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RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

Investigation of Rheological and Mechanical Properties of Polypropylene During Recycling Processes

Polipropilenin Geri Dönüşüm Süreçleri Boyunca Reolojik ve Mekanik Özelliklerinin Araştırılması

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Abstract
In this study, the changes in the molecular structure, rheological and mechanical properties of polypropylene (PP), which is the most widely used industrial polymer, were investigated quantitatively during the recycling processes. In order to represent the recycling process, neat PP-homopolymer was subjected to recycling by extrusion and granulation process for five times, and rheological properties, molecular weights and molecular weight distribution of the samples obtained after each step were examined by a rotational rheometer, and then the tensile test results of the samples prepared in the film forms were evaluated. It was observed that the molecular weight decrease in the recycling processes was mainly occurred in the first recycling process and the decrease continued in each recycling process. It has also been determined that the mechanical strength of the samples below a certain molecular weight causes deterioration in a way that does not even allow forming of film samples.
Keywords: Polypropylene, Recycling, Extrusion, Rheology, Mechanical properties.

Öz
Bu çalışmada, en yaygın kullanılan endüstriyel polimer olan polipropilenin (PP) geri dönüşüm prosesleri sırasında moleküler yapısında, reolojik ve mekanik özelliklerinde meydana gelen değişimler incelenmiştir. Geri dönüşüm sürecini temsil etmek için, saf PP-homopolimer beş kez ekstrüzyon ve granülasyon işlemi ile geri dönüşüme tabi tutulmuş ve her aşamadan sonra elde edilen numunelerin reolojik özellikleri, moleküler ağırlıkları ve moleküler ağırlık dağılımı bir rotasyonel reometre ile incelenmiş ve daha sonra film formlarında hazırlanan numunelerin çekme testi sonuçları değerlendirilmiştir. Geri dönüşüm proseslerinde moleküler ağırlık azalmasının ağırlıklı olarak ilk geri dönüşüm prosesinde gerçekleştiği ve her bir geri dönüşüm prosesinde azalmanın devam ettiği görülmüştür. Ayrıca belirli bir moleküler ağırlığın altındaki numunelerin dayanımının, film numunelerinin oluşmasına bile izin vermeyecek şekilde bozulmaya neden olduğu tespit edilmiştir.
Anahtar Kelimeler: Polipropilen, Geri dönüşüm, Ekstrüzyon, Reoloji, Mekanik özellikler.

I. INTRODUCTION

Polypropylene (PP) is a well-known polymer which have been commonly using in industrial applications such as automotive, construction, consumer goods, packaging etc. Providing sustainability and cost reduction of PP without sacrificing its mechanical and rheological properties has been one of the important aims in polymer science. For this purpose, physical, mechanical, and rheological properties of recycled polypropylene (rPP) and using it in different structures has always been a trend topic investigated by researchers. These researches are generally focused on mechanical and rheological properties of rPP [1-4], rPP blends [5-7] and its composite structures [8-14]. Composites structures of rPP such as rPP/microcrystalline cellulose composite [9], rPP/rubberwood flour composite [10], rPP/wood composite [11], rCF/(rPP+Maleic Anhydride grafted Polypropylene) composite [12], rCF/rPP composite [13], rPP/hemp composite [14] perform better properties than its neat form in terms of tensile, flexural and creep.

Aurrekoetxea et al. [1] investigated the effects of recycling process on microstructure and mechanical properties of isotactic PP. It was determined that melt viscosity is the primary parameter affected by recycling due to the molecular weight decreasing. Recycled PP performed higher crystallization rate, crystallinity and equilibrium melting temperature than that of virgin grade. Elastic modulus and yield stress increased with the number of recycling steps while elongation at break and fracture toughness decreased. Rogueda-Berriet et al. [2] performed a study on the effects of the recycling process on the mechanical behavior of polypropylene (PP)/elastomeric, talc particles filled and non-filled. They applied different tests such as tensile (small and finite strain), bending

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and creep. Creep test results showed the impact velocity was less important with the talc filled polymer. Stoian et al. [3] studied improving thermal stability and melt processability of recycled PP. PP waste/ virgin PP blends were prepared and the effect of waste PP on thermal and mechanical properties was investigated. All polymer blends performed better thermal stability when they are compared to the virgin PP. Their results recommend the blends including 30–50% virgin PP for the PP recycling waste from raffia in high performance applications. Szpieg et al. [4] developed and characterized a composite material constitutes from fully recycled CFR maleic anhydride grafted polypropylene modified polypropylene. Viscoelastic behavior of the material had a linear trend while viscoplastic strain was following a power law. In addition, results of tensile test having constant stress rate was compatible with material model even at the around of rupture stress. Zdiri et al. [15] investigated the effect of reinforcement of recycled PP by nanoparticles addition. Different nanofillers were added to the structure of rPP such as $CaCO_3$, SiO_2, carbon clack and CNT etc. It is concluded that nanofillers may have positive effect on rPP like improving mechanical and rheological properties.

In this study, effect of recycling on mechanical and rheological properties of PP homopolymer having two different molecular weights was investigated. Results were comparatively presented for virgin PP and each of recycled forms. This study will bring a detailed understanding of the mechanical and creep properties of different molecular weight PP throughout their recycling processes.

II. MATERIAL AND METHOD

2.1. Material

Two different industrial grade isotactic PP homopolymer grade materials were used in the study. Their melt flow index (MFI) values were 11 g/min and 2.5 g/min, respectively. These two samples will be mentioned as PP3 (210.000 g/mol) and PP4 (300.000 g/mol) throughout this study.

2.2. Method

In order to represent the recycling process, virgin PP-homopolymer was subjected to extrusion and granulation processes five times. Samples were prepared in a co-rotating twin-screw extruder which has a granulator equipment and screw has a diameter 16 mm, L/D = 40. Temperature profile was 185–220–230–240 °C from the feeding zone to the die. All sample granules were dried in an oven at 60 °C for 24 h before melt processing. Rheological and solid-state tensional properties, molecular weights, and molecular weight distribution (in term of polydispersity index-(PDI)) of the samples measured (or calculated) after each step.

The rheology tests were performed by a rotational dynamic oscillatory rheometer has a 25 mm diameter parallel plate. The measurements were performed at 200 $^{\circ}$C with 1000 μm distance between plates. First, a dynamic strain sweep test was done to the specimens to find their linear viscoelastic region (LVR). Then, a frequency sweep test was performed between 600–0.1 rad/s at a strain value in LVR (1%). Additionally, solid state creep tests were conducted under 5 MPa constant stress.

Tension test was applied according to the ASTM 882–02 test standard at different temperatures such as 30, 40, and 50 $^{\circ}$C for each specimen by using a hybrid rotational rheometer has tension grips. The tests were done at 3 mm/min and continued up to 100% elongation. Dynamic mechanical analysis (DMA) in tension mode were performed by using a hybrid rheometer at a 1 Hz frequency in the temperature between 30–200 °C with a 3 °C/min heating rate.

III. RESULT AND DISCUSSION

In Figure1a, c and Figure1b, d, G'-ω and G"- ω were presented, respectively. Both modulus values decrease in all samples with the decreasing angular frequency. Decreasing modulus value can be explained by the relaxation characteristics of the polymer chains. The reason of observing higher modulus value at high frequencies is that non-reorganized polymer chains present a rigid behavior. On the other hand, the reason of low modulus value at low frequencies is the viscous deformation, which is more effective at long-time deformation.

It is also noted in the graphs that while the module values decrease in each recycling process. This difference can be clearly observed at the low frequency region. Finally, it is seen that reduction in the modulus values decreases more effectively compared to the others, especially in the first recycling process, and the G' value, which is the indicator of elastic properties, decreases more than the G" value. From this point of view, it has been evaluated that the ability of the materials to elastically store the energy during deformation during each recycling process decreases and the viscous character becomes more effective.

Figure 2 presents the changing in molecular weight and polydispersity index values which were calculated by the modeling frequency scanning test results during the recycling period. Evaluation of the molecular weight changing in the recycling process shows that the molecular weight values decrease with each recycling process and this decrease is especially effective in the first recycling process.

In addition, the fact that the PP-3 sample did not have the mechanical strength to make a film after the third recycling suggested that recycled PPs would not be

suitable for film applications when the Mw value dropped below approximately 70,000 g/mol. Finally, when the molecular weight distribution values in the polymer chains are examined by considering the PDI parameter (Mw/Mn), it is seen that the PDI values decrease in each recycling process and that even different PP derivatives have similar PDI values after the third recycling.

Figure 3 presents viscosity behavior depends on shear rate. Herein, viscosity getting reduces with the number of recycling due to the molecular weight of samples getting reduces. It is also seen that newtonian behavior at the shear rate range of the samples becomes wider with recycling process which is probably caused by reducing in PDI.

Creep test results of the samples can be seen in Figure 4. Only first and second recycled samples of PP-3 could be tested because the other recycled samples could not form a stable polymeric film. Any tertiary creep region did not observe because the creep tests were conducted in the linear viscoelastic region. When the maximum strain values were compared, it can be observed recycled polypropylene samples generally performed less maximum strain than their virgin forms. In the case of PP3, its first recycled form showed some higher maximum strain value than its original one. This behavior may be caused from first recycled form of PP3 could not perform enough molecular orientation to gain higher crystallinity. Therefore, it exhibited more strain value than original PP3. But other forms of samples showed less strain because their molecular structure re-oriented after every recycling process and this caused an increasing their crystallinity. There is an inversely proportional relationship between crystallinity and maximum strain value.

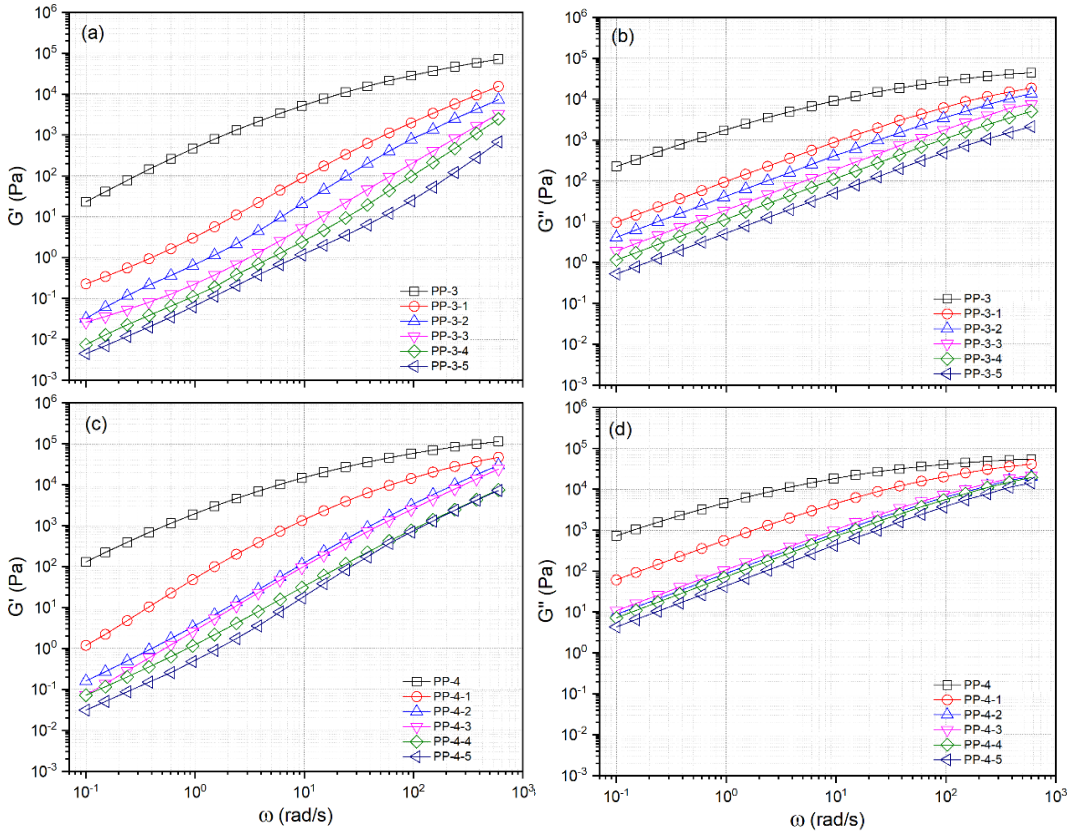

Figure 1. G'-ω and G''- ω graphs of pure and recycled PPs

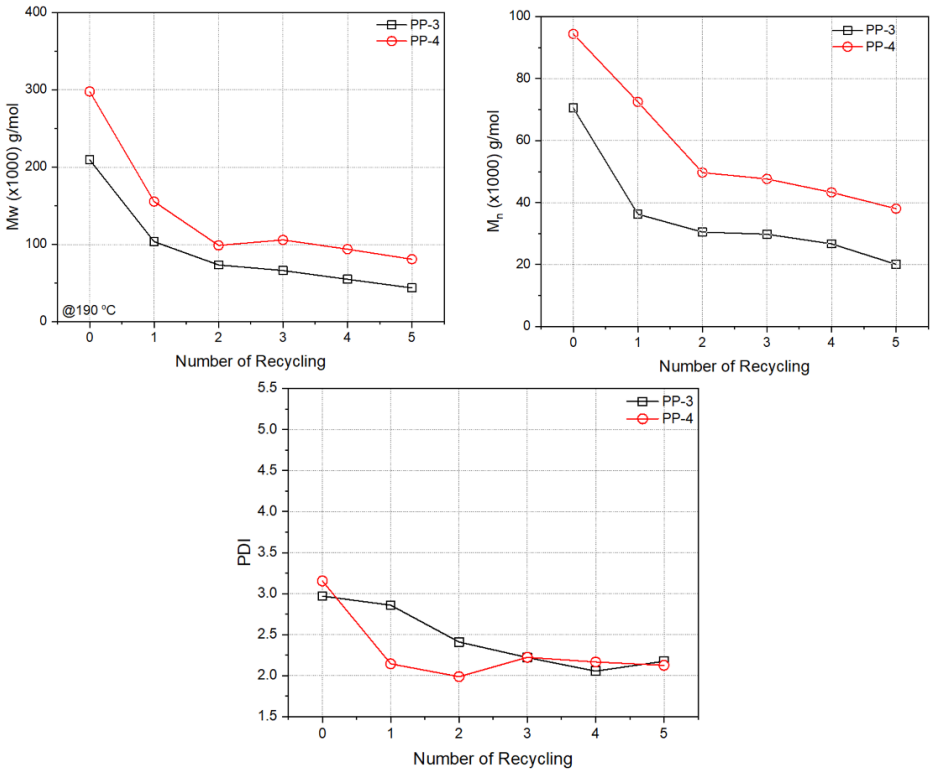

Figure 2. Changing of M_w, M_n and PDI values depend on the number of recycling

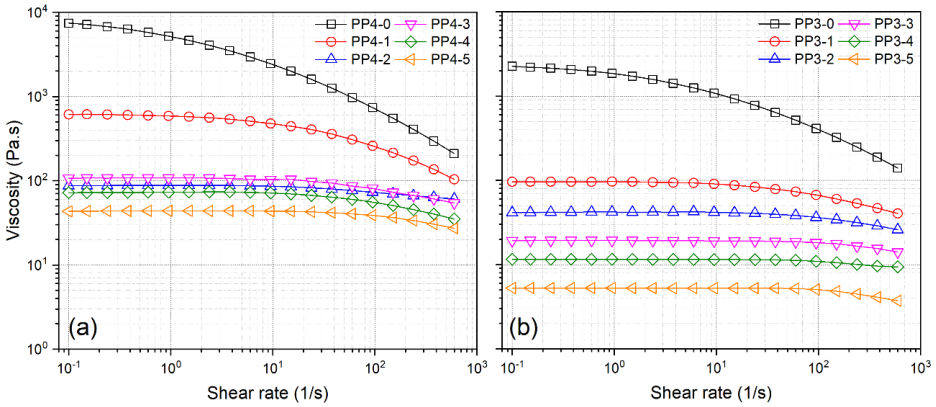

Figure 3. Rheological properties of pure and recycled PPs

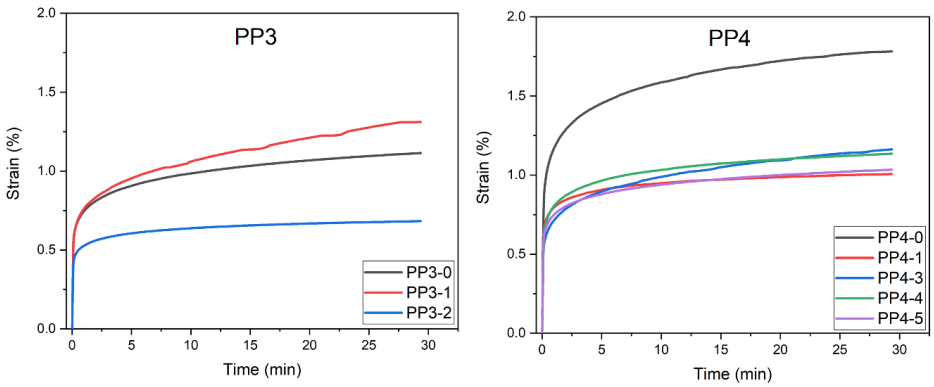

Figure 4. Creep test results of pure and recycled PPs

Table 1 summarizes to tensile test results of the samples at 30 °C. Strain at break values of samples can be compared to each other to understand the mechanical behavior of samples at each step. 4th and 5th recycled samples of low molecular weight PP could not be tested because they are extremely brittle. Conversely, high molecular weight PP could be tested, and it can keep its elastic character even its fifth recycle. It can be observed from Table 1 that elastic modulus of PP4 getting increased with the increasing number of recycle. This behavior may be explained polymer chains in PP4 can perform enough arrangements. Thereby, high molecular weight PP can be assumed as more environmental because it can resist more recycling process without loss its mechanical properties.

Figure 5 and Figure 6 show stress-strain graphs for each form of polymers at 30, 40 and 50 °C temperatures. As it is mentioned before, PP3 performed so brittle behavior after third recycle that it could not be tested. Mechanical behavior of PP3 is compatible with number of recycle. Its elastic behavior getting decrease with the increasing number of recycling. As expected, it performed more viscous behavior with increasing number of recycling. It can be concluded from Figure 6 that PP4 can preserve its elastic properties at high temperatures. This behavior originates from its high molecular weight structure, and it can keep its chain arrangement even the temperatures above room temperature.

Recycled polymers perform better characteristic than their virgin forms because of the polymer structure recrystallized after each recycle. This situation provided higher stiffness rigidity and ultimate tensile strength than its neat form to the structure. It was stated elastic properties of the samples showed in Figure 2 getting lost after their second recycling. However, it can be seen how the elastic behavior progresses in Figure 5 and 6, especially for PP4. The difference of these two situations is due to the tests and sample forms applied. Since the samples were in the film forms and the applied load was the tensile force in the tensile tests, the samples were able to perform strength due to the recrystallization and their reorientation.

Figure 7 presents storage modulus changing depends on temperature for PP3 and PP4. Fourth and fifth recycled PP3 samples could not be tested because of their high crystallinity. PP3 behaves stable until its third recycling in term of storage modulus. There is a decreasing in the modulus value at the third recycled sample until around the temperature of 90 °C. All neat and recycled samples behave compatible with each other after this value because the crystalline structure degrades, and their behaviors completely turn over viscous character. But the high molecular weight PP (PP4) did not show a large degradation behavior and modulus decreasing because it could keep its elastic properties even its fifth recycled form. A scaling view was added to PP4 graph because six curves closely matched to each other. It can be concluded from the second detail view of PP4 graph that there is a small amount of difference between fifth recycle of PP4 and the others because of the increasing crystallinity. Melting temperatures of the samples were determined from the graphs in Figure 7. Melting temperature of the sample is the point which shows sudden drop in storage modulus. So, melting temperatures of the samples are 160 °C and 175 °C for the PP3 and PP4, respectively.

Table 1. Tensile test results of the samples at 30 ^{o}C

Sample Code	E' (MPa)	Ultimate Stress (MPa)	Strain at Break (%)
PP-3	7.4	19.7	no.
PP-3-1	6.78	20.43	12.18
PP-3-2	7.07	19.2	6.88
PP-3-3	5.43	7.53	1.92
PP-4	6.53	14.94	no.
PP-4-1	6.91	16.06	no.
PP-4-2	7.58	20.09	no.
PP-4-3	7.61	15.2	no.
PP-4-4	7.64	18.52	no.
PP-4-5	8.52	13.18	13.03

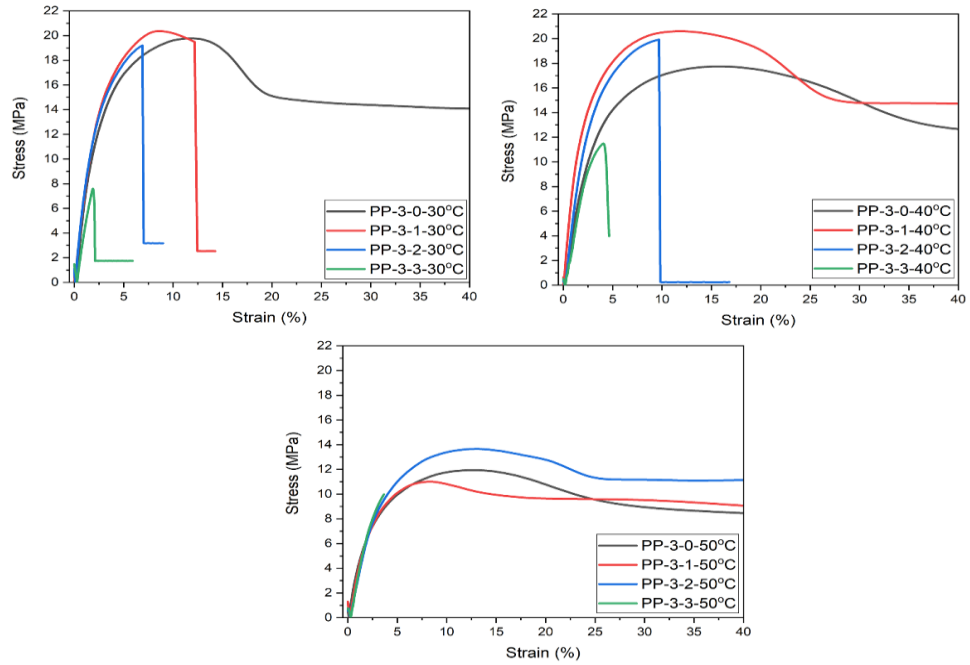

Figure 5. Tensile test results of PP3 sample for every recycle at different temperatures.

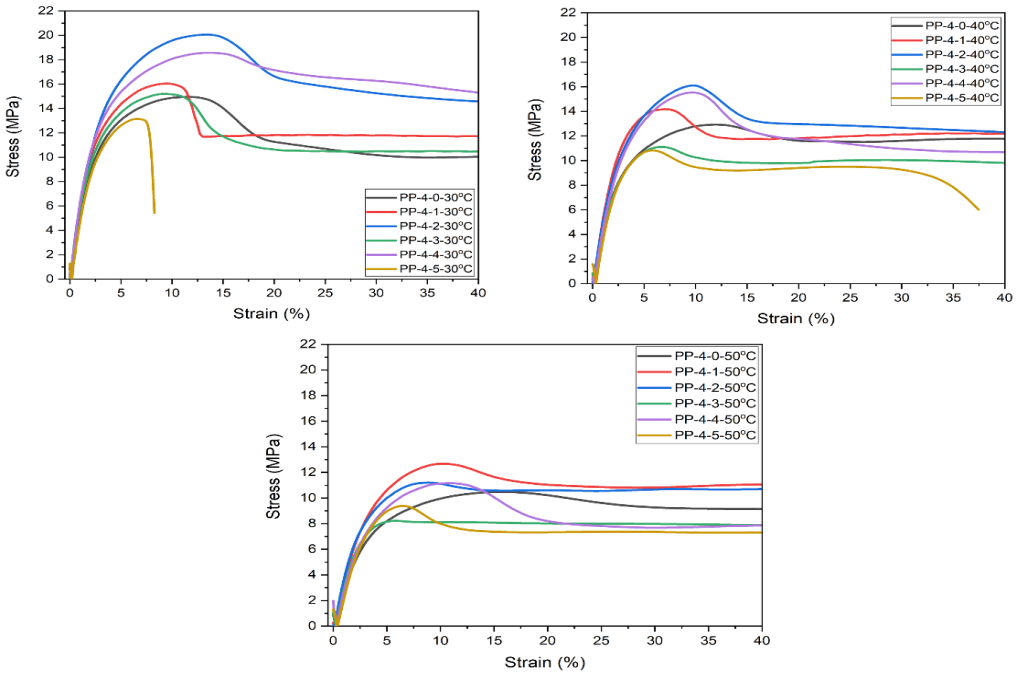

Figure 6. Tensile test results of PP4 sample for every recycle at different temperatures.

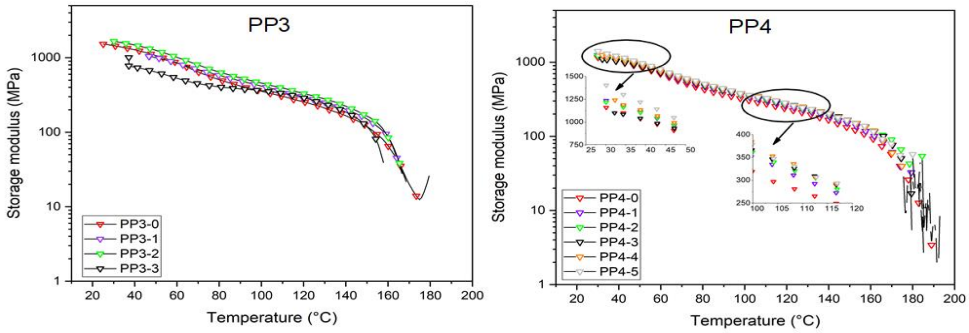

Figure 7. DMA test results of PP3 and PP4 samples for every recycle at different temperatures.

IV. CONCLUSION

Results of this study shows that high molecular weight PP exhibits better characteristics in terms of mechanical and rheological properties. As the recycling number increases, samples showed brittle behaviors due to their crystallinity getting higher. In spite of this, higher molecular weight sample can resist against the loading even at its fourth or fifth recycle. These results can bring a different perspective for environmental issues. For example, using polypropylene having a molecular weight above a defined value may be a requirement to provide several times of recycling.

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