Annales de Chimie - Science des Matériaux
Vol. 48, No. 5, October, 2024, pp. 721-727
Journal homepage: http://iieta.org/journals/acsm

Effect of High Processing Temperature on the Rheological and Morphological Properties of Recycled Polypropylene

Noor Alhuda Sabah Jassim[1*], Marwa A. Anber[2], Salah M S Alhar[3]

[1] Department of Mechanical Technical, Al-Mussaib Technical Institute, Al-Furat Al-Awsat Technical University, Babylon 54001, Iraq
[2] Material Engineering Department, College of Engineering, Mustansiriyah University, Baghdad 14022, Iraq
[3] Prosthetic Dental Techniques Department, Najaf Technical institute, Al-Furat Al-Awsat Technical University, Najaf 54001, Iraq

Corresponding Author Email: huda24576@gmail.com

https://doi.org/10.18280/acsm.480513

Received: 2 March 2024
Revised: 16 August 2024
Accepted: 29 August 2024
Available online: 29 October 2024

Keywords:
polypropylene, injection molding, rheology, morphology, recycling

ABSTRACT

This study investigates the effect of high processing temperatures used in the medical syringe factory in Iraq on some rheological and morphological properties of polypropylene. Ten samples consisting of 50% virgin (pure) PP and 50% recycled PP were processed. The mold temperature was varied in the range of 190°C to 210°C, while maintaining the pressure and secondary time at 78 bar and 0.5 seconds, respectively. The results showed that the density decreased by 45% as the injection temperature increased. In contrast, the Melt Flow Index (MFI) increased by 60% with rising injection temperatures. The results also indicated a severe effect of high processing temperatures on the samples, which was evident in the FTIR test, where the intensity of the peaks changed significantly compared to virgin PP. The DSC test revealed that the Tg value increased to 15.1°C for recycled PP, compared to 9.8°C for the virgin sample.

1. INTRODUCTION

Plastics fall into four main categories: thermoplastics, elastomers, thermosets, and polymer compounds. The class and physical properties of a plastic are determined by its macromolecular structure. Elastomers and thermosets exhibit soft and hard elasticity, respectively, with resins that cannot be melted for recycling. On the other hand, thermoplastics can be either amorphous or semi-crystalline, with amorphous resins having disordered macromolecules, such as polycarbonate and polystyrene, while semi-crystalline resins, such as polyamide and polypropylene, have nearly ordered macromolecules embedded with crystalline phases. Our focus here is on polypropylene, a semi-crystalline plastic [1].

Discovered in 1954, polypropylene (PP) quickly gained popularity for being the least dense among commodity plastics. With excellent chemical resistance, PP can undergo various processing methods, such as injection molding and extrusion. Catalytically prepared from propylene, its notable advantage lies in its high-temperature resistance, making it ideal for sterilizable items in clinical settings. PP, a downstream petrochemical product derived from propylene, is created through addition polymerization. This process involves combining propylene monomers using heat, radiation, and an initiator or catalyst. The polymerization routes include solution, suspension, bulk, and gas-phase methods, which influence polypropylene (PP) properties based on conditions, copolymer components, molecular weight, and distribution. As a vinyl polymer, polypropylene stands out with every carbon atom linked to a methyl group [2]. Polypropylene, a key material among polyolefins, holds significance for three main reasons: its exceptional properties—low density, high melting temperature, chemical inertness, and cost-effectiveness—make it optimal for long-life applications. Polypropylene is highly versatile, allowing for diverse structural designs and mechanical properties. Different morphological structures of PP can be achieved by using fillers, reinforcing agents, and blending with other polymers, resulting in superior characteristics [3]. Typically, melt temperatures are adjusted within the range of 165°C to 250°C. In traditional injection molding, lower melt temperatures can lead to a reduced Young's modulus, primarily due to the presence of pellets. However, in thin section moldings, rapid cooling induces high molecular orientation, potentially outweighing the effect of pellets and favoring low melt temperatures for achieving heightened stiffness. Additionally, lower melt temperatures may enhance impact resistance in thick section moldings produced at elevated mold temperatures, where a higher phase content tends to be observed [4, 5].

The optimal mold temperature for processing polypropylene (PP) is 60°C. Mold temperatures below this value yield a thick skin with a layer of premature pellets. The term 'skin' refers to the region displaying premature pellets, including a very thin layer with an oriented morphology resulting from extensional flow, as described in Tadmor's model for mold cavity filling [6]. Processing cycles may lead to the deterioration of PP properties. Diminishing degradation during processing is crucial to maintaining or enhancing material properties. By preventing degradation, PP can be utilized for higher-quality applications, increasing recycling profitability and the recycling ratio. The three main degradation mechanisms are thermal, mechanical, and thermal oxidative. A precise understanding of each mechanism is crucial for effective prevention. Recycling primarily affects melt viscosity, which is associated with an increase in melt flow rate (MFR) and a decrease in molecular weight [7]. Efficiently addressing environmental pressure, recycling PP offers various technical solutions. Mechanical and chemical recycling, with mechanical recycling being predominant, involve milling post-consumer goods, followed by extrusion and pelletizing. Despite PP's favorable properties, easy processability, and cost-effectiveness, substantial degradation occurs during melt processing and exposure to environmental factors. Incorporating a robust stabilizing system in the initial material can mitigate thermo-oxidative and mechanical degradations during processing and use [8].

The properties of recycled polypropylene include: Density: Typically ranges between 0.90 and 0.93 g/cm³.Melting Point: Around 160-170°C.Flexibility: Good, but may be slightly reduced compared to virgin polypropylene. Stiffness: Young's Modulus is typically between 1000 and 1500 MPa. Tensile Strength: Generally, ranges from 20 to 30 MPa. Water Absorption: Very low, usually less than 0.03%. Chemical Resistance: Maintains strong resistance to acids, alkalis, and oils. Color and Appearance: May vary slightly depending on the source material and recycling process. Hardness: Typically, between 60 and 80 Shore D. Thermal Stability: Slightly lower compared to virgin polypropylene, particularly after multiple recycling cycles.

In this research, the morphology and flow properties of samples from the medical syringe factory in Iraq will be studied, as they face problems in processing syringes due to the addition of recycled polypropylene to the injection shipment. Some of these problems relate to the shape and transparency of the syringes, while others pertain to their rough surface finish. This research includes studies on the effect of high temperature on recycled polypropylene, given the significant impact of high temperature on polypropylene, which indicates thermal deformation. The increase in temperatures of recycled polypropylene leads to changes in properties such as superior hardness, high hardness, scratch resistance, and a large bending modulus. High temperatures have notable effects on the rheological and morphological properties of recycled polypropylene. Here are the key impacts:

1. Viscosity and Melt Flow: High temperatures can cause thermal degradation in recycled polypropylene, leading to a decrease in molecular weight. This degradation reduces viscosity and increases the melt flow rate of the polymer. The material becomes less viscous and more fluid, which can affect its processability during manufacturing [9].
2. Shear Thinning Behavior: Recycled polypropylene tends to exhibit more pronounced shear thinning behavior at elevated temperatures. This means that under shear stress, such as during injection molding, the viscosity decreases more significantly compared to virgin polypropylene [10].
3. Crystallinity: High temperatures can reduce the overall crystallinity of recycled polypropylene. The repeated heating and cooling cycles during recycling disrupt the crystalline regions within the polymer, leading to a more amorphous structure. This reduction in crystallinity can affect the material's mechanical strength and thermal stability [10].
4. Phase Morphology: The morphology of recycled polypropylene can change with high temperatures, particularly when it is blended with other polymers or fillers. For example, when polypropylene is blended with polyethylene or other polymers, high temperatures can influence the phase separation and compatibility between the different components, resulting in varying morphological properties [11].

2. MATERIALS USED

Polypropylene (PP) was used, with formation temperature ranges between 220 and 280°C. The melt flow index (MFI) value for this material is between 20 and 25 g/sec [12], and its technical specifications are PP J 801. The PP used in the study was not entirely virgin; instead, it was a blend comprising 50% virgin PP and 50% recycled PP (the factory's regular shipment), incorporating byproducts like runners, sprues, and gates from the production process. Tests were performed on this material using an MFI device, and the results were recorded. The MFI for virgin polypropylene is 24.9 g/10 min, which is within the permissible limit.

Using a 50% blend of virgin polypropylene and 50% recycled polypropylene in a study on the impact of cold and hot molds on mechanical and rheological properties serves several purposes:

Performance Comparison: This ratio allows for a clear comparison of how the properties are affected when using virgin versus recycled materials. It helps measure the extent to which mechanical and rheological properties change with recycled content.

Balance Between Quality and Sustainability: A 50/50 blend aims to balance the final product's quality with environmental sustainability. Virgin materials usually offer better mechanical and rheological properties, while recycled materials reduce environmental impact.

Mold Effect Study: When forming materials in cold or hot molds, the final properties may vary depending on the content of virgin and recycled materials. The 50/50 mix helps assess how each material type influences these properties under different manufacturing conditions.

Improving Final Properties: Some studies use different ratios of virgin and recycled materials to enhance the final product's properties. A 50/50 ratio provides a good starting point to explore the overall performance impact of this blend.

In summary, using a 50/50 mix of virgin and recycled polypropylene allows for a comprehensive study of how different manufacturing conditions affect the mechanical and rheological properties of the material.

3. EXPERIMENTAL PART

A measured mixture of 50% virgin PP and 50% recycled PP was charged into the hopper of the injection molding machine. The parameters of the processing machine are mentioned in Table 1. The samples were manufactured using a Korean-made JMI/SPI-150 injection machine with a mold closing force of 150 tons, which consists of a three-part mold with dimensions of 450 x 500 x 436 cm and contains 24 cavities. Initially, five cycles of PP products were manufactured to establish operational stability, after which samples were selected for additional testing.

Table 1. The injection molding process parameters

No. of Sample	Secondary Time (sec)	Processing Temperature (°C)	Holding Pressure (bar)
1	0.5	210	78
2	0.5	208	78
3	0.5	206	78
4	0.5	205	78
5	0.5	202	78
6	0.5	200	78
7	0.5	198	78
8	0.5	195	78
9	0.5	193	78
10	0.5	190	78

A Chinese MIF device by SHI JIA ZHUANG ZHONG SHI was used to determine the degree of fluidity of the polypropylene used (PP 801). The temperature of the device was set at 230°C, which is the melting point of polypropylene, using a standard load of 2.16 kg. This is according to the international standard ASTM D 1238. The FTIR test was performed using a device of Japanese origin (Kyoto, Japan), manufactured by Shimatzu Corporation, type IRAFFINITY-1. The Scanning Electron Microscope (SEM) images were analyzed for both the sample with the highest and lowest injection molding operation temperatures. This comparison, achieved through two images captured at 500x and 10,000x magnifications, aimed to provide a comprehensive understanding of the temperature's impact. The SEM device was of Czech origin and manufactured by TESCAN. To measure the density of the manufactured samples, a factory device produced by MASTUHAKU Company, model (GP-120S), was used. The device was of Chinese origin. The electronic scanning calorimetric DSC device was utilized to determine the extent of the changes occurring in the sample's thermal properties (Tm, Tg, Tc) under the injection conditions recorded in Table 1. The device was of Swiss origin, manufactured by Mettler Toledo, model (DSC1).

4. RESULTS AND DISCUSSION

4.1 FTIR and SEM results

Sample No. 1 in Table 1 was used for these tests. By examining Figure 1, the FTIR diagram for polypropylene, the figure highlights a disparity in peak intensity between pure virgin PP and the diagram of the sample influenced by parameter variations. This distinction is attributed to elevated temperatures causing alterations in the polymer, thereby accounting for the observed difference. Accordingly, the absorption of recycled PP will decrease with increasing processing temperature because, with increasing temperature, more molecules will occupy excited vibrational states. This means that the absorption coefficient will decrease with increasing temperature [13].

The morphology of PP observed in the SEM images (Figure 2) shows a significant change between virgin PP and recycled PP. From examining the images, the surface of virgin PP has a smoother finish compared to recycled PP (as shown in Figure 3). This is a strong indication of the negative effect of recycled additives and their poor mechanical properties.

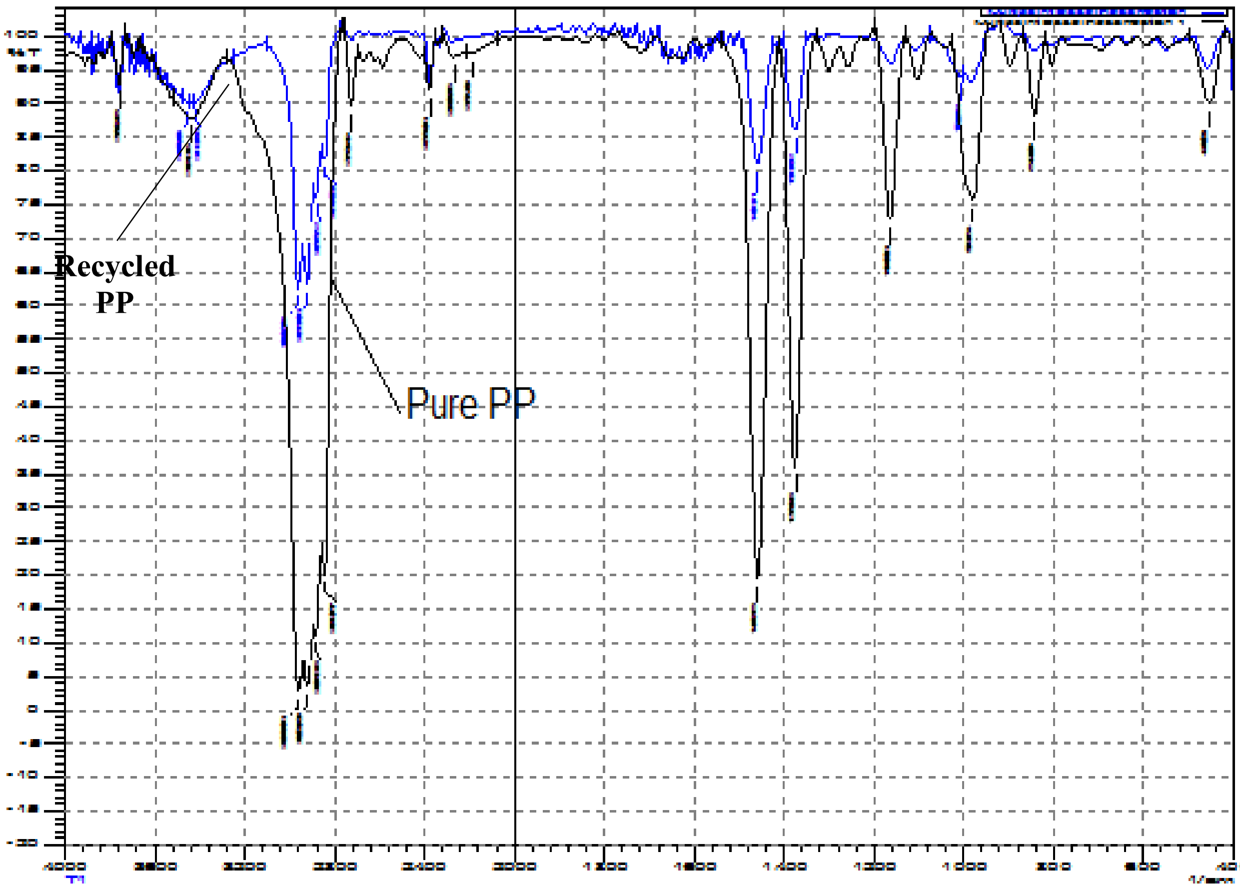

Figure 1. FTIR images of virgin (pure) PP + recycled PP at 210°C

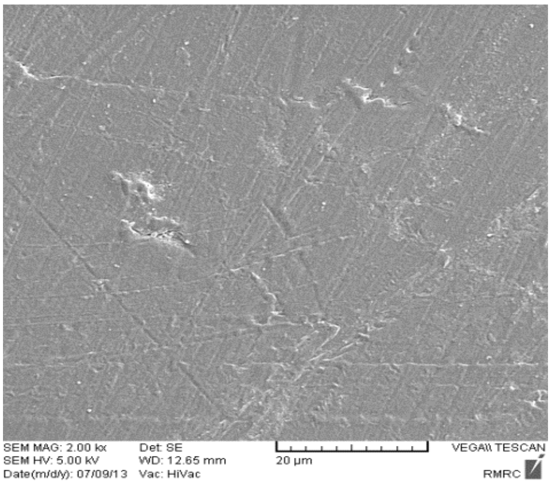

Figure 2. SEM image of virgin (pure) PP + recycled PP at 210°C

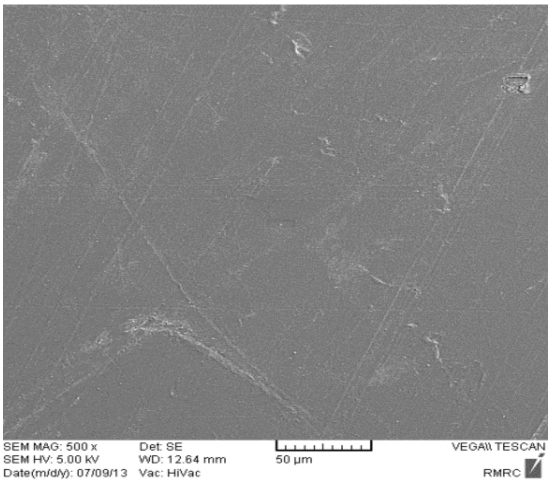

Figure 3. SEM image of virgin (pure) PP at 210°C

4.2 DSC (Differential scanning calorimetric)

The DSC results at high processing temperatures for PP are given in Figure 4 and Figure 5. It is noted that the heat value of the reaction reached 163.62°C, while in the case of virgin PP, this value reached 163.34°C. In the case of the exothermic reaction, it was found that the heat value of the sample produced at a variable temperature reached 121.22°C. However, in the case of virgin PP, it reached 120.61°C. From these results, it was noticed that both reactions of the recycled PP produced at a high processing temperature are slightly higher than in the case of virgin PP. This is evidence that the change in temperature has led to this difference due to the change in the crystalline structure of the produced sample. The reason for this difference is the possibility of chain breaking in the produced sample as a result of the high injection temperature [14]. However, when observing the Tg value, we find that it has increased significantly to 15.10°C in the case of changing the temperature compared to the original sample, whose Tg value reached 9.8°C. This change occurs because the polymer chains became more regular as a result of the heat, which resulted in an increase in the Tg value of the recycled PP sample.

4.3 Melt flow index (MFI)

This test was submitted after the production of the samples. From Figure 6, this illustrates the relationship between temperature change and fluidity change, the values of fluidity increase with increasing processing temperature, reaching their highest value (29 g/10 min) at a temperature of 210°C. However, this is due to the increase in the volume of the melt, which leads to an increase in the distance between the polymer chains, thereby decreasing viscosity as the temperature rises. Most polymeric melts decrease in viscosity (increase fluidity) with increasing temperature [15].

Another reason for this difference is the increase in the processing temperatures of the melt, which allows the chains to move more freely and enables them to slide over each other. The resistance to flow decreases as viscosity decreases with the increase in shear rate [16]. This is due to the increase in the volume of the melt and the increase in the distance between the polymer chains, which leads to a decrease in viscosity with increasing temperature. This agrees with the findings of the researcher, as most polymeric melts decrease in viscosity with increasing temperature.

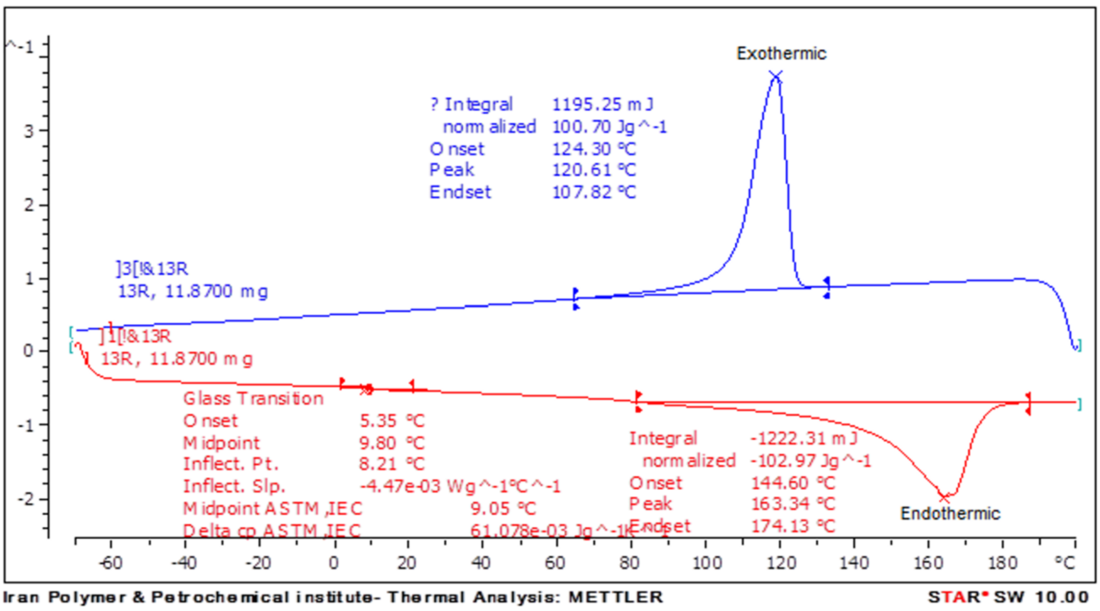

Figure 4. DSC test results for virgin PP

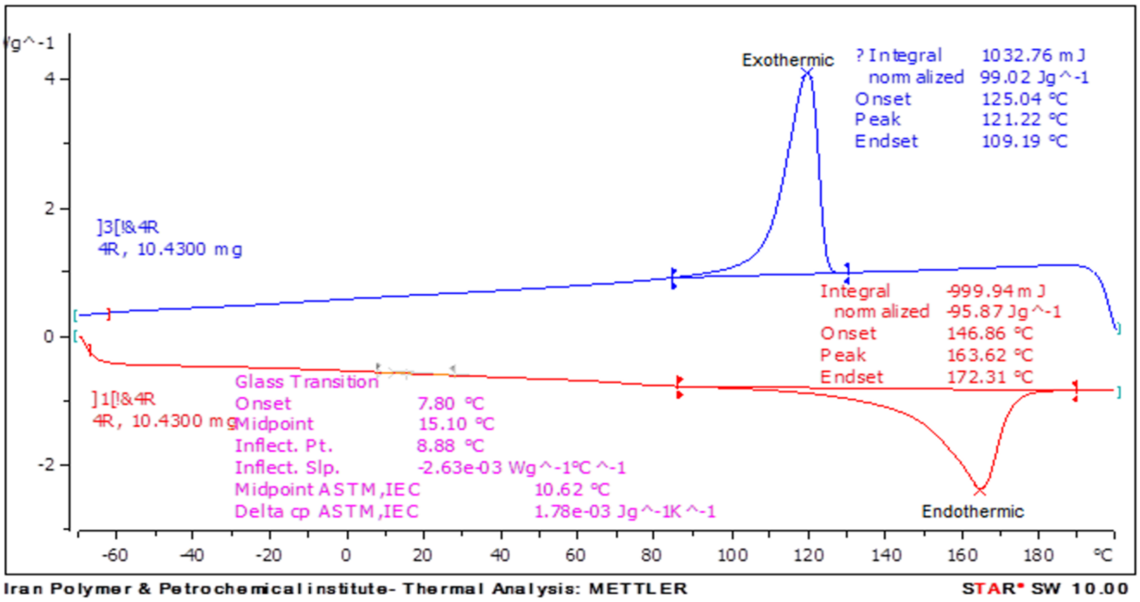

Figure 5. DSC test of virgin (pure) PP + recycled PP at high processing temperature

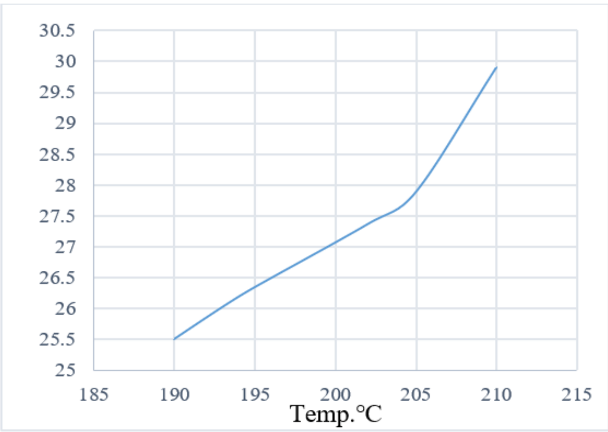

Figure 6. MFI Behavior with processing temperature change

Recent research has shown that the effect of high temperatures on RPP can vary based on processing conditions such as cycling time and polymer quality. Research indicates that high temperatures can improve some mechanical properties if processing conditions are carefully controlled, but can lead to significant deterioration if overheated [17, 18].

4.4 Density test

Elevating the molding temperature leads to a gradual rise in sample density. This outcome is attributed to heightened crystallinity in polypropylene (PP) and a reduction in the quantity of voids and porosities within the composites, highlighting that increased crystallinity contributes to a higher PP density [19]. From Figure 7, which represents the relationship between injection molding processing temperature and density, it was noted that increasing the processing temperature reduces density. This is due to the fact that increasing the temperature leads to an increase in the fluidity ratio resulting from a decrease in the viscosity ratio, which increases the distances between the polymeric chains. This dilution of the substance (i.e., a decrease in its concentration per unit volume) results in a decrease in density ratios with increasing temperature due to the decrease in mass per unit volume. This behavior leads to a reduction in manufacturing costs because of the increased flow rate due to decreasing viscosity and density, which agrees with researchers [20]. However, by observing the density behavior at the lowest manufacturing temperature, the density reached 0.933 g/cm³ at a temperature of 190°C, while the density reached 0.858 g/cm³ at a temperature of 210°C, indicating that the lower temperature led to higher density values. At high temperatures, this is significantly due to the increase in the viscosity of the melt at lower temperatures compared to higher temperatures, which resulted in an increase in density in this manner [20]. This is attributed to the temperature increase, which leads to a complete increase in the viscosity ratio, causing the distances between the polymer chains to increase (reducing the substance, i.e., decreasing its concentration). In volumetric units, this resulted in a decrease in the density ratio with the increase in temperature due to the decrease in mass in the volumetric unit, which is completely opposite to the behavior observed with increasing pressure. Here, there is an increase in the shear rate, which works to reduce the percentage of shear flow, affecting the viscosity by reducing it during shear thinning and heat application. This leads to an increase in the flow rate of the melt, as a decrease in the density rate results in a reduction in manufacturing costs. This aligns with the findings of other researchers [21-23].

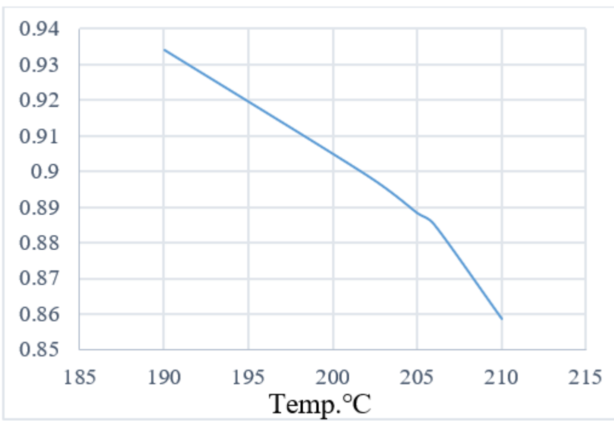

Figure 7. Density behavior with processing temperature change

5. CONCLUSION

The aim of these studies is to determine the effect of different temperatures on the mechanical and rheological properties of recycled polypropylene. According to the results obtained, it was shown that high temperatures have a significant impact on all properties, with optimal properties achieved at the appropriate temperature. The results indicated that increasing the manufacturing temperature led to an increase in fluidity and a decrease in density inversely related to temperature. As for the FTIR test results, they demonstrated a clear change in peak intensity, which also applied to the SEM test results, as the images revealed a noticeable difference between the original manufactured and recycled samples. This difference was documented by the results of the DSC test, which showed a clear change in the thermal properties of the produced samples, as the degree of glass transition (Tg) differed between the virgin and recycled samples. After examining the results, it was noted that the recycled samples did not have a good surface finish, in addition to weak flow properties and a clear impact on the strength of the peaks due to the high heating of the recycled samples, which caused them to lose the properties that qualify them for use. From the above, the factory should reduce the percentage of recycled material in the charge and lower the processing temperature to a level that allows for the improvement of the properties of the recycled samples. Future studies need to focus on improving processing techniques to mitigate the effects of high temperatures and enhance the thermal stability of recycled polypropylene.

ACKNOWLEDGMENT

This work was supported by training provided by the College of Materials Engineering, Department of Polymers and Petrochemical Industries, University of Babylon, Iraq. The authors would like to thank the Medical Syringe Factory-Iraq for their assistance in training and manufacturing samples.

REFERENCES

[1] Mark, J.E. (2017). Thermoset elastomers. In Applied Plastics Engineering Handbook. William Andrew Publishing, pp. 109-125. https://doi.org/10.1016/C2014-0-04118-4

[2] Maddah, H.A. (2016). Polypropylene as a promising plastic: A review. American Journal of Polymer Science, 6(1): 1-11. https://doi.org/10.5923/j.ajps.20160601.01

[3] Tang, C.C., Chen, H.I., Brimblecombe, P., Lee, C.L. (2019). Morphology and chemical properties of polypropylene pellets degraded in simulated terrestrial and marine environments. Marine Pollution Bulletin, 149: 110626. https://doi.org/10.1016/j.marpolbul.2019.110626

[4] Spoerk, M., Holzer, C., Gonzalez-Gutierrez, J. (2020). Material extrusion-based additive manufacturing of polypropylene: A review on how to improve dimensional inaccuracy and warpage. Journal of Applied Polymer Science, 137(12): 48545. https://doi.org/10.1002/app.48545

[5] Fernandez, A., Muniesa, M., Javierre, C. (2014). In-line rheological testing of thermoplastics and a monitored device for an injection moulding machine: Application to raw and recycled polypropylene. Polymer Testing, 33: 107-115. https://doi.org/10.1016/j.polymertesting.2013.11.008

[6] Baum, M., Jasser, F., Stricker, M., Anders, D., Lake, S. (2022). Numerical simulation of the mold filling process and its experimental validation. The International Journal of Advanced Manufacturing Technology, 120(5): 3065-3076. https://doi.org/10.1007/s00170-022-08888-9

[7] Spicker, C., Rudolph, N., Kühnert, I., Aumnate, C. (2019). The use of rheological behavior to monitor the processing and service life properties of recycled polypropylene. Food Packaging and Shelf Life, 19: 174-183. https://doi.org/10.1016/j.fpsl.2019.01.002

[8] Stoian, SA., Gabor, A.R., Albu, A.M., Nicolae, C.A., Raditoiu, V., Panaitescu, D.M. (2019). Recycled polypropylene with improved thermal stability and melt processability. Journal of Thermal Analysis and Calorimetry, 138: 2469-2480. https://doi.org/10.1007/s10973-019-08824-2

[9] Burgoa, A., Arrillaga, A., Schreier-Alt, T. (2024). Effect of multiple recycling on thermo-mechanical and rheological behaviour of PP/EPDM thermoplastic vulcanizates. Journal of Polymers and the Environment, 32(2): 947-961. https://doi.org/10.1007/s10924-023-03042-2

[10] Othman, N., Marzuki, N.H., Din, S.F.M., Arsad, A., Yusoff, N.I.S.M., Wahit, M.U. (2021). Rheological behavior of recycled plastics, blends and composites. In Recent Developments in Plastic Recycling. Springer, Singapore, pp. 193-212. https://doi.org/10.1007/978-981-16-3627-1_9

[11] Bazgir, M., Zhang, W., Zhang, X., Elies, J., Saeinasab, M., Coates, P., Youseffi, M., Sefat, F. (2021). Fabrication and characterization of PCL/PLGA coaxial and bilayer fibrous scaffolds for tissue engineering. Materials, 14(21): 6295. https://doi.org/10.3390/ma14216295

[12] Osswald, T.A., Baur, E., Rudolph, N. (2019). Plastics Handbook: The Resource for Plastics Engineers. Carl Hanser Verlag GmbH Co KG. https://doi.org/10.3139/9781569905609

[13] Qian, C., Zhao, Y., Wang, Z., Liu, L., Wang, D. (2021). Probing the difference of crystalline modifications and structural disorder of isotactic polypropylene via high-resolution FTIR spectroscopy. Polymer, 224: 123722. https://doi.org/10.1016/j.polymer.2021.123722

[14] Banik, M.T.K. (2006). Process-induced long-term deformation behavior of injection molded semicrystalline thermoplastics. http://archiv.tu-chemnitz.de/pub/2006/0127.

[15] Nazarychev, V.M., Vaganov, G.V., Larin, S.V., Didenko, A.L., Elokhovskiy, V.Y., Svetlichnyi, V.M., Yudin, V.E., Lyulin, S.V. (2022). Rhelogical and mechanical properties of thermoplastic crystallizable polyimide-based nanocomposites filled with carbon nanotubes: Computer simulations and experiments. Polymers, 14(15): 3154.

https://doi.org/10.3390/polym14153154
[16] Fujii, Y., Nishikawa, R., Phulkerd, P., Yamaguchi, M. (2019). Modifying the rheological properties of polypropylene under elongational flow by adding polyethylene. Journal of Rheology, 63(1): 11-18. https://doi.org/10.1122/1.5049378
[17] Lu, D., Babaniamansour, P., Williams, A., Opfar, K., Nurick, P., Escobar, I.C. (2022). Fabrication and evaporation time investigation of water treatment membranes using green solvents and recycled polyethylene terephthalate. Journal of Applied Polymer Science, 139(35): e5282. https://doi.org/10.1002/app.52823
[18] Zhou, J., Qiu, Z. (2023). The generation mechanism of demolding force based on the mold-part interface contact mode in micro-injection molding. Polymer Engineering & Science, 63(3): 782-797. https://doi.org/10.1002/pen.26243
[19] Farotti, E., Natalini, M. (2018). Injection molding. Influence of process parameters on mechanical properties of polypropylene polymer. A first study. Procedia Structural Integrity, 8: 256-264. https://doi.org/10.1016/j.prostr.2017.12.027
[20] Aho, J., Syrjälä, S. (2011). Shear viscosity measurements of polymer melts using injection molding machine with adjustable slit die. Polymer Testing, 30(6): 595-601. https://doi.org/10.1016/j.polymertesting.2011.04.014
[21] Gava, A., Lucchetta, G. (2008). Numerical simulation of a PA66 flow behaviour in a hot runner gate. Macromolecular Symposia, 26(1): 53-66. https://doi.org/10.1002/masy.200850307
[22] Kažys, R., Rekuvienė, R. (2011). Viscosity and density measurement methods for polymer melts. Ultragarsas/Ultrasound, 66(4): 20-25. https://doi.org/10.5755/j01.u.66.4.1022
[23] Greene, J.P. (2021). Automotive Plastics and Composites: Materials and Processing. William Andrew.