


RESEARCH ARTICLE

The Impact of Molecular Weight on the Characteristics of Injection-Molded Partially Crystalline Thermoplastic Polyimide R-BAPB

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ABSTRACT

This study investigates the correlation between the molecular weight of semicrystalline polyimide and the properties of injection moldings based on it. It was found that the degree of crystallinity can be increased by annealing of molding. The molecular weight of polyimide materials directly influences their glass transition temperature. An increase in molecular weight leads to a decrease in both the degree of crystallinity and the rate of crystallization within these materials. The mechanical properties of a polymer, such as its tensile strength, elastic modulus, and elongation at break, show a direct relationship with its molecular weight. As the molecular weight of a polymer increases, its strength, stiffness, and ability to elongate at break increase. Crystallization annealing leads to an increase in the rigidity of the material, but at the same time, there is a decrease in its plasticity, which is expressed in a decrease in elongation at break.

1 | Introduction

Polyimides are extensively applied in advanced sectors, namely aerospace, chemical engineering, mechanical and electric power engineering, owing to their remarkable resistance to high temperatures, durability against various chemicals, excellent structural integrity, and a low ability to store electrical charge [1–3]. However, polyimide macromolecules have a rigid structure, as a result of which most of these polymers are insoluble, non-melting compounds, which makes it extremely difficult to process the melt. Conventional processing of polyimides involves either casting the solution of its precursor material into a mold and then converting it to polyimide through heat or chemical treatment or hot sintering of a polyimide powder [4]. Melt

processing is more preferable both in terms of cost and environmental safety. Consequently, the development of thermoplastic polyimides that can be easily processed by melting is a crucial area of research [5].

Fusible thermoplastic polyimides are commonly used in various branches of industry because of their processability, ease of preparation, and storage of finished products. Such polyimides should exhibit good melt fluidity at relatively low processing temperatures [6, 7].

Many commercial polyimides suitable for melt processing have been developed, such as amorphous polyetherimide Ultem developed by General Electric Co. [8, 9], LARC-TPI by Mitsui

Summary

- Crystallizable fusible polyimides of various molecular weights were synthesized.
- Polyimide samples were obtained by injection molding.
- Crystallized polyimide moldings were obtained by annealing.
- Heat-resistant moldings with high mechanical characteristics were produced.

Chemicals Inc. [10], Extem XH and Extem UH produced by SABIC Innovative Plastics [11, 12]. The operational temperature limits of commercially available thermoplastic polyimides are primarily determined by their glass transition temperatures. Due to the amorphous nature of these materials, their maximum operating temperatures generally do not surpass 220°C.

Semicrystalline thermoplastic polyimides (PIs) stand out due to their enhanced properties. Their semicrystalline nature contributes to better thermal endurance, resistance to solvents, and superior mechanical strength [13–16]. Notable examples include LaRC-CPI [17], LaRC-CPI2 [18, 19] created by NASA, as well as New-TPI [20]. Additionally, a number of crystallizable PIs have been developed at the Polytechnic Institute. While certain PIs demonstrate crystallinity, their crystallization typically relies on the presence of a solvent, and they cannot be recrystallized after being melted. Furthermore, the high viscosity or processing temperature of most crystallizable PIs presents a challenge for conventional manufacturing techniques like injection molding or extrusion. Due to specific structural properties, only a select few types of polyimides can crystallize upon cooling from their liquid state. R-BAPB polyimide, a notable example of a thermoplastic polyimide capable of recrystallization from its molten state [21]. This polyimide has already proven itself in the processing of films [22], fibers [23] and resins for fiber-reinforced composites [24].

When developing fusible polyimides that can be processed by advanced methods (injection molding and extrusion), a certain melt viscosity is required. Several research teams employ strategies like incorporating flexible linkages, fluorine-containing moieties, and bulky side chains within the polyimide backbone to modify its properties [5, 25] to regulate its melt viscosity. The simplest ways to reduce viscosity involve controlling molecular weight, blocking the ends of a poly(amido acid), copolymerization, or blending with a polyimide containing more flexible main chains [26, 27]. Among these methods, varying the molecular weight of polyimides is a common and effective approach to control a melt viscosity.

The molecular weight of a semicrystalline polymer significantly impacts both its ability to be processed and its final characteristics. Higher molecular weights lead to increased viscosity, which directly affects the processing of thermoplastic polyimides. Moreover, molecular weight plays a crucial role in determining the properties of the finished product, particularly for polymers capable of forming crystalline structures. It has been shown [28] that the melting point, crystallization behavior, and crystallinity

vary with molecular weight and affect the processing of polyetheretherketone (PEEK), which should be taken into account when obtaining products based on this polymer. Similarly, impact strength is also enhanced significantly. Conversely, elastic modulus in tension exhibits a slight reduction as molecular weight increases. A study [29] demonstrated a consistent correlation between the molecular weight of a polyphenylene sulfide (PPS) material and its physical properties. As the molecular weight decreased, both the glass transition temperature and resistance to fracture declined. The research presented in study [29] demonstrated a correlation between the molecular weight of a polyphenylene sulfide (PPS) material and its physical properties. Specifically, as the molecular weight decreased, both the glass transition temperature and ductility of the PPS material were found to decrease, resulting in increased brittleness. The research concluded that PPS exhibits optimal processability via extrusion within a specific molecular weight range. This range is relatively narrow, spanning from 40 to 60 kg/mol. The authors [6] showed that copolyimides with a molecular weight of 20 kg/mol have good mechanical properties. When the molecular weight is increased up to 34 kg/mol, polyimides exhibit ductile rather than brittle behavior [6]. Not only processability [27], thermal and mechanical properties [30], but gas permeability [31] also are related to the molecular weight of polyimides.

This study examines the relationship between molecular weight and the rheological, thermal, and mechanical characteristics of the semicrystalline polyimide R-BAPB. A series of R-BAPB samples with diverse molecular weights were produced and subsequently subjected to analysis. This research investigates the correlation between the molecular weight of semicrystalline polyimide and the properties of injection moldings based on it.

2 | Materials and Methods

2.1 | Synthesis of Polymers

The synthesis of polyimide P-BAPB was carried out by a two-stage method: at the first stage, polyamide acid was obtained by condensation of 1,3-bis(3',4-dicarboxyphenoxy)benzene (dianhydride R) and 4,4'-bis(4-aminophenoxy)biphenyl (BAPB diamine); at the second stage, chemical cyclization of polyamide acid units was performed according to the procedure described in the work [23]. Its molecular weight was regulated by changing the stoichiometric ratio of the initial monomers during the synthesis of polyamide acids. This was achieved by changing the dianhydride to diamine ratio from 0.98 to 0.93. The synthesis yielded powders of semicrystalline R-BAPB with different dianhydride/diamine ratios: 0.93, 0.95, 0.97, and 0.98.

2.1.1 | Preparation of Moldings From Samples of the Polyimide

The injection molding process utilized specialized micro-scale equipment: an Xplore MC5 microextruder and an Xplore IM5.5 microinjector, both manufactured by DSM in Sittard, Netherlands. Before preparing the samples by injection molding, the synthesized polyimide powder was heat treated at 150°C for 12 h to remove adsorbed water. First, melt homogenization was

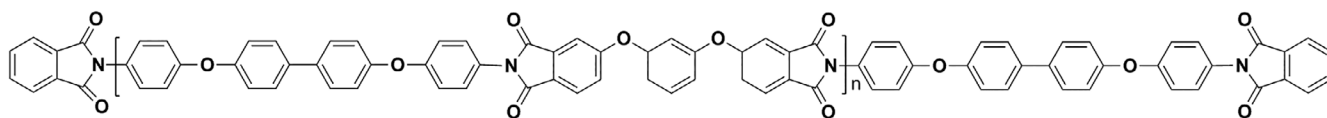


FIGURE 1 | The chemical structure of polyimide R-BAPB.

TABLE 1 | Molecular weights of the samples depending on the ratio between the initial monomers.

R/BAPB molar ratio	Sample	MW, kg/mol
0.93:1	RBAPB 93	22 ± 2
0.95:1	RBAPB 95	26 ± 3
0.97:1	RBAPB 97	29 ± 3
0.98:1	RBAPB 98	32 ± 4

performed at 360°C for 5 min using the microextruder. Then, the polymer melt was loaded into a DSM Xplore IM 5.5 microinjector cylinder heated to 360°C. Next, the polyimide melt was injected into a mold heated to 180°C. Thus, by the injection molding method, samples in the form of a “dog bone” with a width of 4 mm, a thickness of 2 mm and a working part length of 25 mm were obtained. In addition, by the injection molding method, samples in the form of a plate with a thickness of 1.5 mm, a width of 10 mm and a length of 50 mm were obtained. To determine the coefficient of thermal expansion (CTE), samples were obtained in the form of cylinders with a diameter of 15 and 10 mm, a height of 3 and 5 mm, respectively. To ensure the molding samples were in a crystallized state, they underwent further heat treatment. This involved annealing the pre-formed moldings at a temperature of 280°C for a duration of 1 h.

2.1.2 | Instruments

The molecular weight of the produced polyimides was determined in an earlier publication [32].

The flow behavior of molten R-BAPB polyimide was investigated using a rheometer (MCR-301, Anton Paar, Austria). The complex viscosity of the substance was assessed across a temperature gradient ranging from 320°C to 425°C. Measurements were taken at a constant angular frequency of 1 rad per second, with a controlled heating rate of 1°C/min. In addition, viscosity measurements were carried out under isothermal conditions at a temperature of 360°C in the frequency range from 1 rad/s to 100 rad/s.

Thermal analysis of the specimens was conducted using differential scanning calorimetry techniques. Thermal analysis was performed using a NETZSCH DSC 204 F1 instrument. The analysis involved both dynamic heating, ranging from 30°C to 400°C at a controlled rate of 10°C per minute, and isothermal conditions maintained at specific temperatures of 270°C, 280°C, and 290°C. All measurements were conducted in an inert argon environment to prevent oxidation or other reactions. Thermal decomposition analysis was performed using thermogravimetric analysis (TGA) on a NETZSCH TG 209 F1 (Germany)

instrument. The samples were subjected to a carefully regulated heating procedure in an oxygen-free argon environment. Their temperature was gradually increased from 30°C to 700°C at a consistent rate of 10°C per minute.

Dynamic mechanical analysis (DMA) on a DMA 242 C setup (NETZSCH, Germany) provided insight into the temperature dependence of the elastic modulus (E') and loss modulus (E'') in the range from 30°C to 300°C using a three-point bending configuration. The experiment was carried out using a frequency of 1 Hz, a strain amplitude of 0.1%, and a temperature increase rate of 5°C/min.

The coefficient of thermal expansion was determined by dilatometric analysis in the temperature range of 20°C–170°C using a thermomechanical analyzer “TMA402 F1” (“NETZSCH”, Germany). The measurement was carried out with a preliminary sample load (0.02 N) in an argon flow.

The mechanical characteristics of the materials were evaluated using an Instron ElectroPulse E1000 testing machine. “Dog bone” shaped specimens conforming to standard dimensions were subjected to tensile tests at a controlled deformation rate of 1 mm per minute. To guarantee statistically reliable results, a minimum of five samples from each material group were tested.

3 | Results and Discussion

The synthesis yielded powders of semicrystalline R-BAPB with different dianhydride/diamine molar ratios: 0.93, 0.95, 0.97, and 0.98, with the general formula shown in Figure 1. The obtained polyimides were designated as RBAPB 93, RBAPB 95, RBAPB 97, and RBAPB 98, respectively. Molecular weights of the synthesized polyimides varied from 22 to 32 kg/mol; they were determined by light scattering and by studying the characteristic viscosity of solutions of the PAA prepolymer in previous work [32]. The values of molecular weights as a function of the ratio between initial reagents are presented in Table 1. Previous research [23] established the chemical makeup and structural arrangement of the R-BAPB polyimide through Infrared Spectroscopy and Nuclear Magnetic Resonance analysis.

The most important indicator to process fusible polyimides by injection molding is their melt viscosity, because it is not possible to manufacture quality products from a polymer with extremely high melt viscosity. Figure 2 shows the variation of complex viscosity with temperature and angular frequency. For all R-BAPB polyimide samples, the temperature dependence of viscosity goes through a minimum (Figure 2a).

Polyimide melts exhibit a high viscosity (approximately 10^4 Pa·s) at lower temperatures (< 325°C). This viscosity significantly decreases as the temperature nears the material's melting point

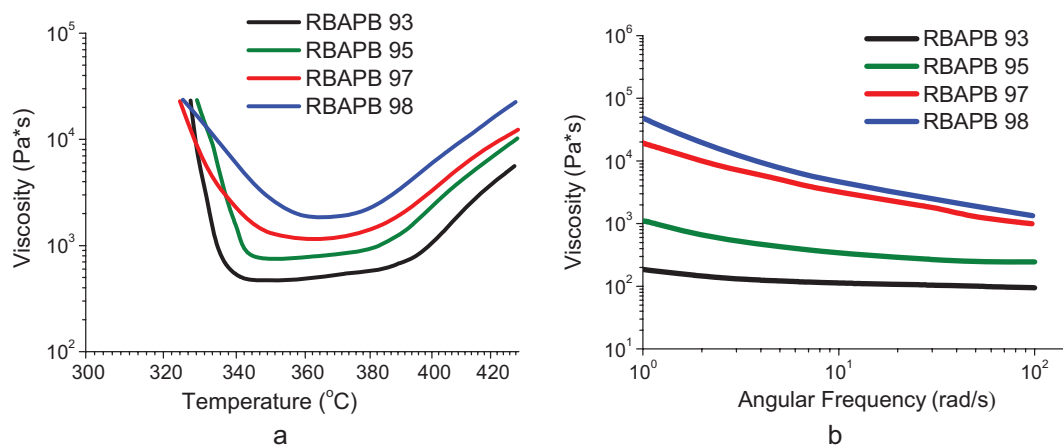


FIGURE 2 | Melt viscosity of samples RBAPB 93, RBAPB 95, RBAPB 97, and RBAPB 98: (a) on temperature; (b) on angular frequency at 360°C.



FIGURE 3 | Samples of polyimides with different molecular weights prepared by injection molding: 1—RBAPB 93, 2—RBAPB 95, 3—RBAPB 97, and 4—RBAPB 98.

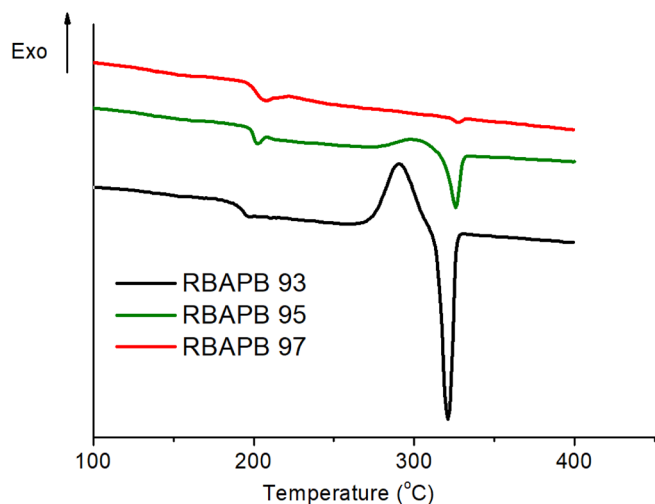


FIGURE 4 | DSC thermograms of the first heating of RBAPB 93, RBAPB 95, and RBAPB 97.

(Figure 2a). When the temperature reaches 360°C, viscosity of polyimide melts stabilizes and reaches minimum values. As the molecular weight becomes higher, the minimum viscosity value increases with temperature. At temperatures above 400°C, there is a persistent rise in the melt's viscosity (as illustrated in Figure 2a). This phenomenon could be attributed to

the occurrence of chain elongation and crosslinking within the molten polymer [33].

Research investigating the melt viscosity of polyimides with varying molecular weights across different angular frequency revealed a consistent increase in viscosity as molecular weight increased, particularly at lower angular frequency. The melt of the sample exhibiting a dianhydride/diamine ratio of 0.93 demonstrated nearly Newtonian flow behavior. However, for samples with higher molecular weights (beginning with a dianhydride/diamine ratio of 0.95), the relationship between viscosity and deformation rate became more apparent. When the ratio of dianhydride to diamine reaches 0.97, a significant increase in viscosity is observed at low shear deformation (as illustrated in Figure 2). This indicates that high molecular weight R-BAPB polyimide exhibits pronounced melt structuring under conditions of low strain rates. The increased viscosity of polymers at high molecular weights is attributed to the entanglement and interweaving of long macromolecular chains. This phenomenon is most pronounced at low deformation rates. The correlation between molecular weight and viscosity is evident: Polyimide samples with the highest molecular weight have the highest viscosity (RBAPB 98). The increased viscosity of the molten polymer, due to its high molecular weight, hinders effective mold filling during the injection molding process (see Figure 3). Due to the impossibility of obtaining a high-quality molding of RBAPB 98, we will not use this sample in our further considerations and studies.

The first scans of the DSC analysis of the studied polyimide samples are shown in Figure 4. The initial moldings are amorphous, that is, they do not have sufficient time to crystallize in the process of preparation. However, during heating in the process of DSC testing, an exothermic crystallization peak in the region of 270°C–290°C is observed, followed by an endothermic melting peak of the crystallized phase (Figure 4). The observation indicates an inverse relationship between molecular weight and the magnitude of both crystallization and melting peaks. As molecular weight increases, the area under these peaks decreases (Figure 4). It is worth noting that in the first scan of the DSC experiment, the sample of high-molecular polyimide (RBAPB 97) shows almost no crystallization peak, and the melting peak has a small area. Analysis of Figure 4 and Table 2 reveals a

correlation between increased molecular weight and enhanced thermal properties. Specifically, as molecular weight rises, there is a discernible increase in both the glass transition temperature and the melting temperature.

Crystallization isotherms in the temperature range of 270°C–290°C (with a step of 10 C) were performed to study the dependence of the crystallization rate on the molecular weight. As an example, Figure 5a displays the isotherms of R-BAPB samples synthesized at the initial monomer ratio of 0.95 at different temperatures. The obtained values of the time required to reach half of the crystallization, or the time to reach the crystallization peak ($t_{1/2}$) depending on the temperature are presented in Figure 5b.

On the plot of the temperature dependence of time $t_{1/2}$, a minimum is observed at temperatures of 270°C and 280°C. Moreover, this minimum shifts slightly from 270°C (for sample RBAPB 93) to 280°C for high molecular weight (sample RBAPB 97). It is known [34] that the crystallization rate is determined by the product of the rates of two processes: nucleation and crystal growth. Probably, the appearance of the extremum on the plot presented in Figure 5b is related to the change in the rate of nucleation and crystal growth with temperature. When

temperatures reach 260°C, the initial stage of crystal formation begins quickly. However, the subsequent growth of these crystals proceeds at a much slower pace. This imbalance between nucleation and crystal growth leads to a prolonged crystallization time overall. As the temperature for crystallization rises, the movement of polymer chains is enhanced. This increased mobility accelerates the process of crystal formation, resulting in a shortened crystallization duration when the temperature reaches 270°C and 280°C. However, when the temperature exceeds 280°C, the crystallization time increases, which is probably due to the decrease in the rate of the nucleation process.

The degree of crystallinity of R-BAPB moldings was determined by the enthalpy of melting obtained from the analysis of the DSC method. The calculation was carried out on the basis of the enthalpy of melting of 100% crystal of R-BAPB polyimide determined earlier [33]. Following heat treatment of the polyimide (PI) molded components, a crystalline structure emerges, constituting between 38% and 46% of the material. The precise percentage of crystallinity is influenced by the molecular weight of the PI used in the molding process. As the molecular weight increases, the degree of crystallinity decreases slightly (see Table 2).

TABLE 2 | Thermal characteristics of polyimide R-BAPB moldings before and after heat treatment.

Sample	Glass transition temperature, °C	Melting point, °C	Melting enthalpy, J/g	Degree of crystallinity, %	Thermal degradation τ_5 , °C	Coefficient of thermal expansion, 10^5
Initial molding						
RBAPB 93	197	—	—	—	562	4.82
RBAPB 95	200	—	—	—	565	4.66
RBAPB 97	203	—	—	—	564	4.56
After annealing						
RBAPB 93	197	321	41.3	45.9	562	4.58
RBAPB 95	200	324	36.2	40.2	565	4.46
RBAPB 97	203	327	34.2	38.0	565	4.38

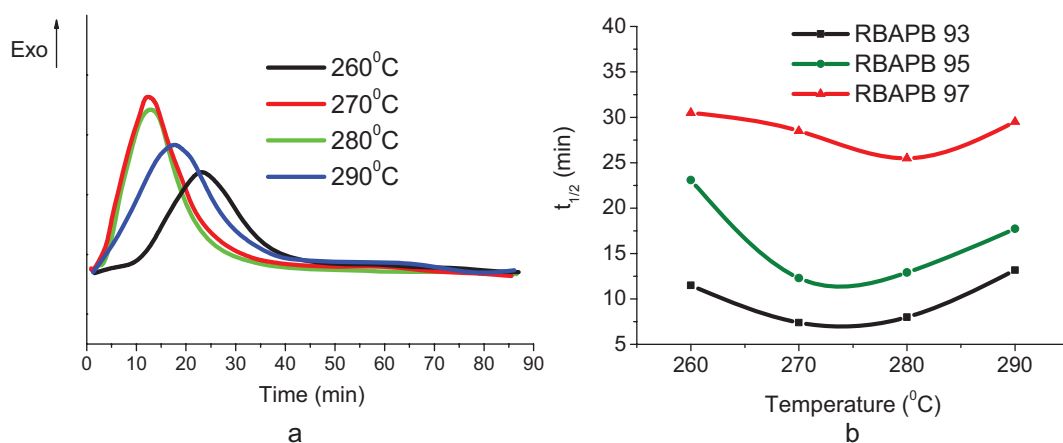


FIGURE 5 | Crystallization isotherms of polyimide samples RBAPB 95 at different temperatures (a) and dependence of time $t_{1/2}$ on crystallization temperature (b).

The obtained moldings were investigated by thermogravimetric analysis (TGA). TGA reveals that the investigated samples demonstrate exceptional resistance to thermal degradation. The material demonstrates thermal stability, maintaining its integrity up to a temperature of roughly 562°C. At this temperature threshold, a 5% reduction in the weight of the polyimide component is observed. Beyond this temperature, thermal degradation processes accelerate significantly (Table 2). Notably, the initiation temperature for thermal degradation remains consistent across polyimides with varying molecular weights.

The increase in molecular weight and the appearance of a crystalline phase in R-BAPB samples lead to a slight decrease in the thermal expansion coefficient (see Table 2). Apparently, more densely packed molecules better withstand thermal effects, which leads to a decrease in expansion and contraction under the influence of temperature.

Figure 6 illustrates the findings regarding the relationship between temperature and both storage modulus (E') and loss modulus (E'') in samples both before and after annealing. Figure 6a shows that there is a significant decrease in the elastic modulus (E') for unannealed samples at temperatures above 175°C. The sharp decrease in the modulus observed in Figure 6a is due to the presence of the glass transition temperature in this temperature region. The highest value of the elastic modulus (≈ 3200 MPa) among the initial (amorphous) moldings was recorded for polyimide RBAPB 97. Following annealing, the behavior of the temperature dependence of E' changes (Figure 6c). After a certain decrease in the modulus value above 180°C, it remains acceptable up to the temperature of 270°C–280°C. The

extent to which the storage modulus decreases is correlated with the molecular weight of the R-BAPB polyimide. Lower molecular weight polyimide (RBAPB 93) exhibits a more gradual decrease in modulus with increasing temperature. As molecular weight increases, the rate of this modulus reduction accelerates (Figure 6c). Significantly, annealing elevates the initial storage modulus to 4500–4600 MPa, compared to 2900–3200 MPa in unannealed samples. These variations in modulus change rate are correlated with differences in crystallinity levels observed among the molded samples. These crystallinity differences, in turn, are dependent on molecular weight (as detailed in Table 2). Analysis of the loss moduli (E'') of the initial (without annealing) moldings as a function of temperature reveals a distinct peak for all molecular weights within a narrow temperature range of 176°C–181°C (Figure 6b). This peak indicates the onset of increased segmental mobility within the polyimide macromolecules. During crystallization annealing, the peaks observed in the loss modulus versus temperature plot broaden and show a shift toward higher temperatures in the range from 188°C to 203°C, as shown in Figure 6d. Analysis of dynamic mechanical analysis data reveals a more pronounced shift in glass transition temperature for the low molecular weight polyimide sample RBAPB 93 compared to samples with higher molecular weights RBAPB 95 and RBAPB 97. This alteration in the temperature dependence of loss modulus curves is attributed to the formation of crystalline phases within the polymers following annealing, as confirmed by Table 2 data. Consequently, the annealed polyimide R-BAPB moldings exhibit enhanced thermal stability, enabling them to withstand loads up to approximately 270°C. In contrast, the operational temperatures of the initial moldings are limited by their respective glass transition temperatures.

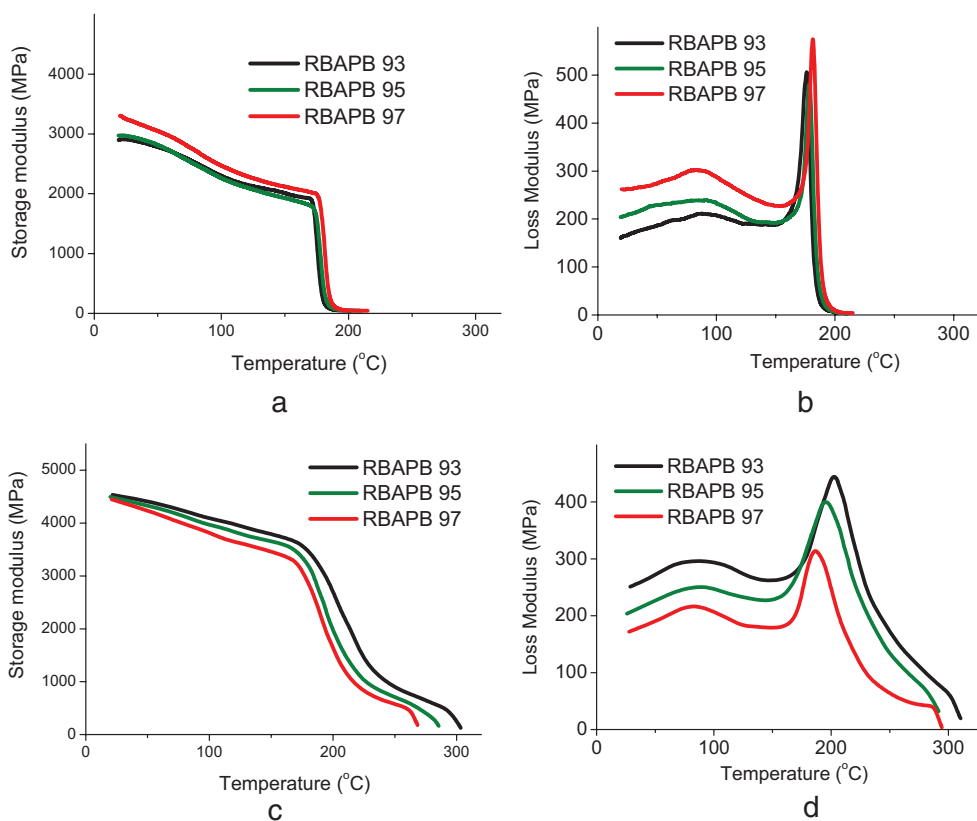


FIGURE 6 | DMA study of the initial (a, b) and annealed (c, d) at 280°C polyimide molding.

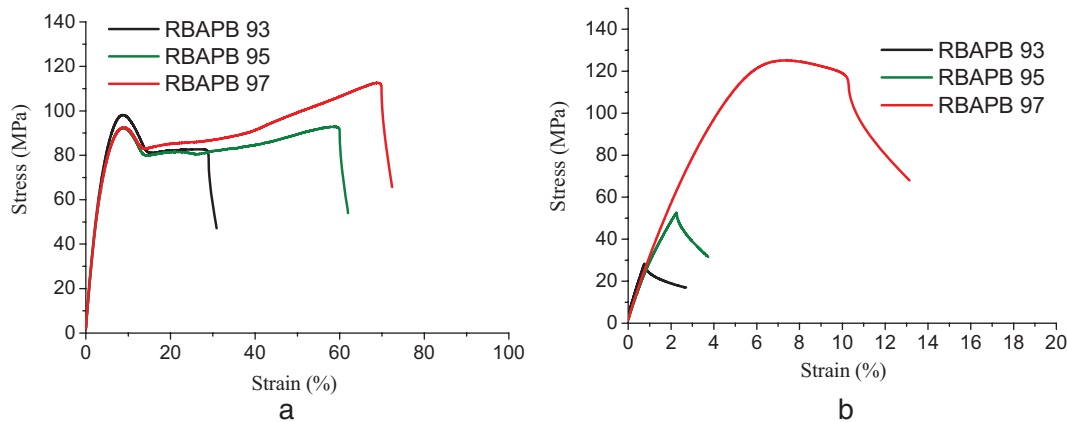


FIGURE 7 | Tensile curves of the initial polyimide moldings (a) and samples subjected to thermal annealing at 280°C (b).

TABLE 3 | Mechanical characteristics of polyimide moldings.

Sample	Elastic modulus, MPa	Yield strength, MPa	Ultimate tensile strength, MPa	Tensile elongation, %
Initial sample				
RBAPB 93	2465 ± 102	93 ± 8	84 ± 5	20 ± 5
RBAPB 95	2450 ± 58	93 ± 3	93 ± 3	58 ± 4
RBAPB 97	2496 ± 53	94 ± 1	106 ± 7	67 ± 10
After annealing				
RBAPB 93	3750 ± 120	—	29 ± 3	1.1 ± 0.3
RBAPB 95	3450 ± 170	—	45 ± 3	3.1 ± 0.6
RBAPB 97	3128 ± 86	—	122 ± 4	9.5 ± 1.4

Figure 7 presents graphical representations illustrating the relationship between stress and strain for the molded specimens. All stress–strain curves show a peak in the range of 8%–9% strain, and the subsequent deformation involves the formation of a neck which spreads over the entire sample. At a deformation of $\approx 40\%$, the strain hardening stage begins, which ends with the destruction of the sample. Furthermore, there is a direct correlation between molecular weight and the prominence of strain hardening: as molecular weight increases, the strain hardening region becomes more pronounced. For example, the sample RBAPB 93 fractures before reaching the strain hardening region. A correlation exists between higher molecular weight and enhanced mechanical properties. Specifically, as molecular weight increases, there is a modest rise in modulus, tensile strength, and ultimate elongation, as illustrated in Figure 7a and detailed in Table 3.

After annealing at 280°C of low molecular weight polyimide (RBAPB 93 and RBAPB 95), the strain curve changes significantly and the ultimate elongation values are reduced (Figure 7b). The observed phenomenon may be attributed to the weak inter-crystallite connections formed by molecular chains within the R-BAPB polyimide [35]. This limited connectivity results in an insufficient number of supporting macromolecules capable of withstanding the stress induced during crystallization annealing. Conversely, the higher molecular weight homolog (RBAPB 97) exhibits increased tensile strength (up

to 122 MPa) upon annealing. Moreover, its elongation at break is less diminished compared to the crystallized lower molecular weight samples (RBAPB 93 and RBAPB 95), as detailed in Table 3. During crystallization annealing, the Young's modulus increases from 2500 to 3700 MPa.

4 | Conclusions

Moldings made of crystallizable polyimide R-BAPB with a molecular weight of 22 to 32 kg/mol were obtained using the injection molding method. The R-BAPB polyimides with molecular weights of not more than 30 kg/mol are suitable for injection molding. The molecular weight affects the thermal behavior of R-BAPB, such as melting point and crystallization rate, which must be taken into account for injection molding processing. There is a direct correlation between molecular weight and thermal properties. In particular, with an increase in molecular weight, the glass transition temperature and melting temperature increase slightly. At the same time, the degree of crystallinity of the samples decreases slightly. To obtain crystallized samples, additional annealing at 280°C is required; at this temperature, the maximum crystallization rate is achieved.

The R-BAPB samples obtained have a sufficiently high heat resistance ($\approx 560^\circ\text{C}$). The increase in molecular weight and the

appearance of a crystalline phase in R-BAPB samples leads to a slight decrease in the thermal expansion coefficient. The heat resistance of annealed, crystallized polyimide samples is significantly enhanced due to the formation of a crystalline structure. These samples can endure mechanical stress at temperatures approaching 260°C–270°C. The mechanical characteristics of R-BAPB moldings, such as breaking strength, tensile elongation, and elastic modulus, rise with increasing molecular weight. The crystallization annealing process allows for the production of molded polyimide products with a tensile strength of up to 122 MPa, an elastic modulus of ~3.5 GPa, and a tensile elongation close to 10%.

Author Contributions

Conceptualization: G.V. Methodology: G.V. and A.D. Formal analysis: G.V. Investigation: E.P. and A.K. Resources: A.D. and V.V. Data curation: G.V., E.P., and A.K. Writing – original draft preparation: G.V. and V.V. Writing – review and editing: G.V. and V.Y. Visualization: G.V. Supervision: V.Y. Project administration: V.Y. Funding acquisition: G.V.

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Data Availability Statement

The authors have nothing to report.

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