im 5:1 1% when compared to PPrOZ 1K-Im 5:1 1% shows higher stability at 70 °C, with an enthalpy of 151.10 J/g in contrast to an enthalpy of 198.46 J/g for PPrOZ 1K-Im 5:1 1K 1%. PEOZ 1K-Im 5:1 1% OCER showing higher stability and latency can be attributed to the higher −OH to Im ratio present in 1K samples and to the microencapsulation of Im taking place in the presence of a hydrophilic polymer such as PEOZ.

To examine the stability of Im 1% and prepared OCERs, four different samples were prepared and stored at room temperature. Since PEOZ 1K-Im 5:1 1% provides better latency according to Table 4, PEOZ 1K-Im 5:1 1% was selected for long-term stability tests among the prepared OCERs. Initial samples were tested upon mixing, while other samples were stored for 3 days under ambient conditions and analyzed. Dynamic DSC analysis was performed to investigate the long-term stability by following the enthalpy changes. Figure 8 shows the results of the stability analysis. When the stability results are examined, the curing enthalpies of the samples at the initial state have higher values than 3 days samples. As the curing reactions progress, Im starts to form a cross-linked structure, thus a reduction in curing enthalpies is observed. When Im 1% and PEOZ 1K-Im 5:1 1% were examined, it was observed that the decrease in the curing enthalpy of PEOZ 1K-Im 5:1 1% was less than that of Im 1%. Based on this result, it can be concluded that OCER containing PEOZ 1K-Im 5:1 1% was more stable than Im 1%.

Rheology Results and Shelf Life Estimation. The stability was also examined by time sweep rheology analyses conducted at 50 °C (18 h), 60 °C (6 h), and 70 °C (6 h) for PEOZ 1K-Im 5:1 1% and DGEBA-Im samples. As can be seen in Figure 9, at 60 and 70 °C PEOZ 1K-Im 5:1 1% OCER showed higher stability in comparison to DGEBA-Im sample with an approximately one h difference in the rise of viscosity. At 50 °C, the DGEBA-Im sample showed a slow increase in the viscosity starting after 100 min. However, PEOZ 1K-Im 5:1 1% OCER exhibited stability up to a 360 min time frame with little to no change in the measured viscosity. Comparing the slope of increase in the viscosity between these samples, it can be inferred that the rate of curing for the DGEBA-Im sample is affected by the temperature. This shows itself as a less steep rise in viscosity at 50 °C compared to 60 and 70 °C. On the other hand, PEOZ 1K-Im 5:1 1% OCER showed the same slope of viscosity increase for 50 and 60 °C after the curing started. For 70 °C, the curing reaction seems to have a steeper increase in viscosity for PEOZ 1K-Im 5:1 1% OCER. This can be attributed to the microencapsulation of Im in PEOZ homopolymer, which inhibits the curing reaction for a certain time period and after this time interval as the microcapsules release the Im curing starts simultaneously at every region of the epoxy resin especially at lower temperatures. For the DGEBA-Im sample, with the chunky fragments of Im seen throughout the resin, the curing reaction proceeds rather slowly.

Shelf life is defined as the time it takes for the viscosity of OCER to double at room temperature. To estimate the shelf life of the chosen OCER at room temperature, the isothermal rheology data at 50, 60, and 70 °C were coupled with
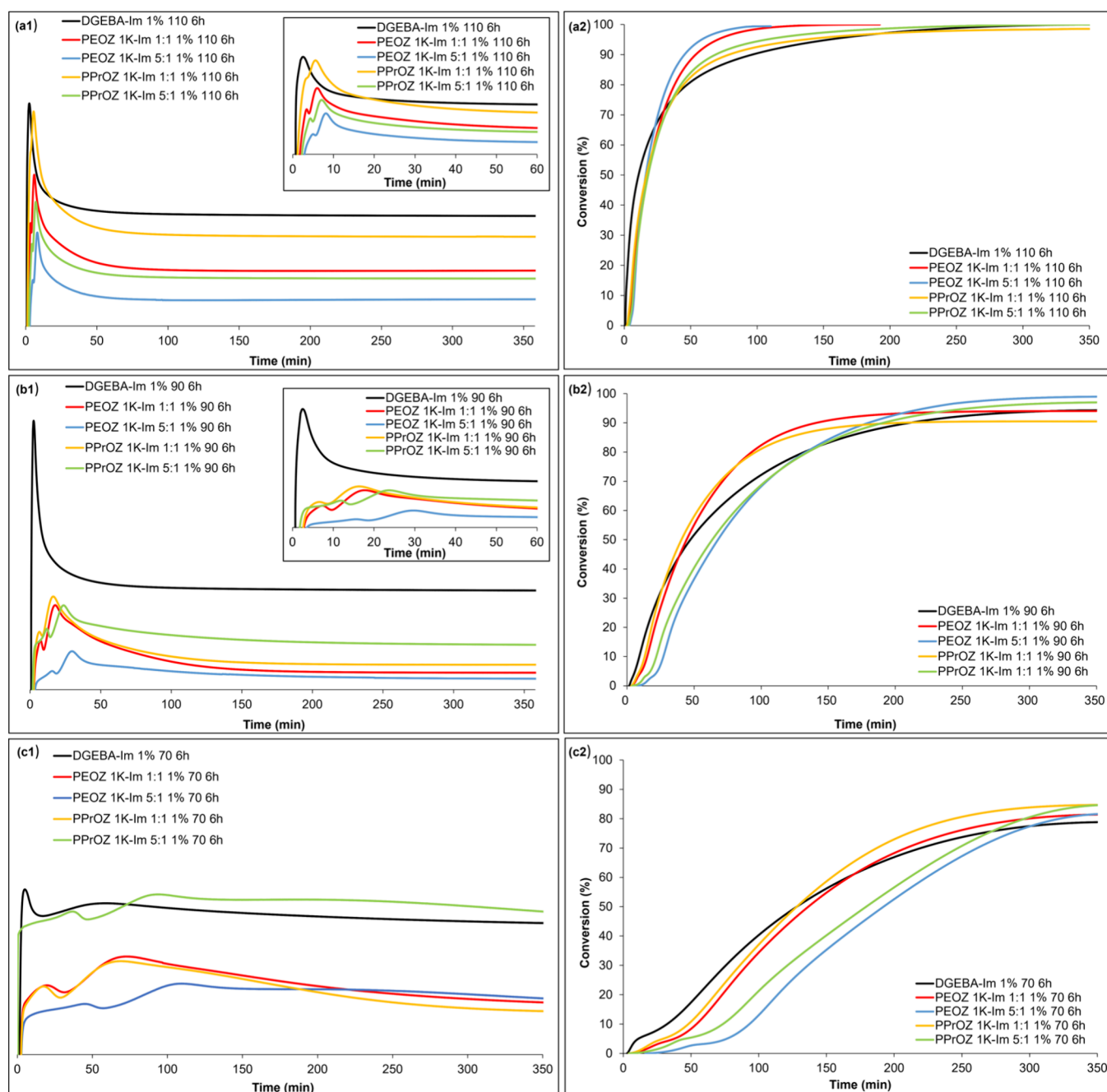
Figure 7. Isothermal DSC thermograms and conversion plots for DGEBA-Im, DGEBA-PEOZ-1K-Im, and DGEBA-PPrOZ-1K-Im systems at (a1, a2) 110 °C, (b1, b2) 90 °C, and (c1, c2) 70 °C.

isothermal DSC results at the same temperatures for this sample. The isothermal DSC results at 50 and 60 °C are given in Figure S13 and Table S7. The conversions corresponding to the time for the complex viscosity to double were found in the isothermal DSC curves. The kinetics of epoxy curing with imidazole were assumed to be of first-order. Using the Arrhenius equation, rate constant values (k) at different temperatures were determined. By plotting the ln k values against $1/T$ and using the linear regression for 50, 60, and 70 °C, k values for −20, 0, and 20 °C were predicted. For conversion at lower temperatures, an average of conversions at 50, 60, and 70 °C was used, and eventually, time required to reach this conversion (shelf life) was determined. The shelf life of PEOZ 1K-Im 5:1 1% OCER was found to be 15.3, 297.7,

and 9191.7 days at 20, 0, and −20 °C respectively. The equations used for predicting shelf life and the corresponding graph are given in detail in SI, Section 7.

Characterization of Cured PEOZ 1K-Im 5:1 1% OCER. *Optical Properties.* As it can be seen in Figure 10a, the prepared mold was filled with the PEOZ 1K-Im 5:1 1% OCER. Optical image of the same sample exhibited a homogeneous distribution of microcapsules in epoxy resin (Figure 10b). After curing (Figure 10c), the sample had a thickness of 2.4 mm and showed a transparent brownish color, which can be attributed to environmental conditions (high temperature and presence of oxygen) of curing. The UV−vis-NIR spectra of the cured sample was measured (Figure 10d). In the visible range,

Table 4. Isothermal DSC and Dynamic DSC Enthalpy Values after Isothermal DSC Samples

| sample name	sample temp (°C)	normalized enthalpy during isothermal experiment (J/g)	residual enthalpy (J/g)
DGEBA-Im 1%	70	120.28	32.28
	90	177.23	10.68
	110	250.17	
PEOZ 1K-Im 1:1 1%	70	250.00	57.00
	90	371.00	23.50
	110	263.00	
PEOZ 1K-Im 5:1 1%	70	151.10	33.89
	90	177.17	1.88
	110	165.71	0.95
PPrOZ 1K-Im 1:1 1%	70	289.85	52.39
	90	324.77	34.15
	110	343.39	5.04
PPrOZ 1K-Im 5:1 1%	70	198.46	35.86
	90	250.77	7.77
	110	204.79	
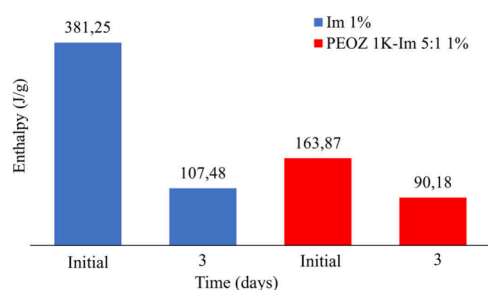
Figure 8. Enthalpy values of DGEBA-Im 1% and PEOZ 1K-Im 5:1 1% samples upon mixing and after 3 days of storage at room temperature.

the sample showed a maximum transmittance of 30% at 700 nm and no transmittance at 380 nm.

Thermomechanical Properties. Dynamic mechanical analysis (DMA) was performed to measure and analyze different mechanical properties of cured PEOZ 1K-Im 5:1 1% OCER, in terms of the storage modulus (E'), loss modulus (E''), and the tan δ. tan δ was obtained from the ratio of the loss to storage
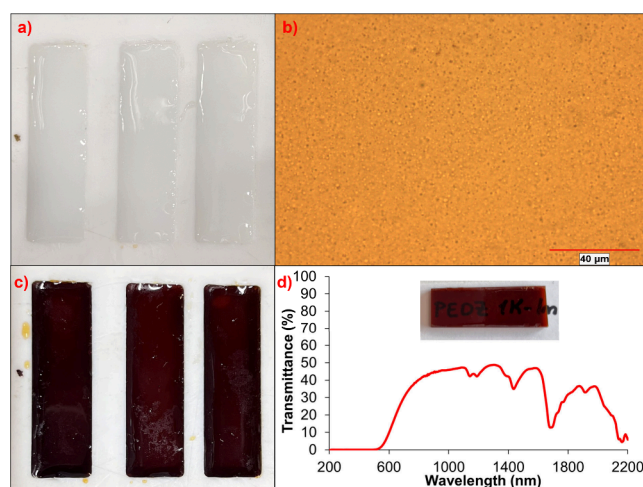
Figure 10. Image of the mold before curing of PEOZ 1K-Im 5:1 1% OCER (a), the corresponding optical image for this sample (b), the image of the mold after curing (c), and the UV−vis-NIR spectra of the cured sample (d).

modulus. Figure 11a shows the DMA results of cured PEOZ 1K-Im 5:1 1% OCER. As the temperature increases, E' typically starts to decline after 57 °C and reaches a minimum at 176 °C. This behavior is generally characteristic of the material that reaches the region of the glass−rubber transition. Thus, DMA was also utilized for the T_g assignment of cured PEOZ 1K-Im 5:1 1% OCER. Different criteria can be selected to analyze the T_g value, such as the onset and offset of the E' peak, the half-height of the E' step, the location of the E'' peak, and the position of the tan δ peak. The E'' peak is often considered the best option for determining the T_g.[35] Using this information, the T_g values of the cured PEOZ 1K-Im 5:1 1% OCER were obtained as follows according to the different criteria: the onset of the E' and the half height of the E'' peak are 57°C and 69.35 °C, respectively. The tan δ peak is observed at higher temperatures compared to the other criteria. As seen from Figure 11b, dynamic DSC result also shows a T_g within an onset at 58 °C and midpoint at 70.37 °C for the cured PEOZ 1K-Im 5:1 1% OCER, which validates the results of the DMA.
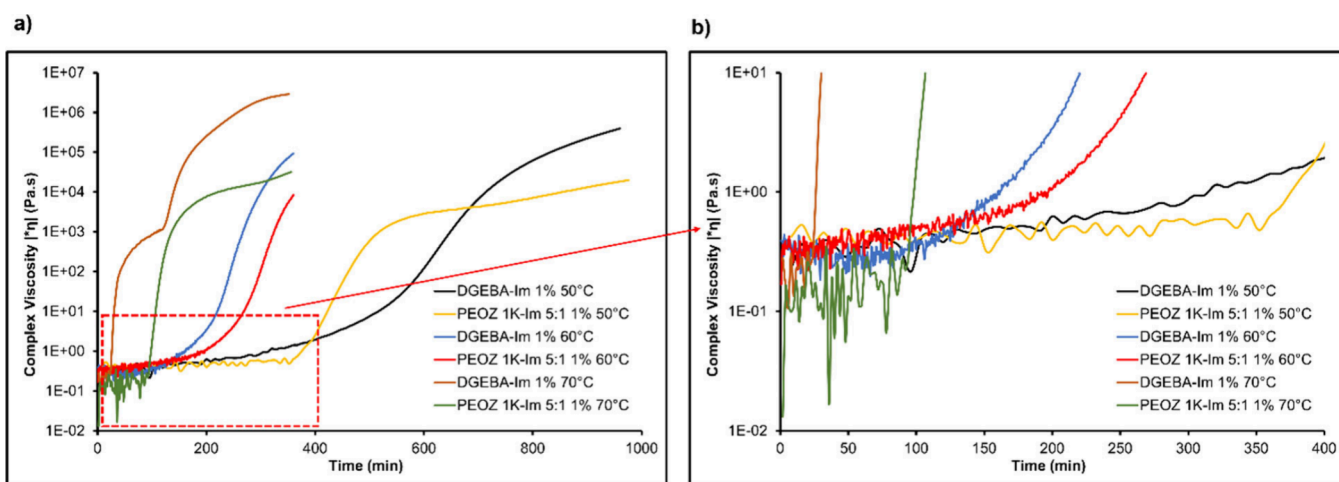
Figure 9. Rheological data for DGEBA-Im 1% and PEOZ 1K-Im 5:1 1% at 50, 60, and 70 °C (a), a magnified view of a specific region within (a) is shown in (b).
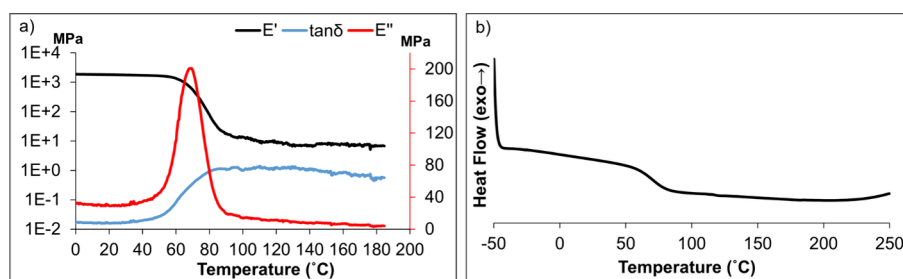
Figure 11. (a) E', E'', and tan δ of cured PEOZ 1K-Im 5:1 1% OCER as a function of temperature, and (b) dynamic DSC result of the same sample.

CONCLUSIONS

OCERs were prepared using newly developed POZ-Im TLCs and DGEBA. Dynamic DSC analysis demonstrated that the curing behavior of the OCERs was influenced by Im concentration, HP:Im ratio, POZ molar mass, and pendant group type. Higher concentrations of HP-Im TLCs in the resin led to lower left limit temperatures and higher enthalpy values, likely due to increased free Im and local exothermic curing reactions. Increasing the HP:Im molar ratio resulted in higher left limit temperatures, with OCERs containing POZ-Im 1:1 TLCs exhibiting greater enthalpies compared to those with POZ-Im 5:1 TLCs due to slower and incomplete Im release. Lower POZ molar mass increased the molar content of hydroxyl end groups, increasing the interaction between these groups and Im, consequently slowing Im release and increasing the left limit temperatures. Optical microscopy revealed superior Im encapsulation in hydrophilic PEOZ and PPrOZ compared to hydrophobic PPeOZ and PPhOZ. Increasing hydrophobicity of the homopolymers resulted in better miscibility of the polymer with DGEBA, decreasing the left limit temperatures. Additionally, PEOZ-Im TLCs exhibited improved thermal latency, supported by stability studies using DSC and a rheometer, confirming their superior performance compared to Im alone. After the screening of the curing behaviors for POZ-based TLCs, the stability of the selected PEOZ 1K-Im 5:1 1% OCER was investigated using isothermal DSC and rheology analysis at 50, 60, and 70 °C. Furthermore, the shelf life of this sample was predicted at −20, 0, and 20 °C. The sample was estimated to have a shelf life of 15.3 days at 20 °C. The mechanical and thermal properties of the said OCER were also examined using DMA and dynamic DSC. From the DMA results, the E', E'', and T_g values were obtained. Subsequently, the T_g value obtained from the dynamic DSC test conformed with the DMA results. Overall, PEOZ HP-Im TLCs show promise as effective thermal latent curing agents for OCERs, owing to their straightforward synthesis and excellent performance.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c03904.

> Synthesis conditions of homopolymers, characterization results of homopolymers, the curing data of 2K and 5K TLCs, and shelf life estimations (PDF)

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■ REFERENCES

(1) Abdellaoui, H.; Raji, M.; Bouhfid, R.; Qaiss, A. E. Investigation of the deformation behavior of epoxy-based composite materials. *Failure Analysis in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*; Woodhead Publishing, 2019; pp 29−49.

(2) Zhao, X.; Huang, Z.; Song, P.; Yang, H.; Zhang, Y. Curing kinetics and mechanical properties of fast curing epoxy resins with isophorone diamine and N-(3-aminopropyl)-imidazole. *J. Appl. Polym. Sci.* **2019**, *136* (37), 1−10.

(3) Mohan, P. A Critical Review: The Modification, Properties, and Applications of Epoxy Resins. *Polym. - Plast. Technol. Eng.* **2013**, *52* (2), 107−125.

(4) Dagdag, O.; El Harfi, A.; Essamri, A.; El Gouri, M.; Chraibi, S.; Assouag, M.; Benzidia, B.; Hamed, O.; Lgaz, H.; Jodeh, S. Phosphorous-based epoxy resin composition as an effective anticorrosive coating for steel. *Int. J. Ind. Chem.* **2018**, *9* (3), 231−240.

(5) Teh, P. L.; Mariatti, M.; Akil, H. M.; Yeoh, C. K.; Seetharamu, K. N.; Wagiman, A. N. R.; Beh, K. S. The properties of epoxy resin coated silica fillers composites. *Mater. Lett.* **2007**, *61* (11−12), 2156−2158.

(6) Jeon, H. R.; Park, J. H.; Shon, M. Y. Corrosion protection by epoxy coating containing multi-walled carbon nanotubes. *J. Ind. Eng. Chem.* **2013**, *19* (3), 849−853.

(7) Haddadi, S. A.; Kohlan, T. B.; Momeni, S.; Ramazani, S.A.A.; Mahdavian, M. Synthesis and application of mesoporous carbon nanospheres containing walnut extract for fabrication of active protective epoxy coatings. *Prog. Org. Coatings* **2019**, *133*, 206−219.

(8) Wright, C. D.; Muggee, J. M. Epoxy Structural Adhesives. *Struct. Adhes.* **1986**, 113−179.

(9) Shin, P. S.; Kwon, D. J.; Kim, J. H.; Lee, S. Il; DeVries, K. L.; Park, J. M. Interfacial properties and water resistance of epoxy and CNT-epoxy adhesives on GFRP composites. *Compos. Sci. Technol.* **2017**, *142*, 98−106.

(10) Ahmadi, Z. Nanostructured epoxy adhesives: A review. *Prog. Org. Coatings* **2019**, *135* (June), 449−453.

(11) Lu, D. D.; Wong, C. P. Materials for advanced packaging. *Mater. Adv. Packag.* **2009**, 1−719.

(12) Olberg, R. C. The Effects of Epoxy Encapsulant Composition on Semiconductor Device Stability. *J. Electrochem. Soc.* **1971**, *118* (1), 129.

(13) Ryu, J. H.; Choi, K. S.; Kim, W. G. Latent catalyst effects in halogen-free epoxy molding compounds for semiconductor encapsulation. *J. Appl. Polym. Sci.* **2005**, *96* (6), 2287−2299.

(14) Pulikkalparambil, H.; Rangappa, S. M. Manufacturing Methods for Fabrication of Epoxy Composites. *Epoxy Composites: Fabrication, Characterization and Applications*; Wiley, 2021, section 1.2.

(15) Saba, N.; Jawaid, M. Epoxy resin based hybrid polymer composites. *Hybrid Polymer Composite Materials*; Elsevier Ltd., 2017; section 3, pp 57−82. DOI: 10.1016/B978-0-08-100787-7.00003-2.

(16) Pham, H. Q.; Marks, M. J. Epoxy Resins. *İçinde Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005. DOI: 10.1002/14356007.a09_547.pub2.

(17) Arimitsu, K.; Fuse, S.; Kudo, K.; Furutani, M. Imidazole derivatives as latent curing agents for epoxy thermosetting resins. *Mater. Lett.* **2015**, *161*, 408−410.

(18) Pascault, J. P.; Williams, R. J. J. General Concepts about Epoxy Polymers. *Epoxy Polym. New Mater. Innov.* **2010**, 1−12.

(19) Ooi, S. K.; Cook, W. D.; Simon, G. P.; Such, C. H. DSC studies of the curing mechanisms and kinetics of DGEBA using imidazole curing agents. *Polymer (Guildf).* **2000**, *41* (10), 3639−3649.

(20) Tomuta, A. M.; Ramis, X.; Ferrando, F.; Serra, A. The use of dihydrazides as latent curing agents in diglycidyl ether of bisphenol A coatings. *Prog. Org. Coatings* **2012**, *74* (1), 59−66.

(21) Antelmann; et al. Use of Urea Derivatives as Accelearators for Epoxy Resins. U.S. Patent US 2007/0027274 A1, 2007.

(22) Lal; et al. One Component Epoxy Curing Agents Comprising Hydroxyalkylamino Cycloalkanes. U.S. Patent 20170342197, 2017.

(23) Xu, Y. J.; Wang, J.; Tan, Y.; Qi, M.; Chen, L.; Wang, Y. Z. A novel and feasible approach for one-pack flame-retardant epoxy resin with long pot life and fast curing. *Chem. Eng. J.* **2018**, *337* (October 2017), 30−39.

(24) Johnson, C. K. Latent Curing Epoxy Compositions Containing a Crystalline Polyphenate Salt of a Polyamine and 2,4,4-Trimethyl-2,4,7-Trihydroxyflavan. U.S. Patent 3,519,576, 1966.

(25) Chen, K. L.; Shen, Y. H.; Yeh, M. Y.; Wong, F. F. Complexes of imidazole with poly(ethylene glycol)s as the thermal latency catalysts for epoxy-phenolic resins. *J. Taiwan Inst. Chem. Eng.* **2012**, *43* (2), 306−312.

(26) Li, C.; Tan, J.; Gu, J.; Xue, Y.; Qiao, L.; Zhang, Q. Facile synthesis of imidazole microcapsules via thiol-click chemistry and their application as thermally latent curing agent for epoxy resins. *Compos. Sci. Technol.* **2017**, *142*, 198−206.

(27) Zhang, S.; Yang, P.; Bai, Y.; Zhou, T.; Zhu, R.; Gu, Y. Polybenzoxazines: Thermal Responsiveness of Hydrogen Bonds and Application as Latent Curing Agents for Thermosetting Resins. *ACS Omega* **2017**, *2* (4), 1529−1534.

(28) Yen, W. P.; Chen, K. L.; Yeh, M. Y.; Uramaru, N.; Lin, H. Y.; Wong, F. F. Investigation of soluble PEG-imidazoles as the thermal latency catalysts for epoxy-phenolic resins. *J. Taiwan Inst. Chem. Eng.* **2016**, *59*, 98−105.

(29) Lowry, M. S.; Connell, E. M. O.; Vincent, J. L.; Goddard, R. J.; White, T. A.; Zheng, J.; Wong, R.; Bitler, S. P. Cure evaluation of Intelimer® latent curing agents for thermoset resin applications: One-component Formulations. Thermoset Resin Formulators Association Meeting, Chicago, Illinois, Sept 15−16, 2008, Air Products, 2008.

(30) Liu, Y.; Zhang, W.; Bao, L.; Xiao, A.; Pauls, S. P. Encapsulated Curing Agents. U.S. Patent PCT/US2011/028938, 2011.

(31) Shin, Y. J.; Shin, M. J.; Shin, J. S. Encapsulation of imidazole with synthesized copolymers for latent curing of epoxy resin. *Polym. Int.* **2017**, *66* (6), 795−802.

(32) Behroozi Kohlan, T.; Atespare, A. E.; Yildiz, M.; Menceloglu, Y. Z.; Unal, S.; Dizman, B. Amphiphilic Polyoxazoline Copolymer-Imidazole Complexes as Tailorable Thermal Latent Curing Agents for One-Component Epoxy Resins. *ACS Omega* **2023**, *8* (49), 47173−47186.

(33) Sahin, Z. M.; Kohlan, T. B.; Atespare, A. E.; Yildiz, M.; Unal, S.; Dizman, B. Polyoxazoline-modified graphene oxides with improved water and epoxy resin dispersibility and stability towards composite applications. *J. Appl. Polym. Sci.* **2022**, *139* (25), No. e52406.

(34) Green, S. P.; Wheelhouse, K. M.; Payne, A. D.; Hallett, J. P.; Miller, P. W.; Bull, J. A. On the Use of Differential Scanning Calorimetry for Thermal Hazard Assessment of New Chemistry: Avoiding Explosive Mistakes. *Angew. Chem.* **2020**, *132* (37), 15930−15934.

(35) Stark, W.; Jaunich, M.; McHugh, J. Dynamic Mechanical Analysis (DMA) of epoxy carbon-fibre prepregs partially cured in a discontinued autoclave analogue process. *Polym. Test.* **2015**, *41*, 140−148.