International Journal of Engineering Inventions
e-ISSN: 2278-7461, p-ISSN: 2319-6491
Volume 12, Issue 11 [November. 2023] PP: 35-42

Effect of the Oleic Acid on Characteristics of Dynamic Vulcanized PP-EPDM blend for automotive weather strip

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ABSTRACT: *The main purpose of this paper is to study to simultaneously improve the flowability and compression set of PP-EPDM TPV for automotive weather strip. Automotive weather strips, in which PP-EPDM TPV is mainly used, must have excellent weather resistance, sealing properties, and durability, so they must be made of materials with good compression ratio and excellent resistance to external environmental conditions. However, in order to improve the compression set and apply it to weather strip, the content of EDPM, a dispersed phase, must be increased and the degree of cross-linking must be increased, but its application is limited due to problems such as processability due to reduced flowability. Accordingly, we attempted to simultaneously improve flowability and mechanical properties by blending low-viscosity oleic acid with white oil, which was previously used as processing oil. When oleic acid is added to PP-EPDM TPV, the double bond of EPDM reacts with the double bond of oleic acid, increasing the chemical bond inside the material and increasing the degree of cross-linking, increasing the internal strength of the material and excellent resistance to external deformation, improving mechanical properties. Therefore, as the oleic acid content increased, tensile strength, modulus, elongation, hardness, and tear strength improved, and compression set also improved. Additionally, the addition of oleic acid, which has a much lower viscosity compared to white oil, improved the flowability of TPV, simultaneously improving the processability and compression set of PP-EPDM TPV with the addition of oleic acid.*

Keywords: *Thermoplastic vulcanizate (TPV);weather strip; oleic acid*

Date of Submission: 01-11-2023 Date of acceptance: 11-11-2023

I. Introduction

Automotive weather strip is located between the door glass and door trim, andpreventsforeignsubstancessuchasrainanddustfromenteringtheindependentinterior,whilealsoblockingwindnoise,doorglass,andvehiclevibrationformtheoutside[1].Automotiveweatherstripshouldhavegoodweather ability,seal-ability,durabilitytoperformitsdutyasbodysealingforvehiclesunderdifferentharshenvironments[2-3].Therefore, it is an important design factor to select a material that has a good compression ratio and does not deteriorate the surface of the skin due to external environmental conditions[4]. EPDM andPVCaremainlyusedasmaterialsforweatherstrips,andcurrently,theuseofthermoplastic elastomers(TPE), which have the advantages of being lightweight and eco-friendly due to their low specific gravity and recyclability, is increasing[5-8].

Thermoplasticelastomer(TPE)isarubberymaterialwithpropertiesandfunctionalperformancesimilartothoseof conventionalvulcanizedrubber,yetitcanbeprocessedinamoltenstateasathermoplasticpolymer[9-10].Thermoplastic vulcanizates (TPVs) are a particular group of high-performance thermoplastic elastomers produced by dynamic vulcanization, which consists of the selective cross-linking of the elastomer and its fine dispersion throughout the thermoplastic phase under intensive mixing[11-13].Unlike static vulcanization, dynamic vulcanization is performed at a high shear rate, which leads to formation of dispersed phase morphology of the blend components.The resulting morphology consists of micron-sized finely dispersed cross-linked rubbery particlesofahighcross-linkdensity embeddedinathermoplasticmatrix[14].Dynamically vulcanized blends show significant improvement in mechanical properties, reduced compression set, higher oil and heat resistance, and improved high-temperature utilization over the unvulcanized blends[15-18].TPVs based on polypropylene (PP) and ethylene propylene diene rubber (EPDM) using activated phenolic resins were widely studied because of their commercial importance.Such a composition combines the advantages of both materials, the relatively high melting point and high crystallinity of PP explains the oil and heat resistance as well as the rigidity of these TPVs and the saturated main chains of the cross-linked EPDM the superior stability against oxygen, ozone and heat[19-21].However, in order to improve the compression set and apply it to weather strip, the content of EDPM, a dispersed phase, must be increased and the degree of cross-linking must be increased, but its application is limited due to problems such as processability due to reduced flowability[22-25].

Thus, the main objective of this paper is to study to simultaneously improve the flowability and compression set of PP-EPDM TPV for automotive weatherstrip. Therefore, a study was conducted by blending oleic acid (cis-9-octadecenoic acid), a monounsaturated fatty acid, with the white oil, which was previously mainly used as process oil. Oleic acid reduces the viscosity of the rubber compound, improves flowability, and has the effect of improving the processability of the compound. In addition, it was judged that the many double bonds present in unsaturated fatty acids could react with the double bonds of EPDM to increase the cross-linking density, thereby improving the properties of TPV.

II. Experimental

1. Materials

WeusedEthylene propylene diene monomer (EPDM), KEP 901N(Kumho Petrochemical., Korea)andPolypropylene (PP), PP HJ4045 (Korea Petrochemical Ind., Korea). Whiteoil-1500(MichangOilInd.,Korea),andOleicAcid(SamchunChem.Co.,Korea)wereusedasprocessoil. Tackirol201(alkylphenol-formaldehyde resin,TaokaChemicalCo.,Japan)wasusedasacureagent. TheformulationisshowninTable1andthemolecularstructuresofOleicacidusedintheexperimentareshowninFigure1.

2. Samplepreparation

EPDM andPPwas mixed in a mixer (BrabenderTechnologieGmbH&Co.,Germany,300cc)at 180°C, 150rpm rotor speed for 2minutes followed by the addition of WhiteoilandOleicacidfor an additional mixing time of 3minutes. Afterthat,Tackirolwasaddedandcross-linkedfor5minutes.The mixtures were sheeted out from a two-roll mill. A rectangular sheet of samples (10cm x15cm x2mm) weremoldedby hot press machine, at 180°Ctemperatureandcooledtoroomtemperature.

3. Characterization

AccordingtoASTMD412,adumbbell-shaped specimen waspreparedtomeasurethemechanicalpropertiesoftheTPV.TensilemeasurementoftheTPVwascarriedoutusinga universal tensile testing machine(UTM 3345,Instron,USA)witha500Nloadcellatroomtemperaturewithacross-headspeedof500mm/min.Hardness of the TPVwas measured by pressing the specimen using a Shore A durometer (Asker's model JIS K 6253, Japan) after overlapping the specimen to thickness of 6mm according to ASTM D 2240.Curingbehavior information wascollectedbyusingaRubberprocessanalyzer (RPA elite 2000,TAInstrument,USA)at180℃ for20minutes. Test for compression set, the samples were set in a cylindrical mold, compressed 25% at 80℃ for 22hours. After compression, the samples were extracted and given a 30-minute recovery period. The final dimensions, particularly height, of the samples were recorded. The Mooney viscosity of the rubber samples was measured using a Mooney viscometer (DWV-200C, Daekyung Engineering Co., Korea) at 125℃ for 4 minutes. Each sample was pre-heated at 125℃ for 1 minute for stabilization prior to the measurement. Melt index was measured bymeltindexer(MP-1200,TiniusOlsen,USA)with 10kg load at 230℃ for 10 minutes.

III. Results and Discussion

Figure2showstherheometriccurvesofOA-0,OA-10,OA-20,OA-30,andOA-40samples.CuringpropertiesofmaximumtorqueMH,minimumtorqueML,thedifferencebetweenmaximumandminimumtorqueΔTorque,andoptimalcuretimeT_{90}(thetimerequiredforthetorquetoreach90%ofthemaximumtorque)areshowninTable2.As can be seen in Figure 2 and Table 2, the compound without oleic acid was confirmed to have the lowest MH value of 0.05Nm. The MH values of the compounds containing oleic acid were 0.06, 0.08, 0.09, and 0.12Nm, respectively, showing that the degree of cross-linking increases as oleic acid is increased by 10 phr.Additionally, the ΔTorque value, which indicates the degree of cross-linking, is 0.02Nm for the compound without oleic acid added, and as oleic acid increases by 10 phr, the degree of cross-linking gradually increases to 0.03, 0.04, 0.05, and 0.06Nm, respectively.T_{90}, which represents the optimalcuretime, decreases as the cross-linking degree increases, so compounds without oleic acid have the slowest optimalcuretimeand the lowest cross-linking degree,andastheoleicacidcontentincreases,theoptimalcuretimegraduallybecomesfaster.These results are judgedto be due to the increase in the degree of cross-linking caused by the reaction between the double bonds present in oleic acid, an unsaturated fatty acid, and the double bonds present in EPDM. Therefore, as the oleic acid content increases, the degree of cross-linkingand the maximum torque value increase and the optimalcuretimedecreases.

Figure3shows thestress-straincurvesofOA-0,OA-10,OA-20,OA-30,andOA-40samples.Thetensilestrength,elongationatbreak,modulusat100%,andhardnessofOA-0,OA-10,OA-20,OA-30,andOA-40samplesareshowninTable3 and Figure 4.Asthe contentofoleicacidincreased,thetensilestrength,100%modulus,elongation,andhardnessareimproved,andthetearstrengthisalsoimproved.ThetensilestrengthofOA-0samplewithout oleic acid was 24kgf/cm^2, which was the lowest compared to the remaining samples with oleic acid added.It was found that the tensile strength of the OA-10, OA-20, OA-30, and OA-40 samples with added oleic acid was 31, 39, 45, and 54kgf/cm^2, respectively, as the oleic acid content increased.Like the tensile strength, the hardness of the OA-10 sample without adding oleic acid was the lowest at 56, while the hardness of the OA-10, OA-20, OA-30, and OA-40 samples was 57, 60, 62, and 67, respectively. It can be seen that hardness increases as the oleic acid content increases.These results can be explained in relation to the cross-linking characteristics. As the degree of cross-linking increases, the chemical bonds between polymer chains increase, which increases the internal strength of the material and thus improves mechanical properties. It is believed that the double bonds present in oleic acid and the double bonds present in EPDM rubber react during mixing, increasing the cross-link density. Accordingly, the 100% modulus,tear strength is also improved.The100%modulusofOA-0samplewithout oleic acid was 18kgf/cm^2, which was the lowest compared to the remaining samples with oleic acid addedandthe 100%modulus of the OA-10, OA-20, OA-30, and OA-40 samples with added oleic acid was 19,20,22, and 24kgf/cm^2, respectively, as the oleic acid content increased.ThetearstrengthofOA-0samplewithout oleic acid was 17.5kgf/cm, which was the lowest compared to the remaining samples with oleic acid addedandthe tearstrength of the OA-10, OA-20, OA-30, and OA-40 samples with added oleic acid was 18.6,23.0,25.1, and 26.6kgf/cm, respectively, as the oleic acid content increased.Therefore, it was found that when oleic acid was added, the degree of cross-linking increased and the mechanical properties improved. As the oleic acid content increased, tensile strength, modulus, elongation, hardness, and tear strength improved.

The compression set is an important property in elastomers and refers to the amount of permanent deformation that occurs when a material is compressed to a specific strain for a specific time at a specific temperature. The compression set was measured after 25% compression at 70℃ and a recovery time of 30 minutes, and shown in Figure 5 and Table 4. This value refers to the elasticity of the material to recover to its original state, and the smaller the value, the better the recovery ability.The low compression set value was observed in OA-40 sample, which is believed to be a result of OA-40 sample containing the most oleic acid, having the highest degree of cross-linking, and excellent internal strength of the material. Likewise, the OA-0 sample, which did not add oleic acid and had the lowest degree of cross-linking, had the highest compression value of 32%. Therefore, the amount of permanent deformation that occurs when a material is compressed to a specific strain for a specific time at a specific temperature is related to the degree of cross-linking. As the chemical bonds inside the material increase, the internal strength of the material increases, resulting in excellent resistance to external deformation. Therefore, adding oleic acid increases the chemical bonds inside the material, resulting in an increase in the degree of cross-linking and an improvement in compression set.

The melt flow index (MFI) is defined as the amount of molten resin passing through a capillary equipment with defined length, diameter, and die geometry under prescribed conditions of temperature, load, and time interval. Melt index values are shown in Figure 6 and Table 5. The OA-0 sample without oleic acid had the lowest melt viscosity at 23.6g/10min. OA-10, OA-20, OA-30, and OA-40 samples with added oleic acid showed 36.6, 42.1, 50.5, and 75.6g/10min, respectively. These results show that melt viscosity increases with decreasing white oil content and increasing oleic acid content. Oleic acid has a much lower viscosity than white oil, so when mixed, the viscosity of the compound decreases and the melt viscosity index increases.With similar results, the results of Mooney viscosity measurement are shown in Table 6. The OA-0 sample without oleic acid had the highest 56.9MU, OA-10, OA-20, OA-30, and OA-40 samples with added oleic acid showed 43.9, 31.0, 21.2, and 17.6MU, respectively.Like the melt viscosity index, Mooney viscosity also showed a decrease in viscosity as the oleic acid content increased.Therefore, adding oleic acid reduces the viscosity of the compounds and thus improves flowability, resulting in excellent processability.

IV. Conclusions

The effect of oleic acid on TPVs was investigated by studying the relationship between the cross-linking properties and mechanical properties of TPVs prepared by adding oleic acid to dynamically vulcanized PP-EPDM blends for automotive weatherstrip. The higher the ENB content of EPDM applied to PP-EPDM TPV, the higher the degree of cross-linking, but there are limits to its application to automotive weatherstrip due to processability problems due to poor flowability. Therefore, we attempted to simultaneously improve flowability and mechanical properties by blending low-viscosity oleic acid with white oil, which was previously used as a processing oil. Oleic acid, an unsaturated fatty acid, has a molecular structure with many double bonds. Thus, when oleic acid is added to PP-EPDM TPV, the double bond of EPDM reacts with the double bond of oleic acid, thereby increasing the degree of crosslinking. It was shown that as the oleic acid content increased, the degree of cross-linking and maximum torque increased and the optimal curing time decreased. In addition, it was found that the chemical bonds inside the material increased and the degree of cross-linking increased, thereby increasing the internal strength of the material and improving its mechanical properties with excellent resistance to external deformation. Therefore, as the oleic acid content increased, tensile strength, modulus, elongation, hardness, and tear strength improved, and compression set also improved.In addition, the flowability of TPV was improved due to the addition of oleic acid, which has a much lower viscosity than white oil, and as a result, the processability and compression set of PP-EPDM TPV were improved simultaneously with the addition of oleic acid.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/orpublication of this article: This work was supported by the Ministry of Trade, Industry, and Energy,Republic of Korea (20010572).

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Table 1. Formulation of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
KEP 901N			70		
PP HJ4045			30		
Tackirol 201			5		
White oil 1500	40	30	20	10	0
Oleic acid	-	10	20	30	40

*phr(perhundredrubber)

Table 2. Cure properties of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
MH [Nm]	0.05	0.06	0.08	0.09	0.12
ML [Nm]	0.03	0.03	0.04	0.04	0.06
Δ Torque [Nm]	0.02	0.03	0.04	0.05	0.06
T_{90} [min]	15.36	15.09	14.96	13.48	9.43
T_{10} [min]	1.72	1.33	1.10	0.93	1.05

Table 3. Mechanical properties of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
Hardness [Shore A]	56	57	60	62	67
Sp.Gr.	0.912	0.918	0.920	0.922	0.924
Tensile strength[kgf/cm^2]	24	31	39	45	54
100% Modulus[kgf/cm^2]	18	19	20	22	24
Elongation at break [%]	330	360	390	460	500
Tearstrength[kgf/cm]	17.5	18.6	23.0	25.1	26.6

Table 4. Compression set of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
Compression set [%] (70℃x25% x22hr)	32	30	26	23	20

Table 5. Melt index of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
Melt index[g/10min] (230℃x10kg)	23.6	36.6	42.1	50.5	75.6

Table 6. Mooney viscosity of the dynamic vulcanized PP-EPDM blend compounds

SampleNo.	OA-0	OA-10	OA-20	OA-30	OA-40
Mooney viscosity [MU]	56.9	43.9	31.0	21.2	17.6

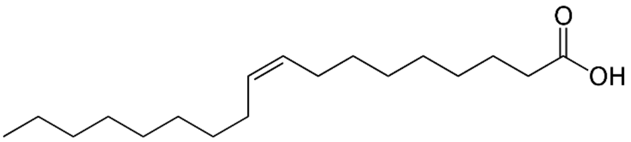

Figure1. Themolecularstructures of Oleicacid(cis-9-octadecenoic acid).

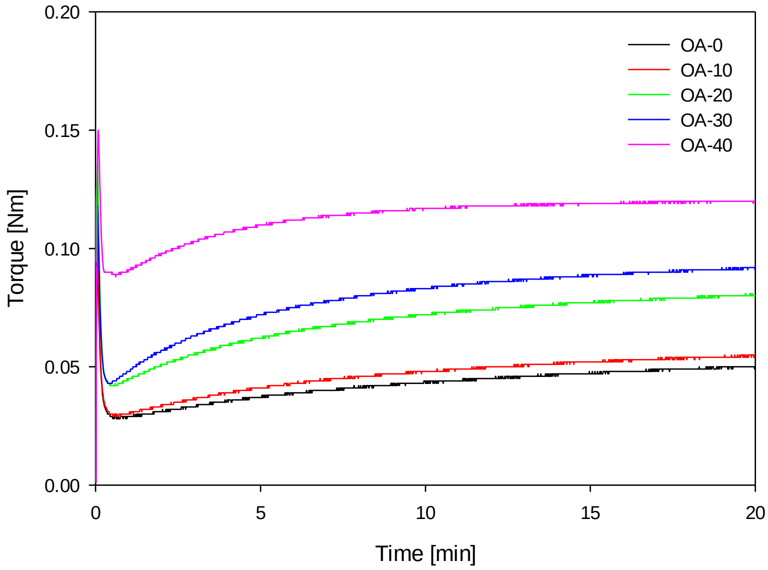

Figure2. Cure characteristics of the dynamic vulcanized PP-EPDM blend compounds.

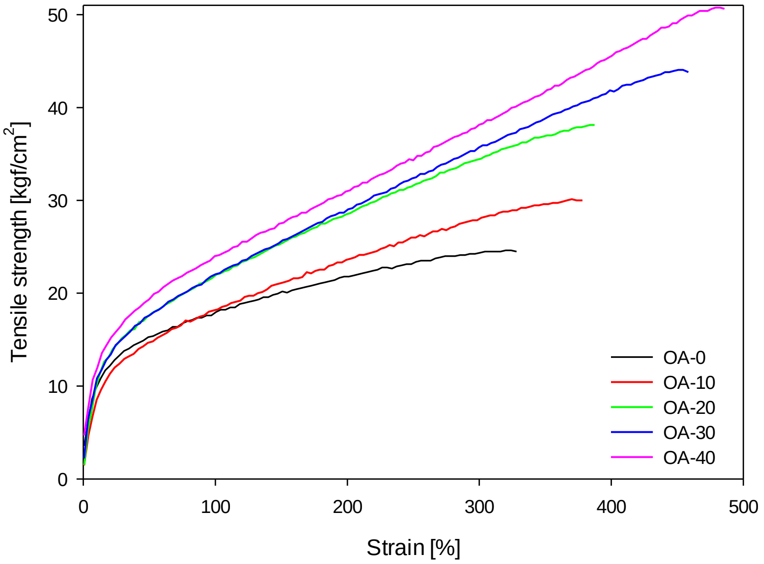

Figure 3. Stress-Straincurveof the dynamic vulcanized PP-EPDM blend compounds.

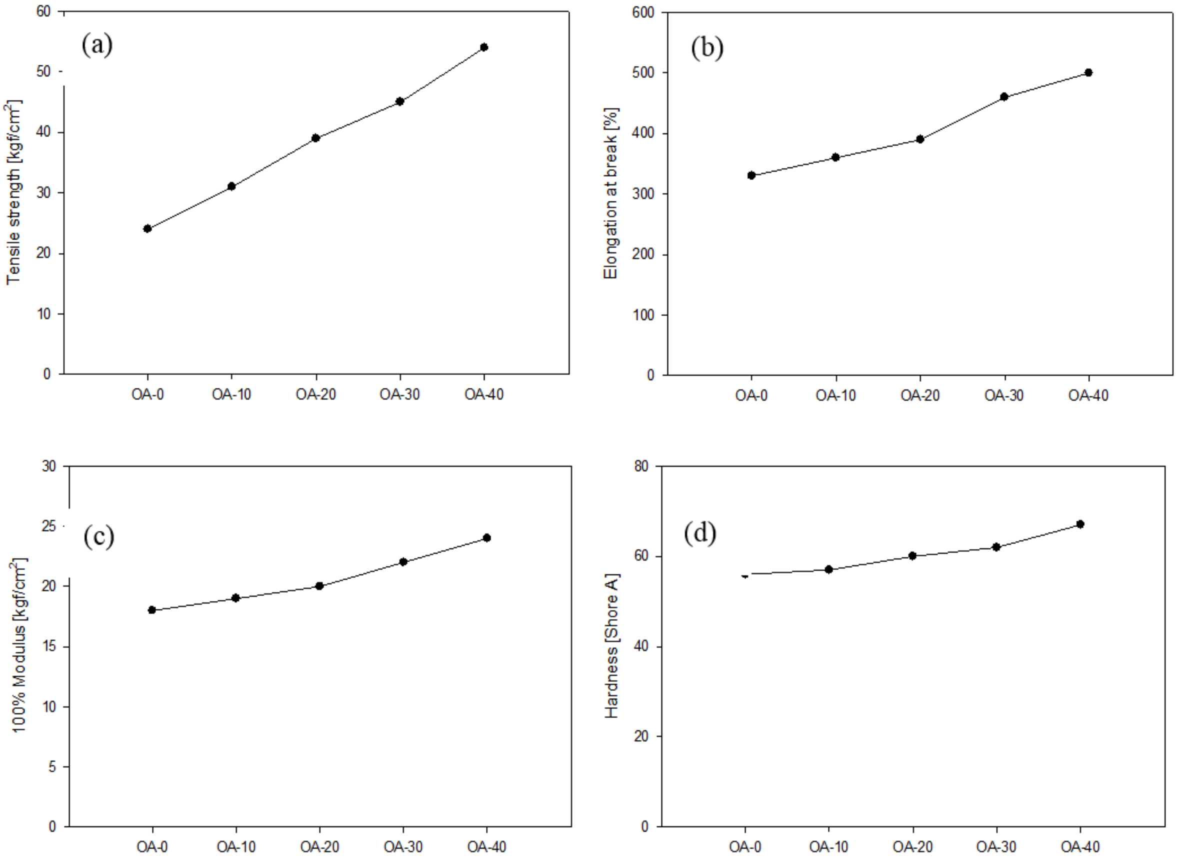

Figure 4. Mechanical properties of PP-EPDM TPV : (a) tensile strength, (b) elongation at break, (c) 100% modulus, and (d)hardness.

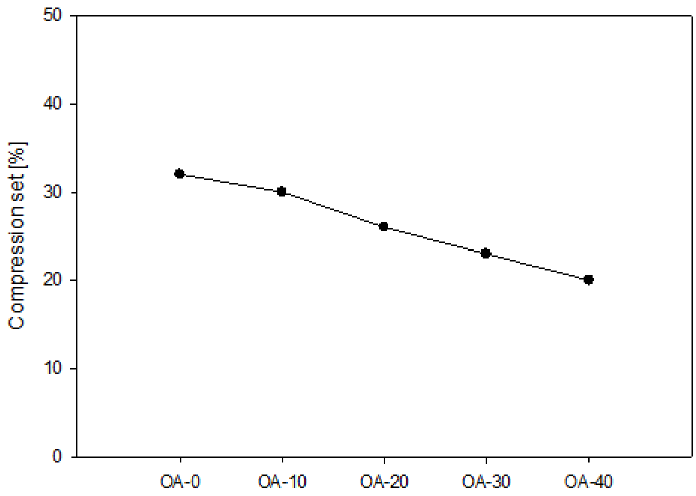

Figure 5. Compression setof the dynamic vulcanized PP-EPDM blend compounds.

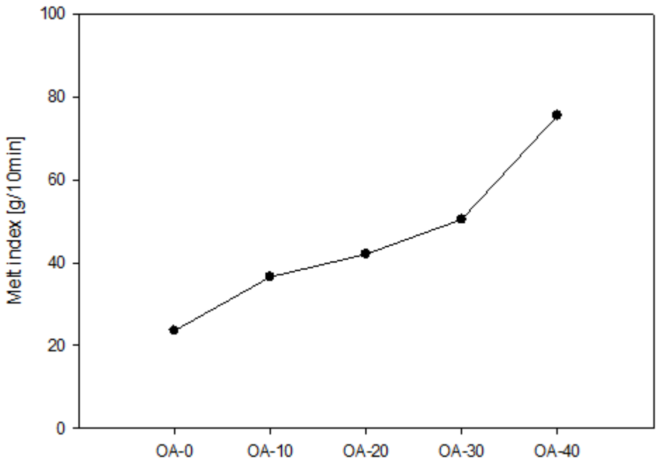

Figure 6. Melt indexof the dynamic vulcanized PP-EPDM blend compounds.