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Research Article

Investigation of the Structural and Mechanical Properties of PET for the Development of Hydrogen Storage Tank Liner Materials

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Abstract: The aim of this study is to investigate the structural and mechanical properties of PET-based materials for potential use as liner materials in high-pressure hydrogen storage tanks. The research focuses on the effect of post-heat treatment, which influences the crystallinity of PET and, consequently, its mechanical behavior. Standardized specimens produced by injection molding were heat treated at 120 °C and 150 °C for different durations (5, 10, 15, and 30 minutes), followed by rapid quenching in ice water to stop the crystallization process. The degree of crystallinity was determined using differential scanning calorimetry (DSC), while mechanical properties were evaluated through tensile testing. According to the results, higher heat treatment temperature significantly increased the crystallinity and improved the tensile strength, while reducing elongation. Based on the findings, the optimization of heat treatment parameters offers an opportunity to fine-tune the properties of PET, and may serve as a basis for future gas barrier and permeability studies.

Keywords: PET; heat treatment; crystallinity; tensile strength; DSC analysis; hydrogen storage; liner material

I. INTRODUCTION

Hydrogen, as a clean and high-energy-density carrier, plays a key role in future sustainable energy systems. One of the fundamental prerequisites for the widespread use of hydrogen technology is its safe and efficient storage, which is currently most commonly achieved in high-pressure tanks. In so-called Type IV pressure vessels, the inner liner material is of crucial importance, as it ensures gas-tightness and separates the stored hydrogen from the external composite reinforcement. In the development of liner materials, not only mechanical resistance but also hydrogen permeability, processability, and thermal and long-term stability must be considered [1], [2].

The aim of the present study is to investigate polyethylene terephthalate (PET)-based liner materials with properties suitable for hydrogen storage applications. One of the main advantages of PET is that its structure especially the degree of crystallinity can be adjusted by post-heat treatment, offering a way to tailor material properties for specific requirements. Increased crystallinity may reduce gas permeability, but it also affects mechanical behavior, which must be carefully balanced [3], [4].

In this phase of the research, we investigate the effect of post-heat treatment on the structure and mechanical performance of PET. The objective is to identify heat treatment parameters (temperature and duration) that optimize crystallinity without significantly compromising mechanical performance. In the long term, the goal is to fine-tune PET properties toward the development of a liner material suitable for hydrogen storage tanks.

II. LITERATURE REVIEW

The storage of compressed hydrogen gas is one of today’s key technological challenges, especially in automotive applications. Throughout the development of storage vessels, several tank types have been introduced, differing in material composition, weight, and performance. Type I tanks are made entirely of metal, while Type II tanks consist of a metallic body partially reinforced with composite materials. Type III tanks incorporate a thin-walled metal liner fully wrapped with composite reinforcement. The widely used and technologically advanced Type IV tanks feature a completely polymer-based inner liner surrounded by a full composite shell. In contrast, the latest development, the Type V tank, is entirely linerless composed solely of composite material, with the composite structure itself responsible for gas containment [1], [2].

The present research focuses on the development of polymer liner materials for Type IV hydrogen storage tanks, with particular attention to the structural and mechanical properties that influence performance. The liner plays a critical role in Type IV tanks, as it ensures gas-tightness and separates the stored hydrogen from the load-bearing composite structure. This separation prevents hydrogen-induced damage such as cracking, material fatigue, and delamination [1], [2].

An increasing number of studies focus on optimizing liner materials. Kis et al. [3] emphasize that while many investigations concentrate solely on external factors such as pressure, temperature fluctuations, and cyclic loading the behavior of the liner is also strongly influenced by internal parameters, including structural configuration, crystallinity, molecular weight distribution, and processing conditions. According to their findings, liner performance is the result of complex interactions, and understanding it requires a thorough consideration of the material’s internal structural characteristics. The Ishikawa diagram presented in their study (**Fig. 1**) clearly illustrates the interrelationship between external and internal factors contributing to liner collapse [3].

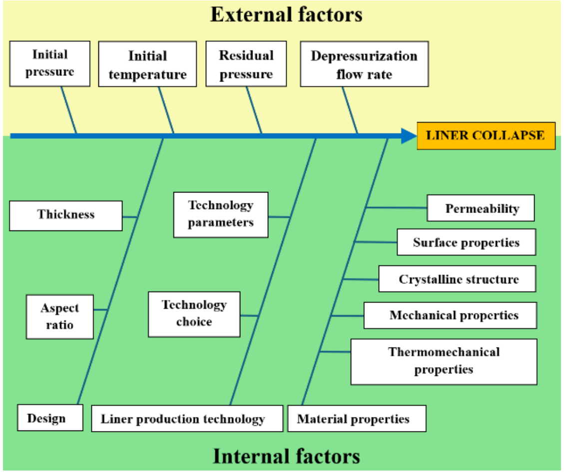

Figure 1. *Ishikawa diagram illustrating the factors influencing liner collapse. Based on [3].*

Research on polyamide 6 (PA6)-based liner materials has brought significant advances in hydrogen storage technology and has also laid the foundation for our current research direction. However, the focus of the present study is on polyethylene terephthalate (PET), which is considered a promising alternative for several reasons. One of the advantages of PET is its lower hydrogen permeability[5], which is a critical factor for meeting the gas barrier requirements of Type IV pressure vessels. This advantage is supported by the findings of Smith et al. [5], who conducted a comprehensive comparative study on various liner materials used in Type IV hydrogen storage vessels. Their results showed that blow-molded PET exhibited significantly lower hydrogen permeability than the other tested liner materials, making it a promising alternative for applications where gas barrier performance is critical. These findings are illustrated in **Fig. 2**.

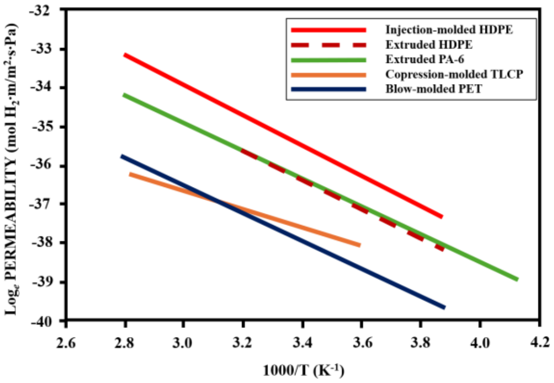

Figure 2. *Temperature dependence of the hydrogen permeability for four tank liner polymers and one thermotropic liquid crystal polymer (TLCP). Based on [5].*

Another advantage is its favorable cold crystallization behavior, which enables the crystallinity to be adjusted by post-heat treatment [4].

Studies conducted by Hiroyuki Kanesugi and co-workers [6] confirmed that an increase in the degree of crystallinity of PET reduces hydrogen permeability. According to their results, crystalline regions act as physical barriers to the diffusion of hydrogen molecules, thus a higher crystallinity level contributes to improved gas barrier properties an essential factor in the selection of liner materials [6].

In the investigation of the structural characteristics and mechanical behavior of PET, Panagiotis G. Karagiannidis and his team [7] conducted fundamental work. In their study, they thoroughly analyzed the relationship between the degree of crystallinity and the mechanical properties under different heat treatment conditions. Differential scanning calorimetry (DSC) was employed to determine the ratio of crystalline and amorphous phases. In addition to tracking changes in crystallinity, tensile tests were performed to evaluate the evolution of strength and deformation characteristics [7].

Further insights into the relationship between structure and mechanical properties were obtained by Fourier-transform infrared spectroscopy (FTIR), which enabled the identification of molecular bonds specific to crystalline and amorphous phases. This method proved particularly useful in independently verifying the degree of crystallinity and provided a deeper understanding of structural changes in PET induced by heat treatment [7], [8], [9].

Hiroyuki Kanesugi and colleagues [6] also developed a hydrogen permeability model specifically for crystalline polymers, which is particularly relevant for high-pressure hydrogen storage. Their model suggests that hydrogen permeability decreases with increasing crystallinity, as crystalline regions act as diffusion barriers for hydrogen molecules. To better understand the enhancement of gas barrier properties, the authors employed various characterization methods, including high-pressure hydrogen permeability tests (HPHP) and low-pressure Temperature Desorption Analysis (TDA), pressure-volume-temperature (PVT) measurements, DSC analysis, and wide- and small-angle X-ray scattering (WAXS and SAXS) [6], [10].

The crystalline layer thickness was determined using the Scherrer equation, while the lamellar spacing was measured by SAXS. These complex measurements aimed to provide a detailed description of the organization of the crystalline structure in PET and its effect on hydrogen permeation. Density measurements of the samples also played an important role in validating the permeability model. The experimental data were interpreted using a modified Nielsen model, which allowed for the estimation of the permeability properties of samples with varying degrees of crystallinity [6], [11].

The comparison of different gas permeation models can help in understanding how the structure of polymer materials particularly the ratio of crystalline and amorphous phases affects hydrogen diffusion. **Fig. 3** presents the most common models found in the literature, illustrating various structural configurations and permeation mechanisms [6]

The tortuosity model describes how gas molecules must travel along a winding path through the structure, where crystalline regions acting as fillers significantly increase the diffusion path length. In the series model, gas passes sequentially through layers with different permeabilities. In contrast, the parallel model assumes that the gas can simultaneously move through multiple types of layers. The spherical dispersion model represents a case where filler particles are distributed in a spherical arrangement within the matrix, thereby hindering the motion of gas molecules [6].

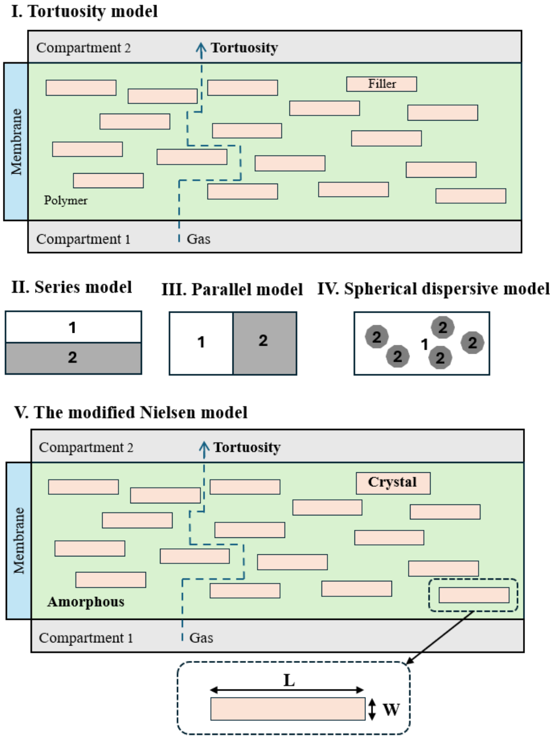

Figure 3. *Gas permeation models: (I.) Tortuosity model; (II.) Series model; (III.) Parallel model; (VI.) Spherical dispersion model; (V.) Modified Nielsen model. Based on [6].*

The modified Nielsen model, applied by Kanesugi and co-workers, integrates the effects of tortuosity, free volume, and pressure dependence. Its novelty lies in treating the crystalline regions as impermeable fillers, while the amorphous regions are considered as diffusion pathways. This approach allows for a more accurate estimation of gas barrier properties at different levels of crystallinity. The model is particularly relevant for PET, as its gas barrier performance strongly depends on the distribution and proportion of crystalline and amorphous phases [6].

The reviewed literature results confirm that properly heat-treated PET can be a suitable liner material for Type IV hydrogen storage vessels. The strong relationship between crystallinity and mechanical properties, as well as the structural parameters influencing gas barrier behavior (such as tortuosity and free volume), support the idea that the PET microstructure can be deliberately tailored through heat treatment. Building upon these insights, the aim of the present study is to investigate the effect of post-heat treatment on the degree of crystallinity and the mechanical properties of PET. The goal is also to define heat treatment parameters that can optimize PET’s properties for future gas barrier and permeability studies, contributing to the development of a long-term viable liner material [6], [7], [8], [9].

III. MATERIALS AND METHODS

1. Raw Material

For the investigations, a food-grade PET (polyethylene terephthalate), NEOPET 80, manufactured by Neo Group (Lithuania), was used. The raw material was available in granulated form and was primarily developed for injection molding and bottle manufacturing applications. According to the manufacturer's technical data sheet, the intrinsic viscosity was 0.80 ± 0.02 dl/g, and the melting temperature was 248 ± 4 °C. The advantages of NEOPET 80 include low acetaldehyde formation, high transparency, and excellent processability.

In selecting the material, a primary consideration was that it possesses structural and processing properties suitable for post-heat treatment, enabling targeted adjustment of the crystallinity to develop a structure optimized for gas barrier properties.

2. Sample Preparation and Heat Treatment Protocol

The raw material was processed into test specimens by injection molding according to the ISO 527-2 Type 1A standard, following prior drying and applying the processing parameters recommended by the manufacturer. The shape and dimensions of the specimens ensured compliance with the standard requirements for mechanical testing. During sample preparation, particular care was taken to ensure consistent processing conditions, allowing the effects of heat treatment on material properties to be evaluated in isolation.

The post-heat treatment was carried out in a laboratory oven at 120 °C and 150 °C for holding times of 5, 10, 15, and 30 minutes. The selected parameters aimed to investigate the influence of temperature and time on the crystallization process. After heat treatment, the specimens were immediately quenched in ice water to halt further crystallization and to prevent post-crystallization or deformations due to slow cooling.

3. Tensile Testing

Mechanical tests were conducted using an Instron 3366 universal testing machine, in accordance with ISO 527-1 and ISO 527-2 standards. The measurements were performed at room temperature on standard Type 1A test specimens.

Preliminary tests were carried out on untreated specimens at various crosshead speeds (5, 10, 20, 50, 100, 200, and 500 mm/min) to determine the most suitable testing speed for the evaluation of heat-treated samples. The results showed the expected trends: an increase in tensile strength and a decrease in elongation with increasing testing speed. Taking into account the observed scatter and the stability of the mechanical behavior, a testing speed of 10 mm/min was selected for the comparative evaluation of the heat-treated specimens.

Fig. 4 illustrates the tensile curves of untreated PET specimens tested at a crosshead speed of 10 mm/min. Due to the variations in elongation at break, the evaluation was limited to the determination of the Young's modulus and the stress at yield.

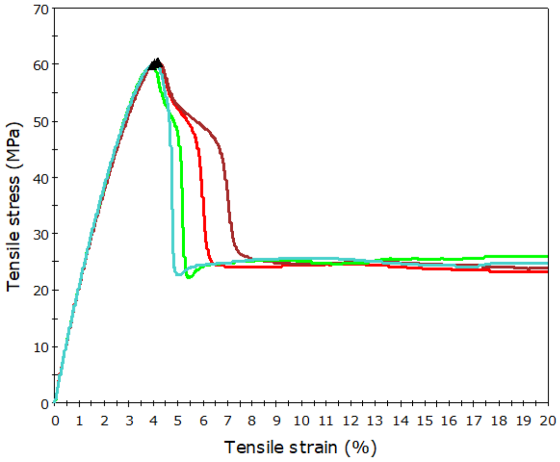

***Figure 4.** Tensile stress–strain curves of untreated PET specimens tested at a crosshead speed of 10 mm/min.*

4. DSC Analysis

The degree of crystallinity was determined using a TA Instruments Q200 differential scanning calorimeter (DSC). Measurements were carried out under a nitrogen atmosphere, following a heating–cooling–heating cycle between 30 °C and 280 °C at a heating/cooling rate of 20 °C/min. For the analysis, samples were consistently taken from the core region at the end of the flow path of the injection-molded specimens to ensure uniform thermal history and crystallization state.

The degree of crystallinity was calculated using the following equation (Equation 1):

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \qquad (1)$$

where:

- ΔH_m is the melting enthalpy J/g
- ΔH_c is the cold crystallization enthalpy [J/g]
- $\Delta H_m^0 = 140\ J/g$ is the melting enthalpy of 100% crystalline PET [J/g]

Fig. 5 shows a typical first heating curve of a sample taken from an untreated PET specimen. The curve clearly reveals the glass transition, the cold crystallization (exothermic peak), and the melting (endothermic peak), which serve as the basis for the calculation of the degree of crystallinity.

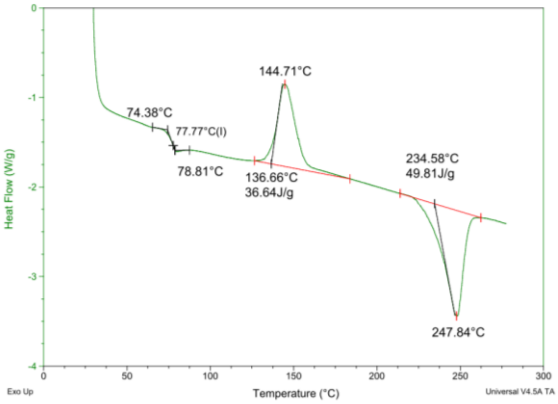

Figure 5. *First heating DSC curve of an untreated PET specimen, showing the glass transition, cold crystallization, and melting peaks.*

IV. RESULTS

1. Change in Crystallinity as a Function of Heat Treatment

The results of the differential scanning calorimetry (DSC) analysis of the PET specimens are summarized in **Table 1**. The table shows that the degree of crystallinity of the untreated sample was only 9%. Heat treatment at 120 °C caused only a moderate change in crystallinity, with values ranging between 11.9% and 13.2% depending on the holding time. This indicates that the cold crystallization process did not proceed fully at this temperature.

In contrast, heat treatments performed at 150 °C resulted in a significant increase in crystallinity. After a short holding time of 5 minutes, the degree of crystallinity already reached 30.2%, and with longer heat treatment times it increased up to 36%. The ΔH_c values of cold crystallization significantly decreased for these samples and completely disappeared with longer holding times, indicating that crystallization had already completed during the heat treatment.

Based on these results, it can be concluded that the crystallinity of PET can be significantly increased through appropriate heat treatment, although the application of suitable temperature and duration parameters is necessary. Heat treatments around 150 °C effectively promote crystallization, which is expected to have a beneficial effect on the mechanical and gas barrier properties of the material. The change in the degree of crystallinity as a function of heat treatment duration is illustrated in **Fig. 6**.

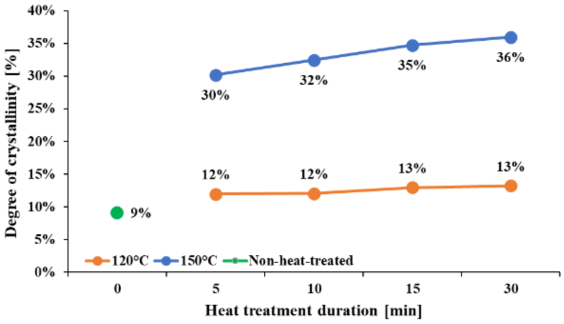

Figure 6. *Change of the degree of crystallinity of PET specimens as a function of heat treatment duration at 120 °C and 150 °C.*

2. Evolution of Mechanical Properties after Heat Treatment

The results of the tensile tests performed on the PET specimens are summarized in **Table 2**. The changes in the values of Young's modulus and yield stress were evaluated as a function of the heat treatment parameters, taking the standard deviations into account.

Table 1. *Results of DSC analysis for PET specimens after different heat treatment conditions.*

Heat treatment	Cold crystallization		Melting		Degree of crystallinity
	T_c	ΔH	T_m	ΔH	X_c
	[°C]	[J/g]	[°C]	[J/g]	[%]
Non-heat-treated	145	36.64	248	49.71	**9.1**
120°C 5min	145	31.34	248	48.54	**11.9**
120°C 10 min	140	31.75	248	49.09	**12.0**
120°C 15 min	142	29.59	248	48.27	**13.0**
120°C 30 min	132	32.64	249	51.69	**13.2**
150°C 5min	128	2.85	248	46.32	**30.2**
150°C 10 min	156	3.07	248	49.82	**32.5**
150°C 15 min			247	50.02	**34.7**
150°C 30 min			248	51.81	**36.0**

Table 2. *Young's modulus and yield stress values of PET specimens after different heat treatment conditions.*

Heat treatment	Young's modulus E [MPa]		Stress at Yield σy [MPa]	
	Mean	SD	Mean	SD
Non-heat-treated	**2178**	*11.4*	**60.3**	*0.31*
120°C 5min	**2297**	*83.7*	**52.3**	*2.26*
120°C 10 min	**2533**	*31.6*	**64.3**	*0.33*
120°C 15 min	**2494**	*49.6*	**65.2**	*0.45*
120°C 30 min	**2535**	*31.0*	**65.8**	*0.24*
150°C 5min	**2014**	*109.4*	**51.8**	*0.39*
150°C 10 min	**2162**	*58.8*	**51.2**	*2.03*
150°C 15 min	**2128**	*42.3*	**50.6**	*2.56*
150°C 30 min	**1944**	*104.2*	**51.3**	*0.92*

In the case of Young's modulus, the specimens heat-treated at 120 °C exhibited a slight increase in modulus over time; however, due to the relatively high standard deviations, these changes cannot always be considered significant. For the specimens treated at 150 °C, the modulus increase observed after 10 and 15 minutes of holding time was detectable even within the error bars, suggesting a probable positive change. In contrast, a decrease in modulus after a 30 minute holding time was considered significant, even when taking the scatter into account. The evolution of the Young's modulus values is illustrated in **Fig. 7**.

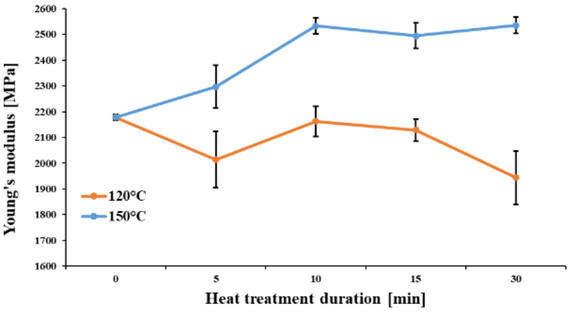

Figure 7. *Change of Young's modulus of PET specimens as a function of heat treatment duration at 120 °C and 150 °C.*

In the case of yield stress, the specimens heat-treated at 120 °C showed minor changes; however, due to the high standard deviations, these changes cannot be considered significant. For the specimens treated at 150 °C, the increase observed after a 10 minute holding time was reliably detectable even when considering the error bars, and the values remained at a similar level for the 15-30 minute treatments. This suggests that the increase in crystallinity had a positive effect on the yield stress values as well. The change in yield stress is illustrated in **Fig. 8**.

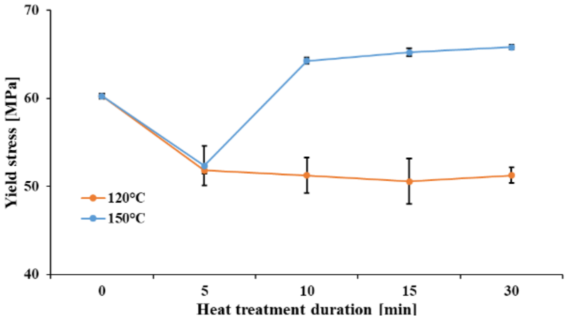

Figure 8. *Change of yield stress of PET specimens as a function of heat treatment duration at 120 °C and 150 °C.*

Overall, it can be concluded that heat treatment at 150 °C, particularly with 10-15 minutes of holding time, improved the mechanical properties, while no clear trend could be observed for the treatments performed at 120 °C due to the large scatter in the results.

3. Relationship between Crystallinity and Mechanical Properties

The relationship between the degree of crystallinity and the mechanical properties is illustrated in **Figs. 9** and **10**.

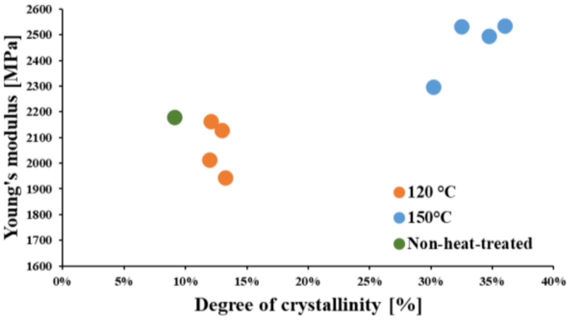

Figure 9. *Change of Young's modulus of PET specimens as a function of the degree of crystallinity.*

As shown in **Fig. 9**, the Young's modulus generally increases with the degree of crystallinity, particularly for the specimens heat-treated at 150 °C. In the specimens treated at 120 °C, however, only minor changes were observed, which can be attributed more to the relaxation of internal stresses rather than to any significant structural rearrangement due to the relatively low degree of crystallinity. Based on the results, it can be concluded that heat treatment at 120 °C functioned primarily as a stress-relief process and did not result in substantial cold crystallization.

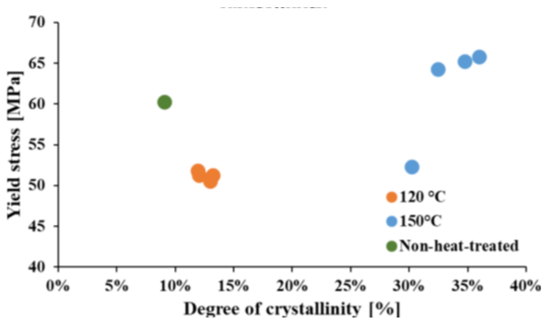

Figure 10. *Change of yield stress of PET specimens as a function of the degree of crystallinity.*

In **Fig. 10**, the variation of yield stress as a function of the degree of crystallinity is presented. It is clearly visible that specimens with higher crystallinity particularly those heat-treated at 150 °C generally exhibit higher yield stress values. In the case of the specimens treated at 120 °C, the decrease in yield stress also indicates that significant crystallization did not occur and that the effect of the heat treatment was primarily limited to stress relief.

Thus, the results demonstrate that the mechanical properties of PET are closely related to the formation of a crystalline structure and that by applying appropriate heat treatment parameters, the desired mechanical behavior can be deliberately adjusted.

V. CONCLUSIONS

The aim of the present research was to investigate the structural and mechanical properties of polyethylene terephthalate (PET) under the effect of post-heat treatment, with special emphasis on changes in the degree of crystallinity. Based on the investigations, it can be concluded that the heat treatment temperature and duration have a significant impact on both the degree of crystallinity and the mechanical behavior.

Heat treatments performed at 120 °C did not result in substantial crystallization; however, their stress-relieving effect contributed to the stabilization of mechanical properties. In contrast, heat treatments at 150 °C led to a significant degree of cold crystallization, which manifested in an increase in the Young's modulus and an improvement in the yield stress values.

The examination of the relationship between crystallinity and mechanical properties confirmed that the structure of PET can be deliberately modified by heat treatment. By applying appropriate temperature and time parameters, mechanical resistance and likely gas barrier properties as well can be improved, which is critical for the development of PET-based liner materials for hydrogen storage tanks.

Future research will aim to further refine the heat treatment parameters, to perform a detailed investigation of permeability properties, and to evaluate the long-term mechanical stability of the material.

AUTHOR CONTRIBUTIONS

P. Hansághy: Conceptualization, Experiments, Theoretical analysis, Writing

F. Ronkay: Review and editing.

A. Bata: Supervision, Review and editing.

DISCLOSURE STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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