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Impact of Imidazolium-Based Ionic Liquids on the Curing Kinetics and Physicochemical Properties of Nascent Epoxy Resins

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ABSTRACT: We investigated the influence of anion type (salicylate, [(MOB)MIm][Sal], vs chloride, [(MOB)MIm][Cl]) of imidazolium-based ionic liquid (IL) and its content on the curing kinetics of bisphenol A diglycidyl ether (DGEBA of molecular weight $M_n = 340$ g/mol). Further physicochemical properties (i.e., glass transition temperature, $T_g$, and conductivity, $\sigma_{dc}$) of produced polymers were investigated. The polymerization of the studied systems was examined at various molar ratios (1:1, 10:1, and 20:1) at different reaction temperatures ($T_{reaction} = 353−383$ K) by using differential scanning calorimetry (DSC). Interestingly, both DGEBA/IL compositions studied herein revealed significantly different reaction kinetics and yielded materials of completely distinct physical properties. Surprisingly, in contrast to [(MOB)MIm][Cl], for the low concentration of [(MOB)MIm][Sal] in the reaction mixture, an additional step in the kinetic curves, likely due to the combined enhanced initiation activity of anion (salicylate)—cation (imidazolium-based), was noted. To thoroughly analyze the kinetics of all studied systems, including the two-step kinetics of DGEBA/[(MOB)MIm][Sal], we applied a new approach that relies on the combination of the two phenomenological Avrami equations. Analysis of the determined constant rates revealed that the reaction occurring in the presence of the salicylate anion is characterized by higher activation energy with respect to those with the chloride. Moreover, DGEBA/[(MOB)MIm][Sal] cured materials have higher $T_g$ in comparison to DGEBA polymerized with [(MOB)MIm][Cl] independent of the IL concentration. This fact might indicate that, most likely, the products of hardening are highly cross-linked (high $T_g$) or oligomeric linear polymers (low $T_g$) in the former and latter cases, respectively. Such a change in the chemical structure of the polymer is also reflected in the dc conductivity measured at the glass transition temperature, which is much higher for DGEBA cured with [(MOB)MIm][Cl]. Herein, we have clearly demonstrated that the type of anion has a crucial impact on the polymerization mechanism, kinetics, and properties of produced materials.

1. INTRODUCTION

Epoxy resins, due to their versatility, are one of the most important groups of thermosetting macromolecules. They are widely used, for example, in the marine and aerospace industry and allow to construct and develop electronic devices, coatings, paints, or adhesives.1−4 Such an impressive number of applications is caused by the fact that the final properties of these materials can be easily tuned by either optimization of the system composition or the curing protocol (choice of pressure, temperature, heating rate, or variation in the external parameters such as light irradiation and sonification).5−12 Consequently, solid-state polymers with well-defined mechanical characteristics, degree of cure, cross-linking density, glass transition temperature, adhesivity, thermal stability, moisture, corrosion, fungal, electric, and chemical resistance can be synthesized.13−15 Recently, a great effort has been made to obtain high-performance materials that link excellent thermomechanical properties with unique features like self-healing, shape memory, or high (superprotonic) conductivity.16−22 In particular, the last feature (conductivity) has attracted increasing attention since highly conductive materials can be used in the low- and intermediate-temperature fuel cell applications, reducing environmental pollution such as CO2 emission.23−25 To produce systems of enhanced conductivity, different strategies are adopted. Briefly, one can mention the synthesis of (i) conjugated polymers with unsaturated bonds such as poly(acetylene), poly(pyrrole), poly(thiophene), and poly(3,4-ethylenedioxythiophene),26,27 (ii) poly(ionic liquid)s (PILs),28,29 and (iii) composites consisting of, for example, doped or ionic liquid-based epoxy resins.22,30,31 Although all of the mentioned classes of polymers have many desired properties and benefits, it seems that because of its excellent...
versatility and general performance, the last group of materials seems to be extremely important and interesting.

It is well-known that epoxy-based conductive materials can be obtained via two different approaches: either direct polymerization with the ionic liquids (ILs) acting as monomers and/or hardening agents or the postmodification of produced classical nonconducting epoxy resins with different fillers (i.e., carbon fibers or nanotubes, graphene, metallic fillers, CPs, or nonreactive ILs). Consequently, we can obtain various conducting materials (polymers or composites) containing the ionic moieties (anions and cations) within the polymer network and therefore enforcing the different charge transport.

Herein, we investigated the influence of anion type (salicylate vs chloride) of imidazolium-based IL as well as its content on the curing kinetics and physicochemical properties (i.e., glass transition temperature, $T_g$ and conductivity, $\sigma_{dc}$) of a hardened bisphenol A diglycidyl ether (DGEBA of molecular weight $M_w = 340$ g/mol). For that purpose, two systems composed of DGEBA and [(MOB)MIm][Sal] (polymerizing system I, PS I) or [(MOB)MIm][Cl] (polymerizing system II, PS II) mixed at various molar ratios (1:1, 10:1, and 20:1) were prepared (see Scheme 1). The studied epoxy-based systems revealed significant differences in the reaction mechanism and thermoconducting properties of newly produced materials.

### 3. RESULTS AND DISCUSSION

The raw DSC data obtained upon the isothermal DSC experiments performed at the following temperatures, $T_{reaction} = 353–383$ K, are presented in Figure 1. For the PS I system ([(DGEBA)$_0$/[(MOB)MIm][Sal]]$_0 = 1:1$), a significant exothermic peak related to the formation of new covalent bonds between substrates, shifting toward shorter times with an increase in temperature, is observed in all cases (see Figure 1a). A similar situation was previously noted for the other systems. However, surprisingly, with a reducing concentration of [(MOB)MIm][Sal] in the curing mixture, one can note the presence of the two well-resolved peaks in the measured thermograms, most likely indicating the occurrence of an additional reaction step (Figure 1c). This effect was not detected for the 1:1 molar ratio mixture. Note that the same (two-peak) scenario can also be observed for [DGEBA]$0$/[(MOB)MIm][Sal]$_0 = 20:1$ (see Figure S2). On the other hand, for the PS II system (DGEBA/[(MOB)MIm][Cl]), a monomodal exothermic peak, whose maximum routinely shifts to the shorter times with increasing $T_{reaction}$, can be seen.
independently of the concentration of [(MOB)MIm][Cl]. A similar sharp monomodal exothermic peak was also previously reported for the curing of DGEBA with 1-(3-aminopropyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide (assigned as [apbim][NTf2]).33

Interestingly, both DGEBA/IL systems studied herein revealed a notable different curing characteristic. Thus, the following questions arise: Why does the two-step curing occur in the case of PS I with low IL concentration? Is it related to the type of used anion (salicylate)? Briefly, it is worthwhile to stress that the multistage reactions are often closely linked to the presence of some anions, dicyanamide [N(CN)2]42,43 thiocyanate [SCN],44 acetate [OAc],45 or phosphinate,5 as well as halogen anions (chloride, [Cl], or iodide, [I]),46,47 combined with the imidazole cation. Some insight into this issue provided investigations on the curing of epoxy—phenol resin with either 1,2,4- or 2,4-substituted imidazole derivatives, where authors postulated to link the existence of additional steps in thermograms with the formation of the exothermic adduct by the imidazole moiety.18–20 Nevertheless, one must remember that in both systems studied herein the imidazolium-based cation was applied, and reactions were performed at temperatures much lower with respect to those examined in ref 48. Thus, considering these facts, one can suppose that the explanation given by Heise et al.48–50 cannot be used to understand our data. Anyway, to test this possibility and rule out the possible thermal decomposition of ILs during curing, which might strongly affect the mechanism and character of this reaction,45 further DSC investigations were carried out. In Figure S1, we have presented thermograms collected upon heating of [(MOB)MIm][Sal] and [(MOB)-MIm][Cl] from room temperature up to T = 573 K. It was found that in the former and latter compound endothermal (T = 500 K) and exothermal (T = 490 K) processes indicating their possible thermal degradation are observed, respectively. However, it is important to note that these characteristic transitions are located much above temperatures at which isothermal curing of DGEBA with both ionic liquids was studied (T = 353–383 K). Hence, even though there might be some side reactions occurring within curing of an epoxy resin with ILs, which, as reported in the literature, might be triggered by the presence of bases, heating, and hydroxyl anions,42,51 their impact on the progress of curing is negligible or marginal.

Thus, to find out the origin of the peculiar curing kinetics in the system consisting of DGEBA and [(MOB)MIm][Sal], further experiments with the IL hardener possessing the quaternary ammonium cation (1-butoxymethyl-1-methyl)-trimethylammonium and salicylate anion (labeled as [(MOB)-N111][Sal]) were performed (see the inset in Figure 1c). The chemical structure of this ionic liquid is presented in Figure S3. Herein, it should be pointed out that, in contrast to the imidazolium-based cation, the [(MOB)N111] cation cannot initiate the curing process. Therefore, this simple experiment can be a direct evidence of the chemical activity of the salicylate anion once polymerization of DGEBA with [(MOB)-N111][Sal] is observed. In this context, it is worthwhile to add that salicylic acid, its derivatives (e.g., those containing halogen...
atoms) and salts, salicylates, are well-known accelerators applied for curing epoxy resins with amine-based hardeners. Their effectiveness with respect to the nonaccelerated as well as accelerated by phenols, triphenyl phosphate, or tertiary amines curing process has been documented in the previous reports. What is more, the presence of salicylic acid also has a direct influence on the structure of the obtained resins through modification of the curing mechanism. This involves, for example, a reduction of ether bonds produced during epoxy hardening, in relation to those formed by primary and secondary amines. However, simultaneously, the initiating activity of salicylates upon epoxy resin curing is much rarely investigated in the literature. As shown in the inset to Figure 1c for [DGEBA]0/[(MOB)N111][Sal]0 = 10:1, simple curing kinetics is observed upon the isothermal annealing at $T_{reaction} = 373$ K, contrary to the main panel of Figure 1c, which demonstrates the respective thermograms obtained for the [DGEBA]-[(MOB)MIm][Sal] composition at the same molar ratio that revealed bimodal kinetics. This clearly indicates that the peculiarity (double exothermic peak) found in the raw data presented in Figure 1c probably originates from the enhanced initiation properties of both the salicylate anion and the imidazolium-based cation. Note that the curing reaction of DGEBA with imidazolium-based ILs is generally a complex process comprising several different initiation pathways such as "carbene", "imidazole", and "counterion" routes.

To investigate the kinetics of the curing process, as first, we have determined the monomer conversion, $\alpha$, for the reactions performed at various temperatures for all systems studied herein. Although $\alpha$ can be estimated from many experimental techniques, i.e., nuclear magnetic resonance (NMR) as well as
Fourier transfer infrared (FTIR) and Raman spectrosopies,40,41,55 one of the most suitable and commonly applied methods for following the conversion of epoxy resin upon the curing process is DSC.39,56,57 Employing the well-established procedure, we estimated the calorimetric conversion, $\alpha_{\text{DSC}}$, from the following equation:

$$\alpha_{\text{DSC}} = \frac{\Delta H_{\text{(iso)}}}{\Delta H_{\text{total}}}$$ (1)

where $\Delta H_{\text{(iso)}}$ is the enthalpy change as a function of the polymerization time at a given temperature (isothermal measurements), while $\Delta H_{\text{total}}$ is the total enthalpy of the studied reaction determined to be a sum of enthalpies from isothermal, $\Delta H_{\text{(iso)}}$, and nonisothermal, $\Delta H_{\text{(non-isothermal)}}$ experiments. Therefore, to estimate $\alpha_{\text{DSC}}$, we have to calculate the value of $\Delta H_{\text{(non-isothermal)}}$. For that purpose, we performed additional dynamic (nonisothermal) DSC scans of isothermally polymerized samples. Representative nonisothermal DSC thermograms recorded for isothermally hardened (solid black lines) and fully cured systems (solid red lines) are presented in Figure 2a,b.

As illustrated in Figure 2a,b, all isothermally polymerized samples measured as a function of temperature revealed the presence of (i) the endothermic process, corresponding to the glass transition, and (ii) a huge exothermic peak that originated from the polymerization of unreacted monomer present in the system (solid black lines). On the other hand, the fully cured epoxy resins exhibited only one characteristic endothermic heat capacity jump ($T_g$) located at much higher temperatures with respect to those polymerized isothermally (solid red lines in Figure 2a,b). The evolutions of $T_g$ recorded before and after the nonisothermal measurements are presented in Figure 2c,d. Interestingly, in the case of the PS I system, $T_g$ of both isothermally and fully cured materials estimated for $[\text{DGEBA}]_0 / [(\text{MOB})\text{MIm}] [\text{Sal}]_0 = 1:1$ are much lower ($T_{g,\text{isotherm}} \sim 300 \text{ K}$ and $T_{g,\text{cured}} \sim 320 \text{ K}$) than those prepared with the smaller content of IL ($T_{g,\text{isotherm}} \sim 350 \text{ K}$ and $T_{g,\text{cured}} \sim 400 \text{ K}$, Figure 2c). However, they are significantly higher in relation to the second IL-based hardener ([MOB]MIm-Cl]). Note that $T_g$ of isothermally polymerized and cured DGEBA/[(MOB)MIm][Cl] systems reached $T_{g,\text{isotherm}} \sim 260 \text{ K}$, and $T_{g,\text{cured}} \sim 350 \text{ K}$, respectively (see Figure 2d). This might indicate that, most likely, the DGEBA/[(MOB)MIm]-[Sal] products are highly cross-linked polymers (high $T_g$), while hardening of the second system yields oligomeric linear polymers (low $T_g$). Moreover, it should be pointed out that all isothermally polymerized systems exhibit lower $T_g$ values than the reaction temperature irrespective of the applied IL hardener. This effect is even more visible in the case of ([MOB]MIm][Cl]. One can recall that, generally, $T_g$ of produced epoxy-based systems is comparable to the reaction temperature, $T_{\text{reaction}}$, due to the reduction of the monomer diffusion upon approaching $T_g$ (which, in fact, is a limiting step of the process). Additionally, it can be stressed that the determined values of $T_g$ of both isothermally polymerized and fully cured systems are either lower than or comparable to those ones reported in the literature. It can be noticed that the glass transition temperatures of epoxy resins cured with the
two 1,3-substituted imidazolium-based IL hardeners possessing different anions (including tetrafluoroborate [BF$_4$], thiocyanate [SCN$^-$], or dicyanamidate [N(CN)$_2$]$^-$) reached $T_g$ = 420–454 K$^2$,$^{42,44,58,59}$ whereas the combination of acetate/phosphonium cation and 2-ethylhexanoate/phosphonium cation as curing agents resulted in $T_g$ varying between 434 and 417 K, respectively.$^{44,60}$

After determining the values of $\Delta H_{\text{mon-ino}}$ we estimated the DSC conversion, $\alpha_{\text{DSC}}$, from eq 1. Herein it should be noted that considering that (i) isostructural reactions proceeded with the high monomer consumption and (ii) there is only partial overlapping of the residual heat of the reaction and heat of the IL’s thermal decomposition occurring at very high temperatures, the latter process has a rather marginal impact on the calculated monomer conversion. The temperature dependence of calculated $\alpha_{\text{DSC}}$ is shown in the inset of Figure 3a. As illustrated, the application of [(MOB)MIm][Sal] as the curing agent leads to a higher monomer conversion when compared to the examined ionic hardener. Note that for the PS I system almost full DGEBA consumption ($\alpha_{\text{DSC}} \geq 90\%$) was reached independently of the IL’s content. Comparable values of $\alpha_{\text{DSC}}$ were also calculated for PS II [(DGEBA)$_0$][(MOB)MIm][Cl]$_0 = 1:1$. However, for this system, $\alpha_{\text{DSC}}$ strongly depends on IL’s concentration. For example, in the case of [DGEBA]$_0$/[IL]$_0 = 10:1$, $\alpha_{\text{DSC}}$ decreases to $\sim 60\%$ at $T_{\text{reaction}} = 383$ K (see the inset in Figure 3a). It is worth mentioning that the final degree of monomer conversion depends on the structural features of the applied hardener and usually fluctuates between 40% and 60% in the case of an ionic curing agent. Note that for cationic hardeners the monomer conversions were comparable to those obtained for the anionic ones, reaching values of 50–70%. Interestingly, for some epoxy/IL systems, after isothermal curing at low temperatures, extremely low monomer conversion ($\alpha \sim 3\%$) was obtained.$^{47}$ Nevertheless, for the epoxy/IL systems studied herein, calculated $\alpha_{\text{DSC}}$ are comparable to those previously reported for nonionic curing agents.$^{41}$ As demonstrated, the application of an imidazolium-based hardener with salicylate anion allows to reach higher conversion at comparable temperature conditions and IL’s concentration. This indicates that the studied [(MOB)MIm][Sal] hardener might be considered as a latent curing agent. On the other hand, it should be pointed out that in the case of [DGEBA]$_0$/[IL]$_0 = 1:1$ the same $\alpha_{\text{DSC}}$ was reached for the shorter time in the case of DGEBA/[(MOB)MIm][Sal] than DGEBA/[(MOB)MIm][Cl], which might suggest, in fact, the better catalytic activity of the salicylate anion.

Next, we plotted the determined $\alpha_{\text{DSC}}$ as a function of time for all investigated systems (see Figure 3). As shown, the type of curing agent/anion and its concentration have a crucial impact on the kinetics curves. For the PS I system [(DGEBA)$_0$/[(MOB)MIm][Sal]$_0 = 1:1$), a typical autocatalytic behavior, characterized by the S-shape, can be observed, whereas with the decreasing concentration of the hardener [(DGEBA)$_0$/[IL]$_0$] to 10:1 yields two clearly visible steps. Note that this phenomenon is also observed, but not as spectacular as in the case of [DGEBA]$_0$/[(MOB)MIm][Sal]$_0 = 20:1$ (see Figure 54). One can recall that the detected S-shaped kinetic curves are generally reported for epoxy resin curing in the presence of the nonionic hardener, i.e., both aliphatic and primary aromatic amines,$^{11,61}$ as a result of the two various curing steps characterized by different constant rates, $k_1$ and $k_2$, and activation barriers, $E_a$. Briefly, the first one is related to the noncatalyzed ring-opening with a ternary transition state of amine or by nucleophile attack (usually characterized by higher $E_a$). By contrast, the second one is believed to be a subsequent process connected to the autocatalytic ring-opening that involves alkoxy and epoxide groups, which may be catalyzed by the hydroxyl groups formed from the already opened oxirane rings.

On the other hand, the $\alpha_{\text{DSC}}(t)$ dependences estimated for the PS II system (DGEBA/[(MOB)MIm][Cl]) revealed an exponential-like behavior, characteristic of the first-order kinetics (see Figure 3b,d).$^{33,62}$ It should be noted that similar exponential kinetic curves were also previously reported for the curing of DGEBA with both 1-(3-aminopropyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide and tetraethylammonium leucine (assigned as [apbim][NTf$_2$] and [N$_4$]$^{44,44}$-[Leu], respectively).$^{33}$ The first-order kinetics were discussed in terms of the polymerization mechanism change, related to the presence of IL hardener acting as both the initiator and the cocatalyst.$^{55}$ Therefore, the exponential kinetics of studied DGEBA/[(MOB)MIm][Cl] systems might also result from the increased catalytic properties of the applied chloride IL curing agent. Hence, as shown and discussed above, the application of imidazole hardeners with different anions affects the polymerization kinetics in various ways.

To get deeper insights into the examined curing kinetics, we analyzed the obtained experimental data with available phenomenological kinetic models. Taking into account a complex and bimodal character of the hardening process, one can stress that applications of mechanistic models would be a challenging task. Fortunately, one can apply phenomenological ones, which can be used without the identification of the species involved in the reactions. This approach is frequently explored in the literature, where different model-free$^{83}$ and model-fitting$^{64}$ methods are commonly applied to study the kinetics of a variety of epoxy resins. The former group is represented by, i.e., the Friedman, Flynn–Wall–Ozawa, and Kissinger–Akahira–Sunose methods, whereas the latter ones are based on model-fitting algorithms, that are the nth order, Avrami, and the autocatalytic model (Kamal model$^{65}$ and its modifications$^{66,67}$). However, we would like to highlight that both types of methods are used mostly to characterize the standard kinetic curve (characterized by the one exothermic process), which precludes their use in a description of the data presented in Figure 3c.

Nevertheless, we previously demonstrated that the original Kamal model or its modified version can be successfully applied to describe the autocatalytic behavior of epoxy curing in the presence of classical aromatic amine–amine, even in a broad range of thermodynamic conditions.$^{13}$ Therefore, the Kamal equation has been chosen as a first approach to determining the kinetics parameters describing the progress of a reaction:$^{86}$

$$
\frac{da}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n
$$

where $\alpha$ is a degree of thermal conversion, $k_1$ and $k_2$ correspond to noncatalyzed and catalyzed reaction rate constants, and $m$ and $n$ are the model constants. The application of this model provides reasonably good fits to the experimental data over the entire range of temperatures for [DGEBA]$_0$/[(MOB)MIm][Sal]$_0 = 1:1$. This is evidenced by the representative example in Figure 55. However, in the case of systems with low IL content [(DGEBA)$_0$/[IL]$_0 = 10:1$ and
the shape of $\frac{d\alpha}{dt}$ vs $\alpha$ became much more complex, as is clearly demonstrated in the inset of Figure 4b. As shown, two evident peaks are visible, which confirms the previous assumption that we are dealing with two curing stages. Probably, the first one is directly linked to the combined imidazolium salicylate activity effect, participating as an initiator and a cocatalyst. According to the applied amount of ionic liquid, DGEBA is fully or partially cured in the case of a 1:1 or 10:1 (and 20:1) molar ratio mixture, respectively. In the latter situation, the initial catalytic effect observed at the beginning of curing, after the primary step, is reduced, which is reflected in a decrease of $\frac{d\alpha}{dt}$. Nevertheless, as the initial stage of curing proceeds with the epoxide ring-opening, newly hydroxyl groups with the catalytic activity are formed. Simultaneously, the imidazole cation activity should still be accessible. As a consequence, the reaction is accelerated to the second peak maximum. Then, the final decrease of the reaction rate is caused by the reduction of monomer concentration and suppressed diffusion.

An analysis of the initial stage of the curing process registered for the $[\text{DGEBA}]_0/[\text{IL}]_0 = 10:1$ mixed in 10:1 molar ratio was performed. This enabled us to determine the $k_1$ parameter in the model-independent way. Subsequently, we fitted the Kamal model to the experimentally obtained dependence of $\frac{d\alpha}{dt}$ vs $\alpha$. From Figure 4a, it can be seen that this approach does not fit the experimental data measured for this system correctly, even though it accounts for the two-step mechanism of the reaction. Consequently, further analysis of the curing processes, especially for $[\text{DGEBA}]_0/[\text{IL}]_0 = 10:1$ and $[\text{DGEBA}]_0/[\text{IL}]_0 = 20:1$, requires the employment of the different model.

To find a solution to this problem and maintain consistency between the constant rates determined for various systems, we decided to exclude the Kamal model from further considerations. Instead, we chose the Avrami approach, which many researchers—including some of us—had successfully applied to study the overall progress of curing. It should
be stressed that because of its simplicity, the Avrami model seems to be the perfect choice for the further modification. Few attempts of that type of approach can be found in the literature.\textsuperscript{25–27} Using the classical Avrami eq 3

\[
\alpha(t) = C - e^{-(kt)^m}
\]

for the systems \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Cl}]_0\) mixed in the following molar ratios 20:1, 10:1, and 1:1 and equimolar composition of [DGEBA] and \([(\text{MOB})\text{MIm}][\text{Sal}]\) polymerized at \(T = 373 \, \text{K}\), we calculated parameters \(k\) and \(n\), which are the temperature-dependent reaction rate and Avrami exponent, respectively. The obtained results are presented in Figure 4 and Figure 5. Subsequently, we propose the following modification of the Avrami model to consider two-stages of curing (herein named “double Avrami” model):

\[
\alpha(t) = C - x \exp(-k_1 t^m) - (C-x) \exp(-k_2 t^n)
\]

where \(C\) is a final (real) conversion, \(k_1\) and \(k_2\) are the reaction rate constants (note that they have nothing to do with \(k_1\) and \(k_2\), which can be obtained from the Kamal model), \(x\) parametrizes the relative contributions of each reaction step, and \(m\) and \(n\) are the fit parameters. Note that the data analysis with the “double Avrami” model yields two reaction rates (\(k_1\) and \(k_2\)), which herein are assigned to the first and second stages of the studied curing process, respectively. Interestingly, contrary to the Kamal and classical Avrami approaches, the use of the “double Avrami” model leads to a satisfactory description of the curing process performed with the use of \([(\text{MOB})\text{MIm}][\text{Sal}]\) for different \([\text{DGEBA}]_0/[(\text{IL})_0\) concentrations (see Figure 4a). Additionally, in the inset of Figure 4a, we presented the predicted by the “double Avrami” model dependence of \(\alpha = \alpha(t) = \alpha_0\) vs \(\alpha\). In this case, the two evident peaks are described by the fits with satisfactory accuracy. Hence, we can conclude that the “double Avrami” model describes the overall curing kinetics \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Sal}]_0 = 10:1\) and \(20:1\) much better than the Kamal model does.

The determined values of the constant rates \(k\) describing curing DGEBA with both ionic liquids \([(\text{MOB})\text{MIm}][\text{Sal}]\) and \([(\text{MOB})\text{MIm}][\text{Cl}]\) are presented in Figures 5a and 5b, respectively. Note that in the case of the 10:1 and 20:1 molar ratios of the DGEBA/[(MOB)MIm][Sal] compositions analysis of the kinetic curves with the use of double Avrami model yields two different rates, labeled herein as \(k_1\) and \(k_2\), whereas for the other systems, only one \(k\) was estimated. As shown, the estimated constant rates increase linearly with the curing temperature and increasing concentration of ILs. However, the constant rates of DGEBA/[(MOB)MIm][Sal] systems increase with increasing temperature more dramatically as compared to PS II.

Further insight into the kinetics of both stages of reactions can be gained by a comparison of activation energies, \(E_a\) which can be estimated by using the Arrhenius equation:

\[
k = k_0 \exp\left(\frac{E_a}{RT}\right)
\]

where \(k_0\) is a pre-exponential factor and \(R\) is the universal gas constant. The determined values of \(E_a\) are presented in Figure S. It was found that \(E_a = 97.4 \, \text{kJ/mol}\) and \(E_a = 123.2 \, \text{kJ/mol}\) as well as \(E_a = 72.4 \, \text{kJ/mol}\) and \(E_a = 72.7 \, \text{kJ/mol}\) for DGEBA mixed with \([(\text{MOB})\text{MIm}][\text{Sal}]\) in the 10:1 and 20:1 molar ratios, respectively (Figure S). As one can expect, the activation energies for the initial stage of curing, marked as \(E_a\), are higher in comparison to \(E_a\), which is consistent with the literature data.\textsuperscript{33} Moreover, the activation energy of the first stage is correlated to the content of \([(\text{MOB})\text{MIm}][\text{Sal}]\). As a consequence, a decrease in IL’s concentration results in an increase in the activation energy of the first step of curing (\(E_a\)). By contrast, it did not affect the activation barrier of the second stage of the process (Figure S). Furthermore, in the case of high ionic liquid loading, \([\text{DGEBA}]_0/[(\text{IL})_0 = 1:1\), we can assume that nearly all of the epoxy groups were catalytically consumed; therefore, the quite low \(E_a\) equal to 79.1 \, \text{kJ/mol}\), was estimated. On the other hand, the \(k(T)\) dependences for the second stage studied herein, DGEBA/ [(MOB)MIm][Cl], and the corresponding estimated activation energies are shown in Figure 5b. As presented, \(E_a = 16.5\) and 19.8 \, \text{kJ/mol}\) for \([\text{DGEBA}]_0/[(\text{IL})_0 = 1:1\) and \([\text{DGEBA}]_0/[(\text{IL})_0 = 20:1\), respectively. It should be pointed out that they are much lower in comparison to those calculated for cation with salicylic anion. Although only a few literature reports discuss the activation barrier for epoxy resin cured with ionic liquids, it should be highlighted that our values are consistent with the results previously presented by Maksym et al.\textsuperscript{33} and Binks et al.\textsuperscript{28} As an example, one can mention ionic liquid with imidazolium-basedcation for which the reported activation energy is \(E_a = 19 \, \text{kJ/mol}\).\textsuperscript{28} Moreover, the activation barriers \(E_a = 72.7\) and 72.4 \, \text{kJ/mol}\) estimated for curing DGEBA with \([(\text{MOB})\text{MIm}][\text{Sal}]\) are in perfect agreement with the respective value for the system reported in ref 78 (where \(E_a = 74 \, \text{kJ/mol}\)). As shown, the values of \(E_a\) are closely connected to the applied monomers, which also affect the dominant curing mechanism. One can expect that due to a common presence of imidazolium-based cation, both studied systems polymerize according to a similar mechanism (probably via “carben” and “imidazole” routes). However, in the case of DGEBA/ [(MOB)IM][Sal], additionally, the “counterion” route might be favored.

Finally, we examined the relationship between the structure of networked epoxy resins, a type of anion, the applied amount of ILs, and the conductivity of fully cured resins. As mentioned in the Introduction, these parameters are unquestionably important for achieving significant progress in energy storage, i.e., to design and produce flexible, solid electrolytes, or separation membranes for Li-ion batteries.\textsuperscript{25} Herein, we measured the ionic conductivity, \(\sigma_{dc}\), of produced resins by means of broadband dielectric spectroscopy (BDS) at \(T_f\) which were previously determined from dynamic DSC experiments. We should highlight that measuring \(\sigma_{dc}\) of all cured materials at \(T_f\) allows for the comparing of systems characterized by the same viscosity and molecular mobility, independent of their structure.\textsuperscript{79} The determined \(\sigma_{dc}\) conductivity at their glass transition temperature for \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Sal}]_0 = 1:1\) and \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Sal}]_0 = 10:1\) was equal to \(\sigma_{dc} = 7.18 \times 10^{-14} \, \text{S/cm}\). On the other hand, for \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Cl}]_0 = 1:1\), \(\sigma_{dc} = 6.1 \times 10^{-15} \, \text{S/cm}\), and for \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Cl}]_0 = 10:1\), much higher values, \(\sigma_{dc} = 1.82 \times 10^{-10} \, \text{S/cm}\), were obtained. The obtained \(\sigma_{dc}\) are lower than those presented in the literature, i.e., for 1-decyl-3-methyl-imidazolium bromide [DMIm][Br], where \(\sigma_{dc} = 10^{-2} \, \text{S/cm}\) at room temperature and \(\sigma_{dc} = 10^{-3} \, \text{S/cm}\) at \(T_f = 443 \, \text{K}\), where the cation part of ILs is covalently linked to the epoxy network to a considerably lower degree. Even higher
conductivity was achieved for 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIm][TFSI]) added to the mixture of DGEBA and tetrafunctional epoxy resins.80 Note that in the discussed cases IL-based hardeners were applied together with the classical nonconducting ones. Moreover, one can also find studies indicating the implementation of ionic groups into networked resin due to the application of ionic monomers (or comonomers) via polyaddition polymerization. In this context, one can notice the diepoxy-functionalized 1,2,3-triazolium ionic liquid39 and glycidyltrimethylammonium bis(trifluoromethanesulfonyl)imide (GTMATFSI),32 which were successfully polymerized to achieve an epoxy network structure with built-in cations and movable anions resulting in a relatively high conductivity, \( \sigma_{dc} = 2 \times 10^{-7} \text{ S/cm (at } T = 303 \text{ K)} \) and \( \sigma_{dc} \sim 10^{-5} \text{ S/m} \), respectively. It is also worth mentioning that slightly lower values of conductivity were obtained for epoxy resin-based polymers and polyanions, where \( \sigma_{dc} = 5 \times 10^{-8} \) and \( \sigma_{dc} = 3 \times 10^{-8} \text{ S/cm at } T_g \) for DGEBA + [apbim][NTf2] and DGEBA + [N4444][Leu], respectively.53 The conductivity of the mentioned examples of epoxy resin-based conductive materials differs significantly, probably due to differences in the chemical structure of the produced network and mobility or the viscosity of the studied materials,32,82,83 which strongly affects the charge transport mechanism.82,83 At this point, it should also be stressed that very often the determined values of \( \sigma_{dc} \) are reported for different temperature conditions, as there is no unifying protocol to present them in a comparable manner. Most of the reports devoted to ionic-based epoxy resins listed values of \( \sigma_{dc} \), measured at room temperature (\( \sim 293–303 \text{ K} \)), which, for various cases, indicates a totally different system viscosity, ion mobility, and dc conductivity. To avoid any misunderstandings, herein, we measured \( \sigma_{dc} \) of all cured materials at \( T_g \), which allows for the comparing of systems characterized by the same viscosity and molecular mobility, irrespective of their structure. As shown, the PS II system (DGEBA/[(MOB)MIm][Cl]) is characterized by much higher conductivity, probably due to the presence of the polar and highly mobile chloride anion, which cannot be built into the polymer structure. Moreover, this kind of polymerization most likely yields oligomeric linear polymers (low \( T_g \)) that contribute to enhanced conductivity. On the other hand, in the case of the second system studied herein, a product is a highly cross-linked polymer (high \( T_g \)), where the mobility of the ions is highly restricted.

4. CONCLUSION

Herein, we studied the isothermal cure kinetics of DGEBA in the presence of imidazolium-based ILs hardeners containing different anions, that is, a salicylate and chloride, denoted as [(MOB)MIm][Sal] and [(MOB)MIm][Cl], respectively. The curing process of epoxy/IL systems was investigated at different (moderate) temperatures through the use of various initial molar ratios of DGEBA/IL. Performed calorimetric experiments for \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Sal}]= 10:1 \) and \([\text{DGEBA}]_0/[(\text{MOB})\text{MIm}][\text{Cl}]= 20:1 \) allowed us to demonstrate that there are two peaks in the thermograms upon the isothermal curing. This phenomenon might be probably assigned to the promoted initiation by the anion (salicylate)—cation (imidazolium-based) combination, whereas in the case of [(MOB)MIm][Cl], only one hardening step was observed. The detailed kinetic analysis performed through the application of the modified Avrami model provided constant reaction rates that enabled us to further calculate activation energies for the curing process for all the systems studied herein. It should be pointed out that we applied a combination of two Avrami equations (assigned by us as “double Avrami”) to describe the two-step kinetics of DGEBA/[(MOB)MIm][Sal]. As observed, the proposed approach works perfectly. Interestingly, the reactions performed in the presence of IL with the salicylate anion are shorter, even though they are characterized by much higher activation energies, with respect to those consisting of the chloride anion. Thus, it seems that in the DGEBA/[(MOB)MIm][Sal] composition the presence of the salicylate anion leads to an additional initiation of epoxy ring-opening, which is absent in the case of chloride anion. Moreover, DGEBA/[(MOB)MIm][Cl] systems have a lower glass transition temperature, \( T_g \) than the second system independently of the applied IL concentration. This might indicate that, most likely, DGEBA/[(MOB)MIm][Sal] products are highly cross-linked polymers (high \( T_g \)), while those consisting of DGEBA/[(MOB)MIm][Cl] are oligomeric linear polymers (low \( T_g \)). However, the latter systems are characterized by significantly higher conductivity (measured at the calorimetric glass transition temperature, \( T_g \)), probably due to the presence of polar and highly mobile chloride anion and oligomeric cations. Our data clearly presented that the type of anion has a crucial impact on the polymerization mechanism, kinetics, and properties of produced materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00783.

Experimental details; Figures S1–S5 (PDF)

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