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# Melt Rheological and Bead Foaming Behavior of Recycled Polyethylene Terephthalate/Polybutylene Terephthalate Blends Modified with a Joncryl Chain Extender

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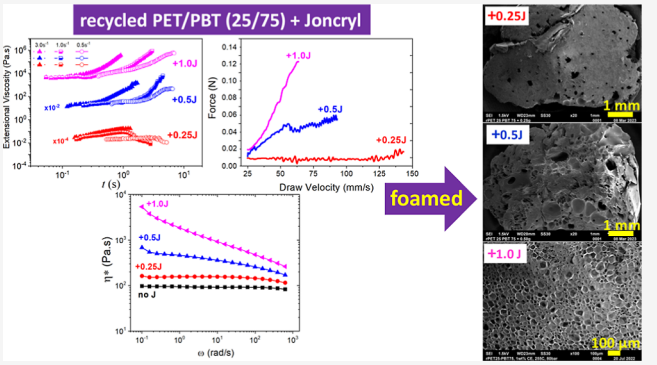
Cite This: *Ind. Eng. Chem. Res.* 2024, 63, 6222−6234



**ABSTRACT:** This study investigates the melt rheological properties and foamability of recycled polyethylene terephthalate (rPET) and its blends with polybutylene terephthalate (PBT) modified through an epoxy-based Joncryl ADR 4468 chain extender. A twin-screw extruder was used to prepare rPET/PBT blends at various weight ratios (i.e., 100/0, 75/25, 50/50, 25/75, and 0/100) and with varying Joncryl chain extender contents (i.e., 0.25, 0.5, 0.75, and 1.0 wt %). The small-amplitude oscillatory shear rheological experiments were conducted to analyze the melt viscoelastic behavior of the samples. The melt strength and strain-hardening behavior of the compounds were examined by measuring the extensional rheology and Rheotens tests. Crystallization analysis was conducted on the processed samples by using differential scanning calorimetry. The bead foaming behavior of the samples was investigated using a batch-based foaming reactor with supercritical $CO_2$. Both compounding with PBT and Joncryl chain modification increased the complex viscosity, melt strength, and strain-hardening behavior of the blends, while their synergistic effect revealed a more noticeable enhancement. Although direct modification of rPET with Joncryl and its direct compounding with PBT could not generate a meaningful foam structure, a homogeneous microcellular foam structure could successfully be induced when 25 wt % rPET was incorporated in blends with PBT modified with 1.0 wt % Joncryl.




## 1. INTRODUCTION

Plastics and their foam structures have been extensively used in commodity and engineering applications. Foam extrusion produces two-dimensional profiles of varying densities and expansion ratios, while foam injection molding creates complex three-dimensional shapes with limited expansions. Bead foaming, however, involves molding and sintering foamed beads, e.g., steam chest molding, to produce lightweight, low-density, three-dimensional foam products.[1] This technology combines extrusion foaming expansion capability with injection molding geometry complexity.[2] Over the years, bead foam products like expanded polystyrene,[3] polyethylene,[4] polypropylene (EPP),[5−8] thermoplastic polyurethane,[9−14] and polylactide (EPLA)[15−19] have been developed for a variety of applications. Nonetheless, existing bead foam materials have low heat resistance, limiting their use in high-temperature applications. In this context, despite their low melt strength and poor foaming ability, engineering plastics such as polyamide,[20] polybutylene terephthalate (PBT),[21−23] and polyethylene terephthalate (PET)[24−28] with high thermal resistance and satisfactory mechanical performance could be considered promising candidates to produce high-temperature-resistant bead foam structures.

PET, a widely used polyester since its first patent in 1949,[29] possesses favorable mechanical and chemical properties.[30,31] Despite the European Union's restrictions on single-use plastics,[32] global PET production continues to grow and contribute to the accumulation of plastic wastes.[33−36] Although recycling postconsumer PET is a key solution to alleviate this problem, recycled PET suffers from suppressed melt strength and processability due to thermal, chemical, and mechanical degradation.[36−40] To mitigate these issues, blending with virgin polymers and chemical modifications could offer a practical and cost-effective approach to restore lost property.[41]

Blending with PBT has been shown to be an effective route to recover the noted properties through enhancing the melt

Received: September 27, 2023
Revised: March 7, 2024
Accepted: March 22, 2024
Published: April 2, 2024







https://doi.org/10.1021/acs.iecr.3c03371
*Ind. Eng. Chem. Res.* 2024, 63, 6222−6234

viscosity, processability, and mechanical performance of rPET.[41−45] This is due to the high compatibility of PBT with PET as a result of their similar terephthalate backbone,[46] as well as the easier processability,[47,48] fast crystallization,[49,50] and good foamability[21,51] of PBT, which is in contrast with those features of PET. While PET and PBT are almost fully miscible in their amorphous phases,[52] the miscibility of their crystalline phases is highly dependent on the processing condition.[53,54] It has been shown that when the processed PET/PBT blends are fast-cooled, crystalline phases are immiscible, whereas slow cooling could cause the cocrystallization of PET and PBT, leading to the full miscibility of PET and PBT polymers.[54] Also, processing at higher temperatures or an increase in processing time could lead to transesterification among PET and PBT molecules, which further influences the occurrence of cocrystallization.[55]

Molecular weight loss through recycling further weakens the melt strength and processability of PET; hence, chain modification through chain extenders (CEs) can, to some extent, restore these losses. The chain modification of PET has been studied using various CEs, including isocyanides,[56,57] phosphites,[58,59] glycerol,[60,61] pyromellitic dianhydride,[62−69] epoxides,[41,54,57,68−80] and other customized chain modifiers.[81,82] The effectiveness of CEs depends on their functionality. Difunctional CEs enable linear chain extension, whereas multifunctional CEs allow for both chain extension and branching. Difunctional[70,71] and tetra-functional[72] epoxides have shown high reactivity with PET, which could increase PET's molecular weight and improve its melt rheological properties. Multifunctional epoxides such as Joncryl ADR exhibit further promising results in improving the melt properties of various polyesters, including rPET.[80] Joncryl ADR, an oligomeric CE with high functionality, introduces chain extension and branching, enhancing melt strength.[68,69,73] Studies have shown how the Joncryl modification could influence the crystallization kinetics[54] and processability[76−79] of rPET.

While melt blending with PBT or Joncryl chain modification can individually enhance certain features of rPET, only a few studies have investigated Joncryl-modified PET/PBT blend systems.[41,54,79] Guclu et al.[41] demonstrated that both blending with PBT and Joncryl modification improved the melt properties of rPET, and their combination generated a synergy, resulting in dramatic enhancements in rPET's melt rheological behavior. Joncryl modification of rPET/PBT blends could also influence the crystallization rate, consequently impacting the occurrence of cocrystallization or separate crystallization.[54] The enhanced melt properties achieved through blending with PBT and Joncryl modification could also address compatibility issues in glass fiber-reinforced rPET.[79]

Modified PET/PBT blend systems could be designed to manufacture high-temperature-resistant bead foams with a double crystal melting peak. Similar to the double crystal melting peak technology applied in EPP and EPLA bead foaming,[8,15−17] the generated double crystal melting peak would help to adjust the steam chest molding temperature between the melting peaks of PBT and PET, where unmolten PET crystals are expected to maintain the generated foam structure, while molten PBT crystals lead to strong intrabead sintering. Hence, while the chain modification and the PBT incorporation could improve the melt rheological properties and thereby the cell nucleation and cell growth stability, the generated double crystal melting peak would also be remarkably beneficial in the steam chest molding stage. In this context, while the foaming behavior of PET[24−28] and PBT,[21−23,51] with or without chain modification, has been explored in very limited studies, the foaming behavior of (r)PET/PBT blends or their chemically modified systems and their foaming dependency on the melt rheological properties have not been explored yet. This study elucidates the melt rheological properties and the resultant bead foaming behavior of Joncryl-chain-modified rPET/PBT blend systems using supercritical $CO_2$. Extensive shear and extensional rheological analyses were conducted to correlate them with the corresponding foaming behaviors. The foaming was conducted through a batch-based bead foaming reactor at various saturation pressures and temperatures, where foaming is induced. The crystallization behavior of the samples was also examined to evaluate the phase miscibility of the blend systems and explore its effect on the foaming behavior of the samples.

## 2. EXPERIMENTAL PROCEDURE

**2.1. Materials and Sample Preparation.** rPET flakes derived from postconsumer bottles and PBT granules were supplied, respectively, by Arçelik A.Ş. subsidiary (Istanbul, Turkey)[84] and Lanxess Co. (Cologne, Germany).[83,85] The weight-average molecular weight ($M_w$) of PBT and rPET were measured to be 62,300[85] and 44,000,[84] respectively. Joncryl ADR 4468 (referred to as Joncryl) from BASF SE (Ludwigshafen, Germany) was used as a chain modifier.[80] The reaction mechanisms of epoxide with polyesters[57] and the final expected molecular structures after Joncryl modification can be found in the literature.[80,85,86]

Unmodified and Joncryl-modified rPET/PBT blends were prepared in a laboratory-scale twin-screw extruder (TSE) (Gülnar Makina Ltd., Turkey) with a corotating screw diameter of 16 mm and an L/D ratio of 30. The processing rotation speed was set at 100 rpm, and the temperature profile was adjusted at 50−220−260−260−260−260 °C (from the hopper to the die). Prior to processing, all formulations were weighed, dry-mixed, and dried in a vacuum oven at 60 °C overnight. Loss-on-drying values were calculated as 0.15% (1500 ppm) for rPET and 0.05% (500 ppm) for PBT.[87]

The rheological testing samples were prepared by using a compression molding machine. Molding was conducted at 260 °C for 5 min under 1.5 ton pressure. In this study, the unmodified "rPET/PBT" and "rPET/PBT + Joncryl" blends were labeled based on their corresponding weight percentages such as "75/25" and "75/25 + 1.0J", respectively.

**2.2. Melt Rheological Analysis.** Small-amplitude oscillatory shear (SAOS) tests were conducted using an MCR-301 rotational rheometer (Anton Paar, Austria) equipped with a 25 mm parallel plate with a 1 mm gap. Frequency and time sweep experiments were performed at 260 °C under a nitrogen atmosphere. Frequency sweep experiments were conducted from a high-to-low frequency, which lasted 11 min. Time sweep experiments were carried out at 1.0 rad/s for 20 min. In all experiments, the strain amplitude was set at 5%, which was within the linear viscoelastic region.

The extensional viscosity of the samples was determined using an RDA3 rheometer from TA Instruments (RDA3, New Castle, USA) at 250 °C under a nitrogen atmosphere and strain rates of 0.5, 1.0, and 3.0 $s^{-1}$.

Melt strength experiments were further analyzed using Rheotens measurements. The granules were vertically extruded through a die ($l$ = 30 mm, $d$ = 2 mm) using a Rheograph 75 capillary rheometer from Göttfert Werkstoff-Prüfmaschinen GmbH (Buchen, Germany). Temperatures were selected to suit


https://doi.org/10.1021/acs.iecr.3c03371
Ind. Eng. Chem. Res. 2024, 63, 6222−6234

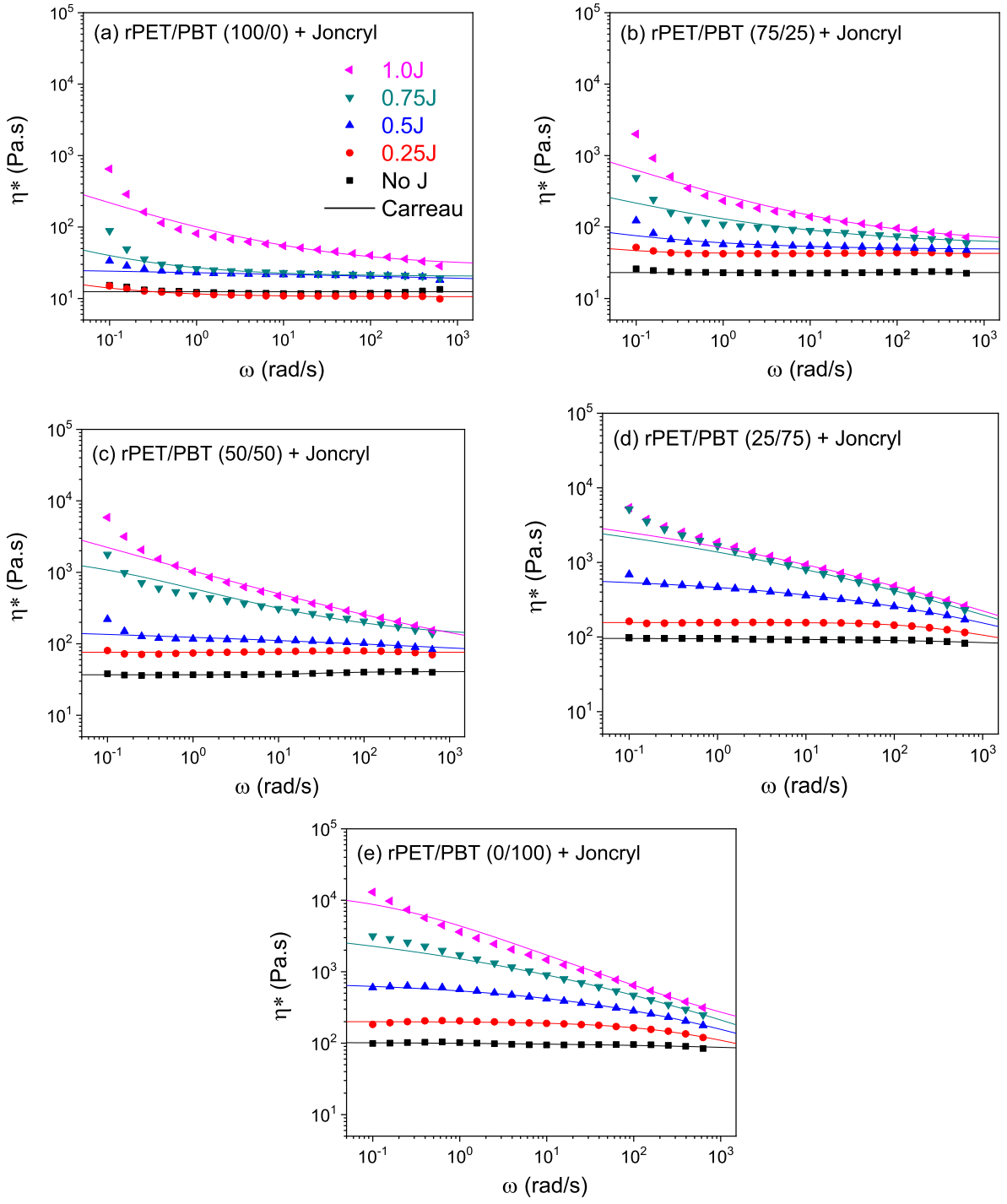



**Figure 1.** Complex viscosity versus frequency of unmodified and Joncryl-modified rPET/PBT blends with blending ratios of (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100 (measurements are conducted at 260 °C).

the blend formulations. The strand was pushed out at 0,208 mm/s and pulled between 25 and 1000 with an acceleration of 6 mm/s$^2$ by two counterrotating wheels of the Rheotens 71.97 device. In order to measure the tensile force applied to the elongated extrudate, the wheel pairs are connected to a force transducer, and the tensile force is then shown as a function of the draw velocity.[21]

**2.3. DSC Analysis.** The crystallization behavior of all rPET/PBT blends was investigated by using a Mettler Toledo differential scanning calorimeter (DSC1, Columbus, USA). The samples were heated from room temperature to 280 °C at 10 °C/min. The degree of crystallinity was calculated from the heating thermograms, considering the theoretical value of the heat of fusion of rPET ($\Delta H_m^0$ = 140 J/g) and PBT ($\Delta H_m^0$ = 145 J/g).[54]

**2.4. Batch-Based Bead Foaming.** The batch-based bead foaming experiments were conducted using a lab-scale reactor. The samples were placed in a preheated vessel and purged with supercritical $CO_2$. The saturation temperature range for foaming was set between 225 and 240 °C for PBT (0/100) and between 235 and 265 °C for rPET (100/0) and the rest of the other blend formulations. The saturation pressure was set between 120−140


https://doi.org/10.1021/acs.iecr.3c03371
Ind. Eng. Chem. Res. 2024, 63, 6222−6234

Table 1. Zero-Shear Viscosity ($\eta_0$) and Apparent Molecular Weight ($M_w$) Values of Unmodified and Joncryl-Modified rPET/PBT Blends

| sample name | no J | 0.25 J | 0.5 J | 0.75 J | 1.0 J |
|---|---|---|---|---|---|
| rPET/PBT (100/0) | | | | | |
| $\eta_0^*$ (Pa s) (Carreau−Yasuda) | 12 | 17 | 34 | 89 | 651 |
| apparent $M_w$ (g/mol) (power law) | 44,791 | 49,478 | 60,314 | 79,400 | 140,196 |
| rPET/PBT (75/25) | | | | | |
| $\eta_0^*$ (Pa s) (Carreau−Yasuda) | 13 | 51 | 123 | 490 | 2000 |
| apparent $M_w$ (g/mol) (power law) | 45,827 | 67,722 | 87,090 | 129,266 | 193,200 |
| rPET/PBT (50/50) | | | | | |
| $\eta_0^*$ (Pa s) (Carreau−Yasuda) | 37 | 76 | 224 | 1780 | 5869 |
| apparent $M_w$ (g/mol) (power law) | 61,789 | 75,898 | 103,360 | 186,873 | 262,778 |
| rPET/PBT (25/75) | | | | | |
| $\eta_0^*$ (Pa s) (Carreau−Yasuda) | 96 | 156 | 789 | 10,220 | 22,785 |
| apparent $M_w$ (g/mol) (power law) | 81,137 | 93,210 | 148,113 | 307,903 | 387,168 |
| rPET/PBT (0/100) | | | | | |
| $\eta_0^*$ (Pa s) (Carreau−Yasuda) | 104 | 205 | 751 | 6725 | 13,000 |
| apparent $M_w$ (g/mol) (power law) | 82,014 | 100,776 | 146,038 | 273,201 | 329,814 |

bar for PBT and between 80−120 bar for rPET and the blends. To ensure a constant saturation pressure, a Teledyne system was used to impregnate the samples with supercritical $CO_2$ (Isco 260D syringe pump, Lincol, USA).

**2.5. Foam Sample Characterization.** The density of the foamed samples was measured using Archimedes' principle. A Mettler Toledo analytical balance (AG245, Columbus, USA) equipped with a sieve and a water container was used for this purpose.

The foam morphology was examined by using a JEOL scanning electron microscope (JSM-6510, Akishima, Japan). Specimens were cut in half. The surfaces were sputtered with gold using a Cressington sputter coater (model 108 auto, Haarlem, the Netherlands) at a current of 30 mA for 60 s. The foam morphology was then characterized under a microscope at various magnifications.

## 3. RESULTS AND DISCUSSION

**3.1. Rheological Analysis.** Figure 1 illustrates the complex viscosities ($\eta^*$) of unmodified and modified blends. Both neat rPET and PBT revealed a wide Newtonian behavior when the complex viscosity of rPET (15 Pa s at 0.1 rad/s) was much lower than that of PBT (99 Pa s at 0.1 rad/s). The complex viscosity of the blends was also proportional to the corresponding weight fractions of rPET and PBT across the measured frequency range. The complex viscosity of the 75/25 and 25/75 blends at 0.1 rad/s increased from 26 Pa s to 97 Pa s, respectively. Moreover, the addition of Joncryl increased the complex viscosity of all samples, specifically at low frequencies, depicting a noticeable shear-thinning behavior.[41,68,69,73] The increase in Joncryl content more dramatically caused such viscosity increments and the corresponding shear-thinning behavior. In rPET-dominated formulations, Newtonian behavior was still more visible after sharp shear thinning at low shear rates. In PBT- and PBT-dominated blends, however, changes in shear-thinning behavior were more gradual as the Joncryl content increased. These differences in complex viscosity after Joncryl modification can be attributed to the higher initial molecular weight of PBT, resulting in stronger physical entanglements after Joncryl modification. On the other hand, chain modification of rPET with much lower inherent viscosity could not be very dominant to reflect a remarkable shear-thinning behavior. Hence, physical entanglements were still weaker in the modified rPET samples compared to those in their modified PBT counterparts.[41,73,74,87,88] It should also be noted that in Figure 1a, the similar melt behavior of 0.25 wt % Joncryl-modified PET to that of unmodified rPET could be generated from the dominancy of two competing parameters of chain modification with Joncryl and polycondensation that occur among the PET molecules.

To better understand the effect of Joncryl modification-related chain branching and molecular weight increase, the Carreau−Yasuda (eq 1) and power-law (eq 2) models were used. Through the Carreau−Yasuda model, zero-shear viscosity values were obtained, which were used to determine the apparent molecular weight. The following Carreau−Yasuda model was used

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}} \quad (1)$$

where $\eta_0$, $\eta_\infty$, $n$, $\dot{\gamma}$, $\lambda$, and $a$ are, respectively, zero-shear viscosity, infinite-shear viscosity, power exponent, shear rate, relaxation time, and transition control factor. It is important to note that an increase or decrease in complex viscosity values outside of the power-law region shifts the calculated zero-shear viscosity values accordingly. The power-law model is also given below

$$\eta_0 = K + M_w^\alpha \quad (2)$$

The power law between the zero-shear viscosity of linear molecules and weight-average molecular weight ($M_w$) is dependent on the pre-factor ($K$) and power exponent ($\alpha$). The power exponent was determined to be 3.5 from the literature,[65,68] and the prefactor was determined to be $6.2 \times 10^{-16}$ from the experimental values for unmodified rPET.[84] Zero-shear viscosity and apparent molecular weight values calculated from these models are presented in Table 1. It should be noted that the prefactor is calculated based on rPET, which causes PBT values to be calculated higher than their original value even for linear samples. Furthermore, it is known that experimental molecular weight values tend to be lower than apparent molecular weight values in branched molecules, and more branching (higher Joncryl content) causes this disparity to be higher.[65,68,89] The addition of both PBT and Joncryl increased the viscosity of rPET, with Joncryl showing a higher efficiency. While both PBT and Joncryl contributed to increased viscosity values, PBT solely increased the average $M_w$ in the blends, whereas Joncryl enhanced both $M_w$ and branching, leading to stronger physical entanglements.



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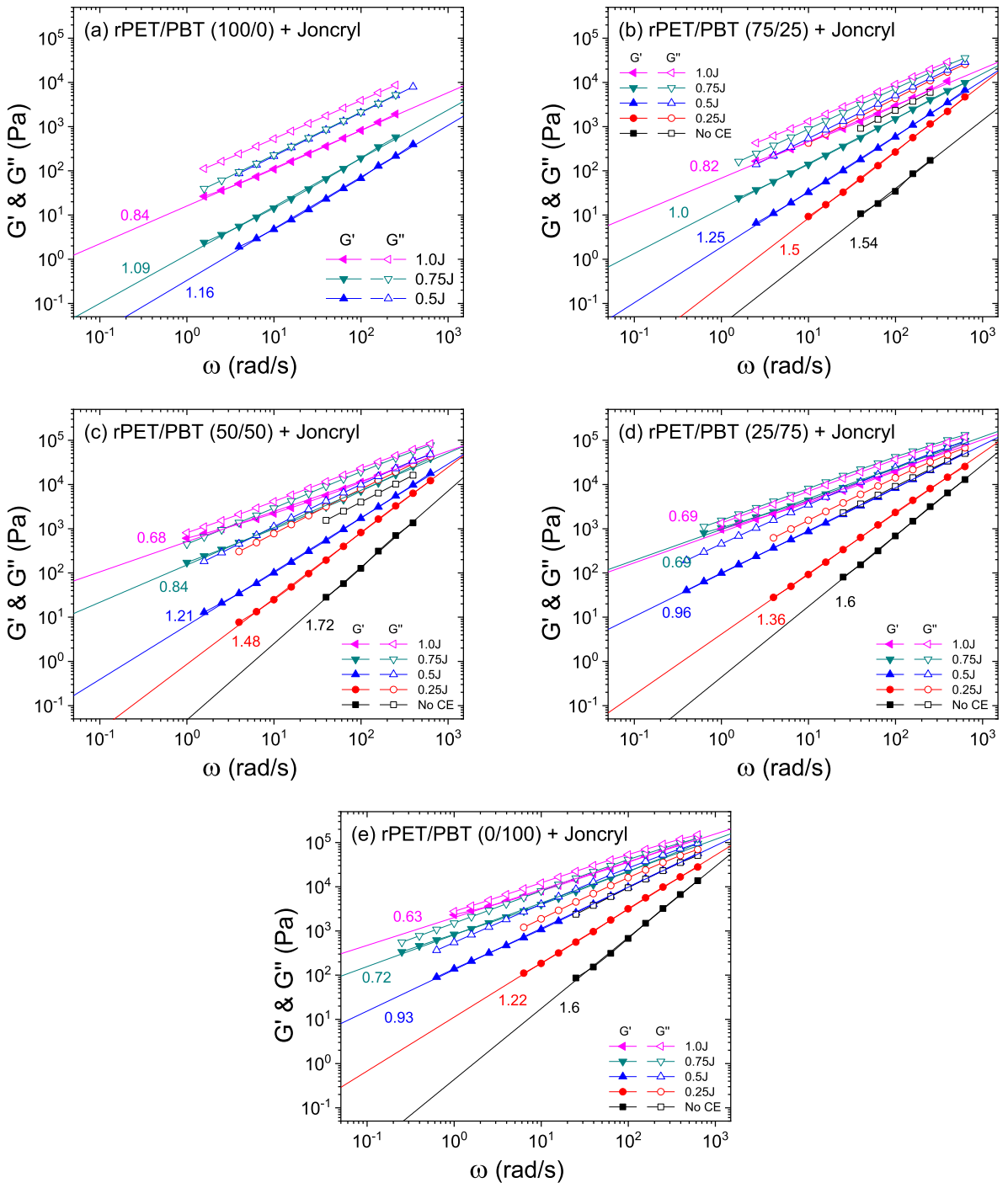


**Figure 2.** Storage modulus versus frequency of unmodified and Joncryl-modified rPET/PBT blends with blending ratios of (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100 (measurements are conducted at 260 °C).

Figure 2 shows the storage ($G'$) and loss ($G''$) moduli of unmodified and modified blends. The fitted curves on $G'$ were used for calculating the slope, which can be used to understand the changes in physical entanglements. It can be seen that unmodified rPET and PBT had $G'$ low frequency slopes higher than 1 and closer to 2, which is typical for linear molecules, and this behavior was also similar to unmodified miscible blends. Joncryl modification reduced the $G'$ slopes of all samples, which shows that branching has occurred with higher modification, causing a greater degree of change in the slopes as more branches are formed. The difference in physical entanglement strength between rPET and PBT also becomes clearer with Joncryl modification, where the storage modulus slopes of PBT decrease more than those of rPET. This difference could stem from the initial molecular weight differences where rPET, having been recycled, has shorter molecules and forms shorter branches when compared to those of PBT, resulting in weaker physical entanglements.

Figure 3 shows the SAOS time sweep experimental results. The complex viscosity of neat rPET (100/0) increased over time due to polycondensation among PET molecules. While Guclu et al.[41] illustrated this phenomenon, they also reported that such a



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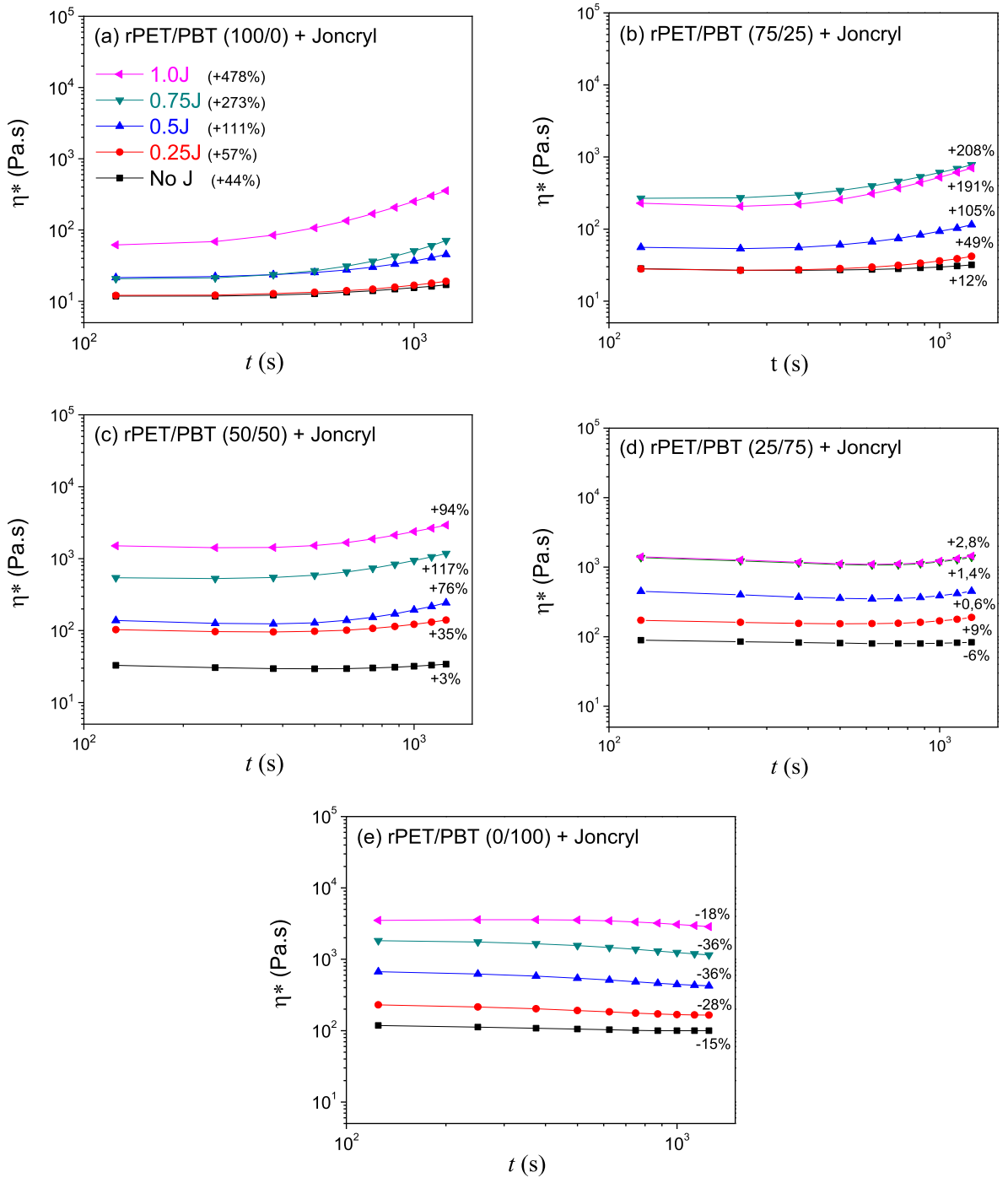


**Figure 3.** Complex viscosity versus time of unmodified and Joncryl-modified rPET/PBT blends with blending ratios of (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100 (measurements are conducted at 260 °C).

polycondensation reaction expedites at higher testing temperatures. In contrast, as shown in Figure 2e, PBT (0/100) encountered a steady degradation over time. Joncryl modification, however, increased the initial viscosity of all samples, while such an increase was more dominant in PBT-dominated blends. Joncryl modification in rPET-dominated samples also increased the samples' viscosity more dominantly over time. This is more remarkable in neat rPET. Such a remarkable viscosity increase over time in rPET and rPET-dominated samples modified with Joncryl could stem from the combined effect of polycondensation among PET molecules and further reaction of the remaining unreacted Joncryl molecules with rPET.[41] In a previous study,[85] it was shown that the majority of reactions between PBT and 1.0 wt % Joncryl molecules occur within the first 3 min, and afterward, the degradation becomes dominant. This was explained as increasing molecular weight and degree of branching hindering the diffusion and reactivity of Joncryl. Furthermore, higher CE content can cause high amounts of gel to form,[68,69,74] which can further hinder diffusivity. Similarly, in PBT-dominated samples, specifically in the neat PBT, the viscosity increase over time was not observed with Joncryl modification and degradation becoming dominant over time.[87]



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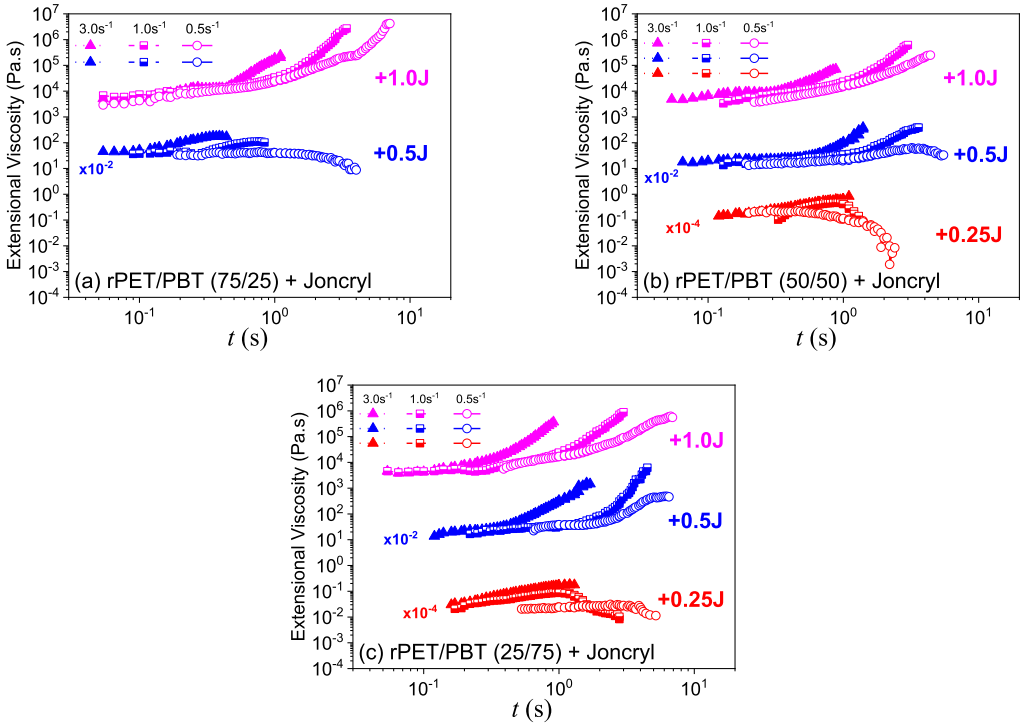


**Figure 4.** Extensional viscosity versus time of Joncryl-modified rPET/PBT blends with various blending ratios of (a) 75/25, (b) 50/50, and (c) 25/75 (measured at 250 °C).

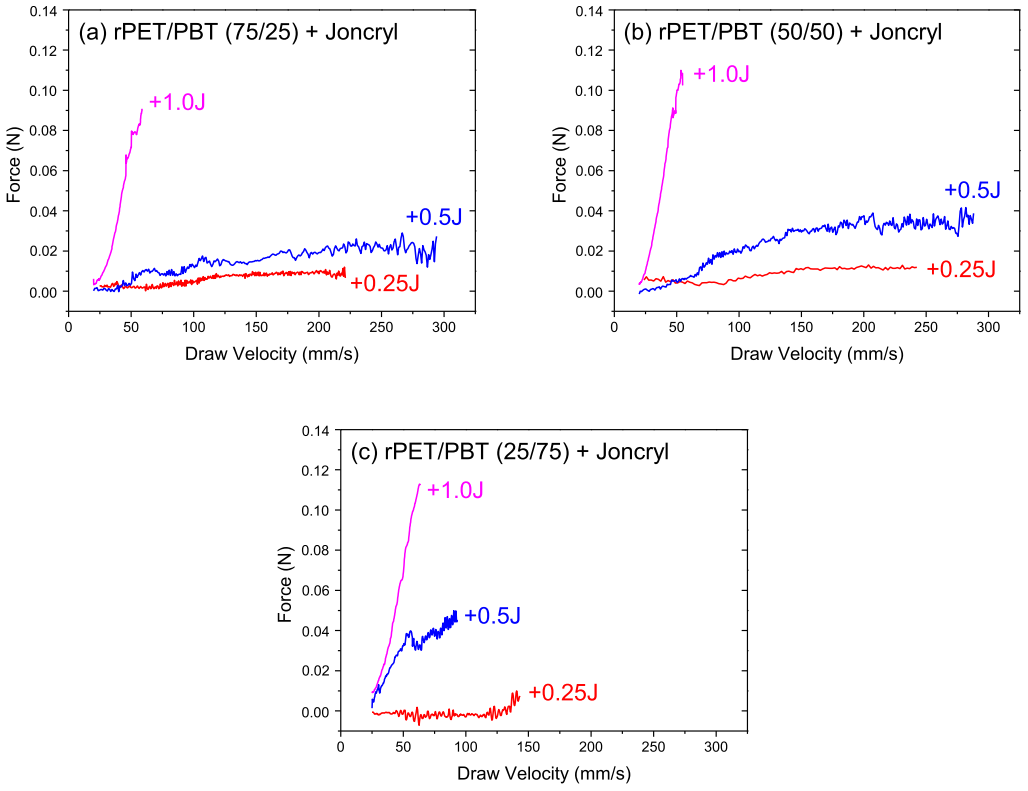


**Figure 5.** Draw velocity versus draw force of Joncryl-modified rPET/PBT blends with various blending ratios of (a) 75/25, (b) 50/50, and (c) 25/75.

Extensional viscosity can be correlated more closely with foaming behavior where higher extensional viscosity values correspond to more cell stability during the cell growth with minimized cell coalescence and more homogeneous foam expansion.[65,68,69,90] Figure 4 shows the extensional viscosity of the Joncryl-modified rPET/PBT blends. While the extensional viscosity results of PBT (same grade as used in this study) are reported elsewhere,[21] no usable data could be obtained from the unmodified and modified rPET samples due to their extremely low melt strength. While it was also not possible to run



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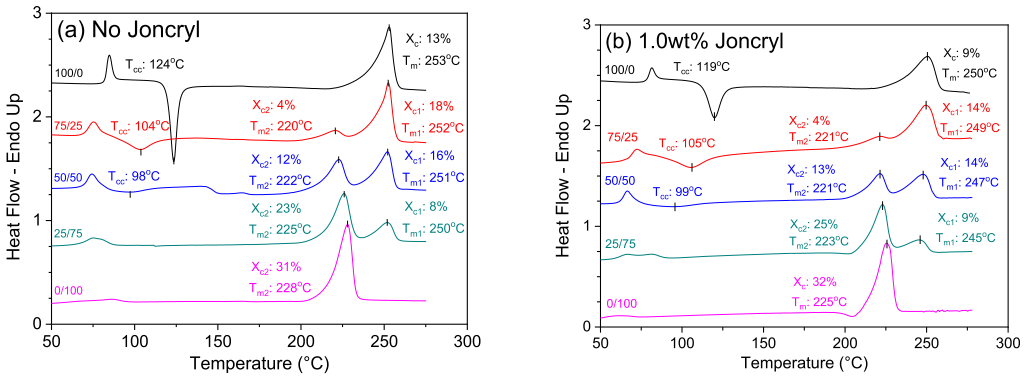


**Figure 6.** First heating DSC thermograms of all blends with and without 1.0 wt % Joncryl modification.

measurements for unmodified blends as a result of the low melt strength of incorporated rPET, results could be obtained for Joncryl-modified blends (except rPET/PBT with 0.25 J) due to the synergistic effect of blending and Joncryl modification. While Joncryl addition could dramatically enhance the extensional viscosity as well as the strain-hardening behavior, PBT addition with a higher viscosity could proportionally increase the extensional viscosity of the blend. It can be seen that the Joncryl content increase resulted in higher extensional viscosity, strain hardening, and melt strength that are essential for foaming.[21] While the strain hardening was quite noticeable in all blends with 1.0 wt % Joncryl, such improvement with 0.5 wt % Joncryl was observed more significantly in blends with higher PBT contents. With 0.25 wt % Joncryl, no significant enhancement in strain hardening was detected.

Since the extensional viscosity measurements could not really illustrate noticeable melt strength differences among the modified blends, Rheotens measurements were also employed to further clarify the difference among the melt strengths of the samples. Figure 5 illustrates the Rheotens measurements of the Joncryl-modified rPET/PBT blends. Similar to the results obtained from the extensional rheology measurements, unmodified neat and blend samples and all modified rPET samples were unable to generate any tangible readings from the device because of their very low melt strength. The experiments could again be conducted only on modified blends. According to Figure 5, in all modified samples, the Joncryl content increase up to 1.0 wt % induced a significant enhancement in the melt strength and strain hardening of all blends. Moreover, the PBT-dominated blend (i.e., 25/75) showed strain-hardening behavior at even lower Joncryl contents, which is consistent with the shear rheological experiments where Joncryl modification leads to higher complex viscosities. These results are consistent with those shown in Figure 4. As will be discussed in Section 3.3, the foam morphology of the PBT-dominated blend was also much finer and more homogeneous when compared to that of other blend systems.

**3.2. DSC Analysis.** While rPET and PBT are miscible in their amorphous phases, the miscibility of the crystalline phases is highly dependent on the applied cooling rate.[54] Since the foaming experiments are performed with the processed samples, it is essential to analyze the differential scanning calorimetry (DSC) first heating thermograms. Figure 6 depicts the first heating thermograms of fast-cooled unmodified and Joncryl-modified blends. In all blends, the fast-cooled samples revealed two distinct melting peaks that belong to PBT and rPET, reflecting the immiscibility of crystalline phases. Joncryl modification does not also influence the miscibility of the crystalline phases.[54] Joncryl modification, specifically with 1.0 wt %, reduced the cold crystallization of rPET and reduced the degree of crystallinity of neat rPET. On the other hand, during the first heating cycle, while the rPET sample demonstrated distinct cold crystallization behavior, increasing PBT content improved the crystallization rate of the blends and hindered the cold crystallization occurrence. Therefore, as PBT content increased in blends, the faster crystallization in PBT-dominated blends could better contribute to the cell nucleation during the foaming step.

Moreover, with Joncryl modifications, both double melting peaks of the blends were slightly shifted to lower temperatures, indicating the less perfection of the crystallites with the induction of chain extension and branching in the blends.[54,91,92] Possible transesterification reactions among rPET and PBT in the presence of Joncryl could also reduce the symmetry of the polymer backbone, thereby shifting them to lower temperatures.[58,93]

To demonstrate the miscibility and immiscibility of the crystalline phases subsequent to slow or fast cooling, Figure 7

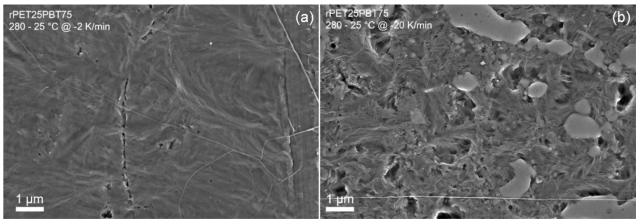


**Figure 7.** SEM images of the (a) slow-cooled (2 K/min) and (b) fast-cooled (20 K/min) unmodified rPET/PBT (25/75) blend.

presents the scanning electron microscopy (SEM) micrographs of the 25/75 blend subsequent to slow (Figure 7a) and fast (Figure 7b) cooling conditions. While a homogeneous structure was observed in the slow-cooled sample, distinct, separate phases are detectable in the fast-cooled case, which supports the earlier DSC results. In a previous study, it was demonstrated that when the processed PET/PBT blends are fast-cooled, crystalline phases are immiscible, whereas slow cooling could cause the cocrystallization of PET and PBT, leading to the full miscibility of PET and PBT polymers.[54] The crystallization kinetics of the 25/75 blend sample, which confirms our discussion, is comprehensively studied elsewhere.[94]

**3.3. Bead Foaming Behavior.** Figure 8 shows the cellular morphology of the bead foams of rPET and blend samples


https://doi.org/10.1021/acs.iecr.3c03371
Ind. Eng. Chem. Res. 2024, 63, 6222−6234

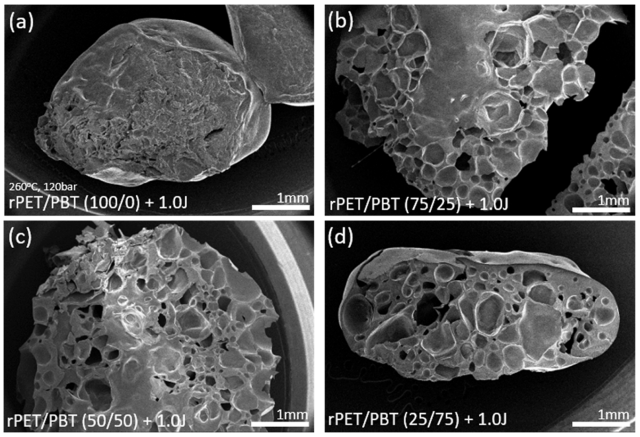


**Figure 8.** SEM micrographs of rPET and blend samples modified with 1.0 wt % Joncryl (saturation was conducted at 260 °C, 120 bar, and 30 min).

modified with 1.0 wt % Joncryl obtained under a given saturation condition (260 °C, 120 bar, and 30 min). rPET failed to form any cellular structure even after using 1.0 wt % Joncryl, which is expected according to results obtained from the extensional rheology and Rheotens measurements. A similar behavior was also seen in unmodified blends where foaming was either unsuccessful (75/25, 50/50) or foam structures were barely achievable (25/75) (not shown here). However, as shown in Figure 8, the modified blends could be foamed when modified with 1.0 wt % Joncryl. This is due to the induced higher melt strength, which prevents catastrophic cell collapse and coalescence.

Figure 9 shows the foam morphology of the modified 50/50 blends with various Joncryl contents under a given saturation

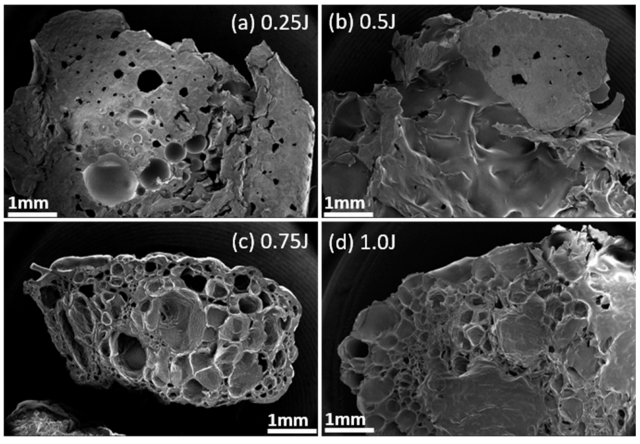


**Figure 9.** SEM images of a 50/50 blend with various Joncryl modifications foamed at 260 °C and 80 bar after 30 min of saturation.

condition (260 °C, 80 bar, and 30 min). The use of 0.25 and 0.5 wt % Joncryl was not very effective in inducing any foam structure due to the very low melt strength (Figures 3 and 4). However, the increase in Joncryl content to 0.75 and 1.0 wt % enabled the formation of some cellular structures, although they are still not considered homogeneous foam structures. The existence of rPET with low melt strength within the blend seems to be still very effective in preventing the formation of a uniform foam structure under various foaming conditions.

Figure 10 shows the foam morphology of all blend formulations (100/0, 75/25, 50/50, 25/75, and 0/100) modified with 1.0 wt % Joncryl. The foam density of each case is also presented in the same figure. It should be noted that each sample underwent a series of foaming experiments with various saturation conditions to identify the foaming window for each formulation separately. Figure 11 illustrates the effect of various saturation temperatures on the density of the bead foams of the unmodified and 1.0 wt % Joncryl-modified samples. Both in unmodified and modified rPET samples, the saturation temperature had no discernible effect on bead foam density. This is due to the very low melt strength of rPET even after Joncryl modification. The foam structure of 1.0 wt % Joncryl-modified rPET could only be obtained in one condition (i.e., 265 °C, 120 bar, and 30 min), and the cellular morphology of this foamed sample is shown in Figure 10a. According to the SEM images shown in Figure 10, with the decrease in rPET content, more homogeneous foam structures could be induced, and in 25/75 and 0/100 cases, even microcellular foam structures could be obtained with densities of about 0.28 and 0.09 g/cm$^3$, respectively. Figure 11 shows that the bead foam density of the blends, specifically PBT-dominated cases, reduced with the increase in saturation temperature, specifically when modified with 1.0 wt % Joncryl. This is due to the synergistic effect of blending with PBT and Joncryl modification, which remarkably improves the strain-hardening behavior and increases the melt strength of the modified samples. Furthermore, the foaming window appears to be wider in PBT dominated blends when modified with 1.0 wt % Joncryl.

Figure 12 shows the bead foam densities of blends modified with various Joncryl contents. As also discussed earlier, the density of rPET with various Joncryl contents could not be reduced noticeably as foaming could not properly occur. On the other hand, blends have shown much lower densities even with low amounts of Joncryl modification, stemming from the much higher melt strength of PBT and its synergistic effect with Joncryl. Increasing Joncryl modification allowed lower densities to be obtained by preventing cell collapse as a result of both higher melt strength and inducing strain-hardening behavior. While higher melt strength prevents widespread cell collapse during foaming, the strain-hardening behavior both provides stable cell growth and restricts the viscoelastic contraction from occurring, which could further decrease the foam density.

## 4. CONCLUSIONS

This study comprehensively investigated the rheological, thermal, and bead foaming behaviors of Joncryl-modified rPET/PBT blends. Reactive compounding through a twin-screw extruder and subsequent foam preparation in a lab-scale autoclave using supercritical $CO_2$ as a blowing agent were employed. SAOS rheological experiments revealed that, even after Joncryl modification, rPET maintained lower viscosity compared to that of PBT. Despite the Joncryl modification of PBT, rPET exhibited noticeable shear-thinning behavior due to its initially low molecular weight. Time sweep SAOS experiments indicated degradation dominance in PBT over time, while rPET exhibited a significant increase due to polycondensation. Joncryl modification increased complex viscosity values, especially in PBT-dominant systems. In Rheotens and extensional rheology experiments, Joncryl modification proved to be more effective, particularly in PBT-dominant systems. DSC thermograms indicated that Joncryl modification decreased crystal melting temperatures and total crystallinity, attributed to


https://doi.org/10.1021/acs.iecr.3c03371
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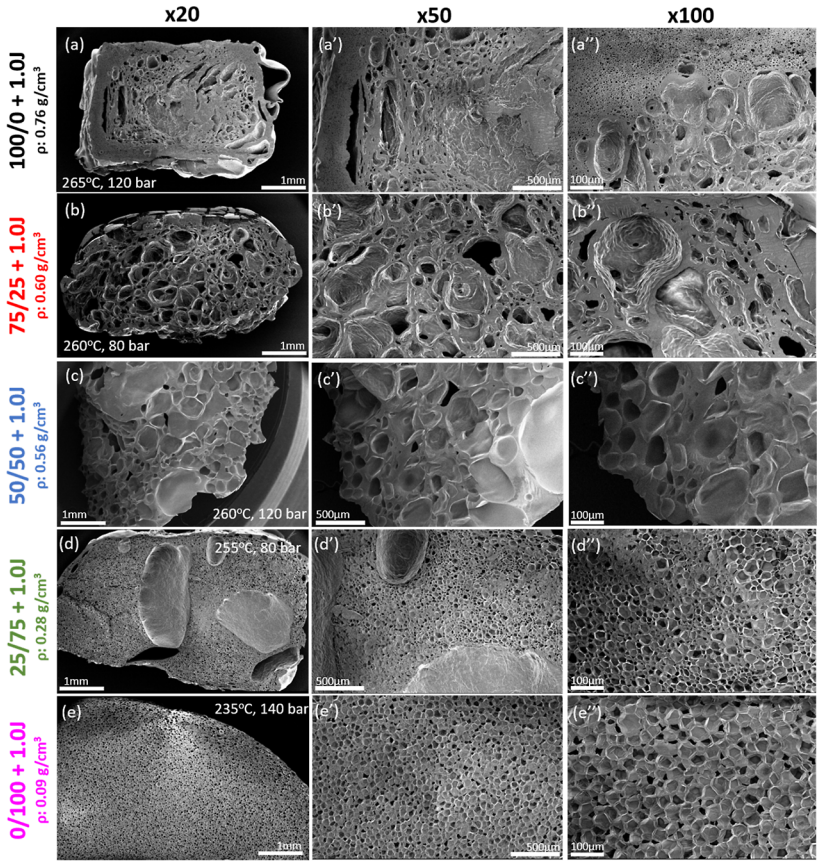


**Figure 10.** SEM images of 1.0 wt % Joncryl-modified formulations at (a−e) 20×, (a′−e′) 50×, (a″−e″) 100× magnifications.

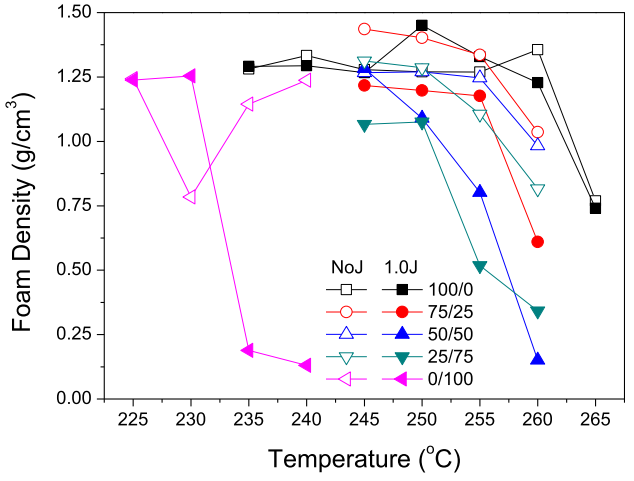


**Figure 11.** Bead foams' density of all unmodified and 1.0 wt % Joncryl-modified formulations at various saturation temperatures (note: neat rPET and PBT densities are about 1.3 g/cm$^3$).

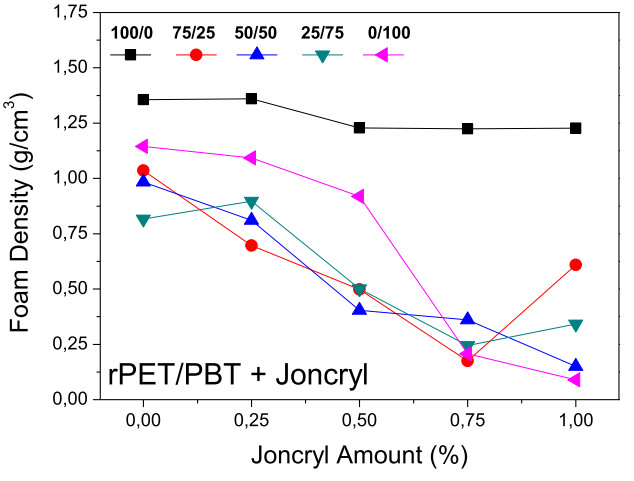


**Figure 12.** Bead foam densities of all formulations with various Joncryl contents. Saturation conditions of rPET and blends were at 260 °C and 80 bar and PBT was at 235 °C and 140 bar.

the reduced crystal packing degree and perfection with branching. For foamability, unmodified rPET and blends lacked cellular structure even with 1.0 wt % Joncryl. However, 1.0 wt % Joncryl-modified blends homogeneously foamed, more pronounced with increased PBT content, resulting in lower final foam densities, particularly in PBT-dominant blends. The lowest-density foam with the finest cell size was observed in Joncryl-modified neat PBT. Still, a microcellular foam structure with about a 4-fold reduction in foam density was induced in the 25/75 + 1.0 wt % Joncryl sample. Consequently, incorporating rPET in modified blends offers an alternative to obtain microcellular foams using recycled PET products in conjunction with PBT and a Joncryl chain modifier.

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https://doi.org/10.1021/acs.iecr.3c03371
*Ind. Eng. Chem. Res.* 2024, 63, 6222−6234

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support provided by the Scientific and Technological Research Council of Turkey (TUBITAK) with project no. 220N342 and the German Research Foundation (DFG) with grant no. AL 474/51-1. We also thank the support provided by the Turkish Academy of Sciences (TÜBA)—Outstanding Young Scientists Award (GEBİP). We would also like to acknowledge Burcu Özdemir, Catharina Stierle, and Janina Rebhan for supporting us in running some of the experiments.

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https://doi.org/10.1021/acs.iecr.3c03371
*Ind. Eng. Chem. Res.* 2024, 63, 6222−6234