In-situ Microfibrillar Recycled PET/Glass Fiber/PP Hybrid Thermoplastic Composites

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Abstract: Hybrid composites of in-situ microfibrillar recycled polyethylene terephthalate (rPET)/glass fiber (GF)/polypropylene (PP) were developed as an economical and environmentally friendly alternative to glass fiber reinforced thermoplastic PP composites. The effect of replacing glass fibers with in-situ formed polymer microfibrils on mechanical and viscoelastic properties of the composites was investigated with tensile, flexural, and dynamic mechanical tests. Characterization results showed that mechanical and viscoelastic performance of 34% glass fiber reinforced PP can be obtained with 24% glass fiber, 10% microfibrillar rPET composites. Compatibilization effect of the maleic anhydride grafted PP (MA-g-PP) was studied using Fourier transform infrared (FTIR) spectroscopy. The scanning electron microscopy (SEM) images confirmed the formation of the rPET microfibrils in the hybrid matrix. Besides, composites with MA-g-PP compatibilizers showed significantly improved fiber-matrix interfacial adhesion on the SEM images.

Keywords: in situ microfibrillar, polypropylene, glass fiber, poly(ethylene terephthalate)

1. Introduction

Compared to traditional fiber-reinforced composites, in-situ microfibrillar composites (MFCs) are lightweight, easy to process, and recyclable. It is also possible to obtain environmentally friendly polymer blends with high mechanical performance using recycled polymer resources through the microfibrillar formation. In general, microfibrillar in situ polymer composites are formed by melt blending or extruding two or more immiscible polymers. During the compounding process, the polymer with a lower melting temperature acts as the matrix, whereas the polymer with a higher melting point acts as the dispersed phase. After melt blending, hot and cold drawing processes are performed to obtain the fibrillar structure from the dispersed constituent. During the extrusion process, the extruder's temperatures should be at the melting point of the dispersed constituent. There should be about 50°C difference between the melting temperatures of the dispersed and matrix constituents for the formation of MFCs. During the drawing process, the dispersed constituent and the matrix constituent are aligned in the direction of drawing. However, during the injection molding process, the primary constituent melts, and the fibrils of the dispersed phase are distributed along with the polymer matrix [1]. The morphological control of the dispersed phase is crucial to obtain desired physical and mechanical properties. The morphology of the MFCs is affected by concentrations, interfacial energies, and viscosities of the constituents, extrusion temperature, drawing ratio, and compatibilizer presence. In the literature, PET is used in various MFC composites as the dispersed phase in different matrix phases such as polyamide 6 [2], low-density polyethylene [3], and polystyrene [4]. However, many studies were focused on the PP matrix [5-13] because of the high melting point difference between the phases, commercial availability, balanced mechanical properties, and low-cost.

After the drawing process, polymer microfibrils are oriented in the direction of drawing. However, the injection molding process, which is performed at temperatures between the melting temperatures of the dispersed phase and the matrix phase, randomly distributes the fibrils in the matrix [9]. The stretch ratio of the composites also affects the glass transition temperature of the polymer matrix.

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Glass transition temperatures obtained by dynamic mechanical analysis shifted to higher temperatures with the increasing stretch ratio. Besides, it is shown that microfibrils significantly affect the mechanical properties at temperatures above the glass transition temperature of the MFC [5].

Recycled PET (rPET) is an environmentally sustainable material option to prepare PET/PP MFCs. In one study, rPET flakes from used water bottles are used to reinforce isotactic PP through melt extrusion and drawing in the presence of maleic anhydride grafted PP (MA-g-PP) compatibilizer. Fiber diameters and mechanical performance of the composites are not affected by the initial size of the PET flakes. Increasing drawing ratio decreased the rPET fiber diameter and resulted in narrow diameter distribution among fibers. Optimum mechanical properties were obtained with 15% rPET fibers [9]. In a recent study, it was shown that using combination of maleic anhydride compatibilizers with different polymer backbones such as PP, ethylene-based polyolefin elastomer (POE) and ethylene-vinyl acetate (EVA) may improve strength and toughness of rPET - PP blends [12]. In another study, in microfibrillar PET - PP blends, different phase morphologies were obtained by changing PET content in the composites. Among different phase morphologies, composites with shish-kebab type phases yielded the highest mechanical properties [13]. Mishra et al. were investigated the tensile, morphological and dynamic mechanical properties of hybrid in situ PET – PP - multiwalled carbon nanotube (MWCNT) composites. Both the presence of the in situ formed PET fibers and MWCNTs have improved the storage moduli of the composites [14, 15].

Even though the formation of in-situ microfibrils in polymer blends is a known method in polymer composite science and technology, a hybrid form of glass fibers and microfibrillar PETs has not been studied previously. To our knowledge, this is the only study that develops and extensively characterizes hybrid microfibrillar PET – glass fiber PP composites. In our previous study, mechanical properties of microfibrillar PET – carbon fiber PP composites were investigated [11]. In this paper, rPET/GF/PP composites were developed as a lightweight, eco-friendly, and economical alternative to conventional GF/PP composites. GF34/PP (34% glass fiber reinforced polypropylene) composition was selected as the reference composite as the industrial application of the material (washing machine tub) uses this formulation.

2. Materials and methods
2.1. Materials
Recycled PET with 2-6 mm flake size and 0.74 – 0.82 dL/g intrinsic viscosity were obtained from Cevre PET Company, Turkey. Injection molding grade PP (12g/10 min at 230°C) was supplied by Borealis AG, Austria. Glass fibers with 13 µm filament diameter and 4 mm chopped strand length was obtained from John Manville, Slovakia. MA-g-PP coupling agent was obtained from BYK Additives, Germany. The coupling agent has 0.9% maleic anhydride content and has a melt flow rate of 20-40 g/10 min.

2.2. Preparation of Recycled PET/Glass Fiber/Polypropylene Hybrid Composites
The composites were prepared using a twin-screw Thermo PRISM TSE24 HC extruder equipped with a side feeder and two gravimetric feeders. The specifications of the extruder and compounding configurations are shown in Table 1.

Table 1. Extruder specifications and compounding configurations.

L/D Ratio	28:1
Screw Diameter	23.6 mm
Torque	6.5 Nm/cm^3
Screw Speed	200 rpm
Temperature profile	200°C/215°C/210°C/240°C/255°C/230°C/220°C

rPET flakes were dried at 75°C for 8 h prior to compounding process. PP, MA-g-PP coupling agent

and rPET flakes were dry mixed and gravimetrically fed into the extruder through main hopper. Glass fibers were gravimetrically fed into the extruder through side feeder. The compounds were produced at a total rate of 8 kg/h. The extrudate was cooled in a water bath and drawn using a custom-made laboratory equipment. Finally, filaments were cut into pellet and dried at 75°C for 8 h prior to injection molding process.

Table 2 shows the rPET/GF/PP formulations that are produced in this study. 34% GF reinforced PP was selected as reference material (with and without MA-g-PP) as it is being used by the home appliance industry to produce washing machine tubs. Specimens for mechanical characterization were produced using an injection molding machine (Arburg Allrounder 320C) with a barrel temperature of 190 – 220°C according to respective ISO standards.

Table 2. rPET/GF/PP formulations

Samples	PP	GF	MA-g-PP	rPET
	(%)	(%)	(%)	(%)
PP/34GF	66	34	0	0
PP/34GF/2MA	64	34	2	0
PP/24GF/10rPET	66	24	0	10
PP/24GF/10rPET/2MA	64	24	2	10
PP/14GF/20rPET	66	14	0	20
PP/14GF/20rPET/2MA	64	14	2	20

2.3. Characterization

Fourier-transform infrared spectroscopy (FTIR) analysis was performed using Bruker Tensor 27 equipped with a germanium crystal. 32 scans were recorded at room temperature at a resolution of 2 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1}. The tensile tests of the rPET/GF/PP composites were carried out at room temperature using a Zwick Z020 universal machine at 50 mm/min cross head speed (ISO-527). Flexural properties were measured by three-point bending tests using an Instron 4505 universal machine at room temperature at 5 mm/min cross head speed (ISO-78). Dynamic mechanical analysis (DMA) were executed by a TA Instruments Q800 DMA. Temperature ramp tests were carried out between 25°C to 150°C at 1 Hz. SEM Analysis were conducted on a Zeiss SUPRA 55VP at 20 kV acceleration voltage. Freeze fractured composite specimens were coated with gold prior to measurements.

3. Results and discussions
3.1. Tensile and Flexural Properties

The effect of rPET and MA-g-PP compatibilizer on tensile strength, flexural modulus, and flexural strength of the hybrid PP/GF/rPET MFCs are demonstrated in Figure 1. Tensile tests show that, with the MA-g-PP compatibilizer, replacing 10% of the glass fiber content of the composites with rPET microfibrils does not significantly affect the tensile strength of the composites as the PET fibers reinforce the PP matrix along with glass fibers. However, replacing 20% of the composite glass fiber content with 20% rPET significantly decreases mechanical properties, possibly due to the PET content that was not transformed into fibers during the compounding process. rPETs that are not transformed into microfibrils possibly lead to micro-crack formation at the polymer matrix interface reducing the tensile strength of the composites. A similar effect was also observed in PP - carbon fiber - rPET MFCs. For the carbon fiber reinforced hybrid MFCs, 5 phr rPET was the optimum rPET content in terms of tensile properties of the composites [11]. MA-g-PP compatibilizer showed a significant effect on the tensile strength of the composites with the rPET microfibrils. For PP/24GF/10rPET MFCs, samples with the compatibilizer showed 35% higher tensile strength than the composites without compatibilizer. Maleic anhydride groups of the compatibilizer covalently bond with the silane coupling agents on the glass fibers and the terminal alcohol and carboxylic acid functionalities of the rPET microfibrils resulting in improved PP

matrix - PET microfibril interfacial adhesion [16]. For the characterization of the MFCs, the stress in the tensile tests is applied parallel to the flow direction, whereas the stress in the flexural tests is applied perpendicular to the flow direction.

The reinforcing effect of the rPET microfibrils on the tensile strength is comparable to the effect on the flexural strength, showing that PP matrix constituent is reinforced by the rPET microfibrils both in the flow and reverse direction. However, the effect of the MA-g-PP compatibilizer on flexural modulus is less prominent than the effect on the flexural strength as modulus is less dependent on the interfacial interactions between matrix and reinforcers than strength [17-19]. For PP/24GF/10rPET formulation, the composites prepared with 2% compatibilizer showed a 29% increase in flexural strength and an 11% increase in flexural modulus.
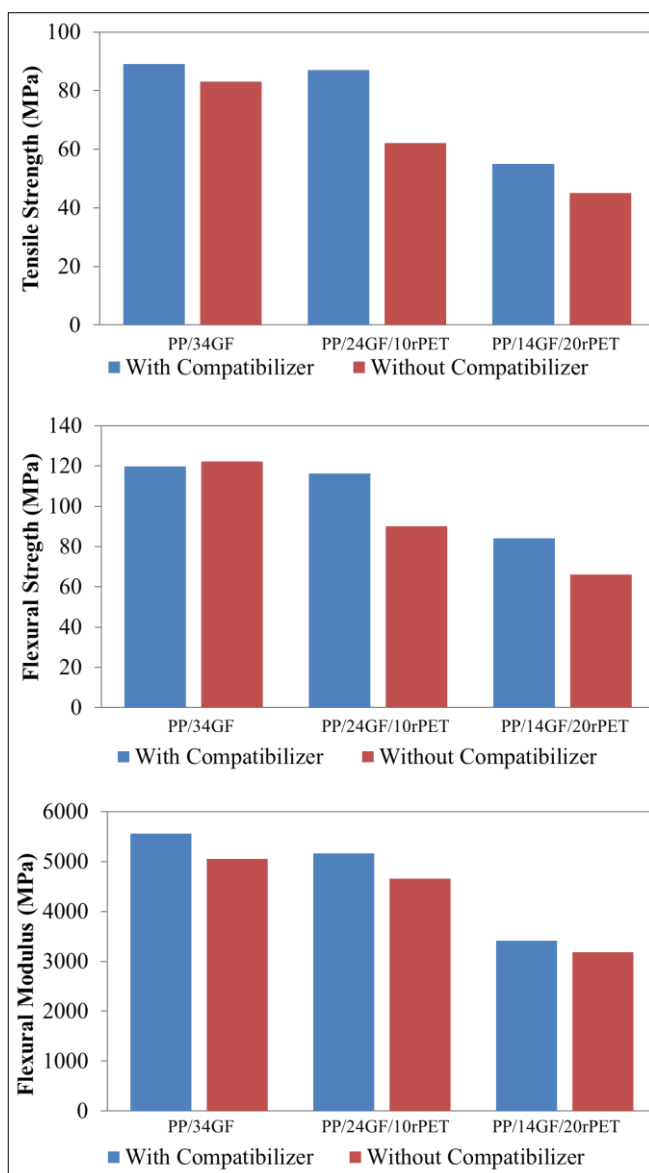

Figure 1. Tensile and flexural properties of rPET/GF/PP MFCs

3.2. Dynamic mechanical properties

The effect of rPET content on the storage modulus of the MFC composites are shown in Figure 2. Similar to the tensile and flexural test results, storage moduli of the PP/34GF/2MA and PP/24GF/10rPET/2MA composites with respect to temperature are almost the same as PET fibers are reinforcing the network at the PET content of 10%. Previously, the strong reinforcing effect of the in situ microfibrillar rPET fibers in in PP network was shown [20]. In this study, the reinforcing effect of the

rPET fibers in the hybrid GF PP composites' storage moduli is demonstrated. There is a slight decrease in the composites' storage moduli with 10% rPET content at temperatures above 80°C as PET fibers soften at temperatures above the glass transition temperatures and lose their reinforcing impact. A similar behavior of the in situ microfibrillar PET fibers was observed in PET-LDPE [21], PET – PP [17] and PET-PP-MWCNT MFCs [14]. However, the composites with 20% rPET content show lower storage moduli as at higher loading values, rPET is not as effective as the glass fibers to reinforce the PP network. A similar phenomenon was also observed with static mechanical tests. In the literature, it was shown that PET phase that are not transformed into fibers during compounding can not reinforce the PP network as effective as the in the fiber form [14, 21].
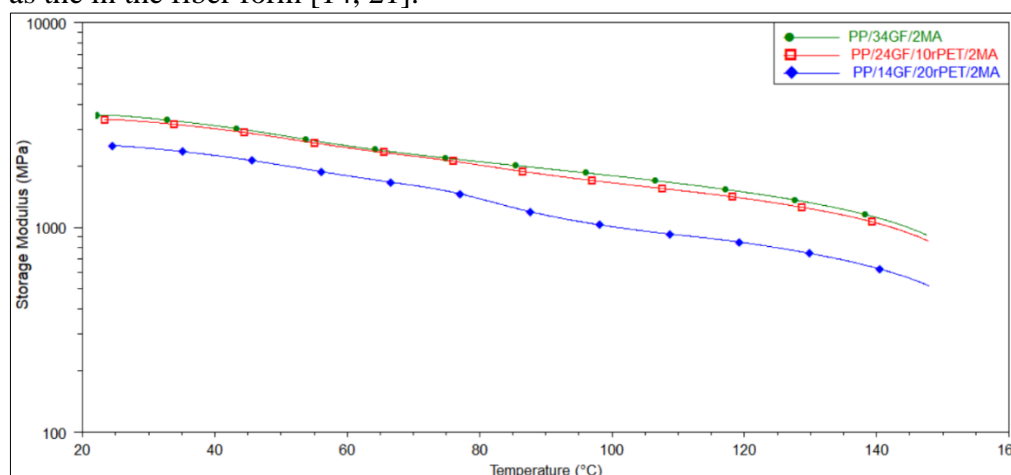

Figure 2. Effect of rPET content on storage modulus of rPET/GF/PP MFCs

The effect of rPET content on the tan delta or loss factor of the MFCs with respect to temperature is shown in Figure 3. Tan delta is the ratio of the loss modulus to storage modulus and it represents the damping properties of the materials. As measured from the maximum tan delta peak, PET phase in both formulations with 10% rPET and 20% rPET had the glass transition temperature of 85°C. At temperatures below 70°C, the viscoelastic dissipation behavior of the composites is very similar. However, as the temperatures approach the glass transition temperature, the PET chains inside the composites start long-range coordinated motions, increasing the energy dissipation of the composites. Since the formulation with 20% rPET has more PET content than the formulation with 10% rPET content, the effect of the PETs on the dissipation at the glass transition temperature is more prominent. In addition, in the composite with 20% rPET, PET relaxation is less restricted since the fiber formation is less prominent than the composite with 10%rPET as discussed in Section 3.1. A similar behavior was previously observed in PET – PP MFCs at PET blend ratios up to 40% [22].
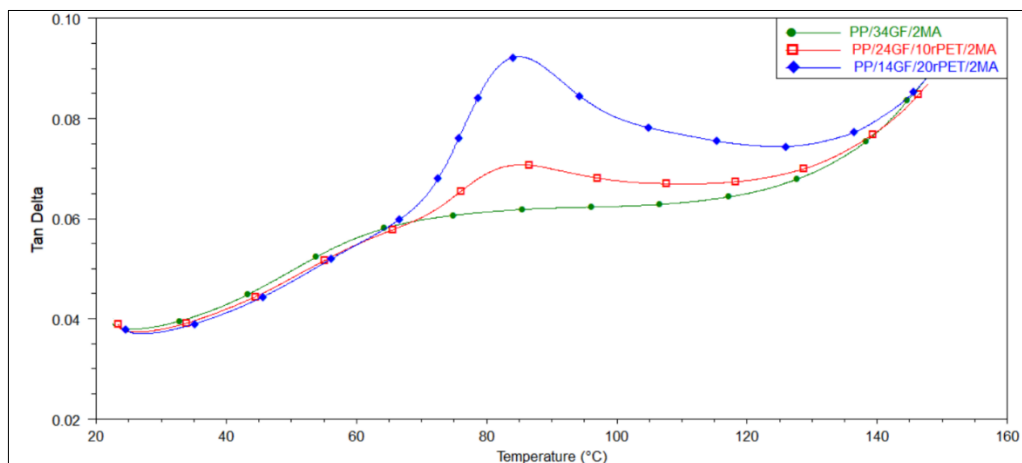

Figure 3. Effect of rPET content on tan delta values of rPET/GF/PP MFCs

3.3. Morphological analysis of rPET/GF/PP MFCs

SEM study was performed to confirm the formation of rPET fibers in the GF/PP composites and to investigate the effect of MA-g-PP compatibilizer on the interfacial adhesion between the PP matrix, glass fibers, and rPET fibers. Figure 4 shows the SEM images of PP/34GF (a), PP/34GF/2MA (b), PP/24GF/10rPET/2MA (c) composites. Figure 4 (b) shows the effect of MA-g-PP on the adhesion between the PP matrix and glass fibers. Due to the interaction of the silane groups on the GFs and the maleic anhydride groups of the compatibilizer, the GFs are well wetted by the PP polymer. However, without compatibilizer, fiber-matrix adhesion is very weak (Figure 4 (a)). SEM images supported the improved tensile and flexural mechanical properties of the compatibilized samples. The formation of the PET fibers from flakes is demonstrated in Figure 4 (c). The curved irregular shaped fiber in the image demonstrates a PET fiber as GFs have a smooth and straight structure. The diameter of the rPET fibers were in the range of 4.4-10.2 µm. Fiber pull-outs are not observed in any formulations suggesting good interfacial adhesion between PP matrix and GFs.
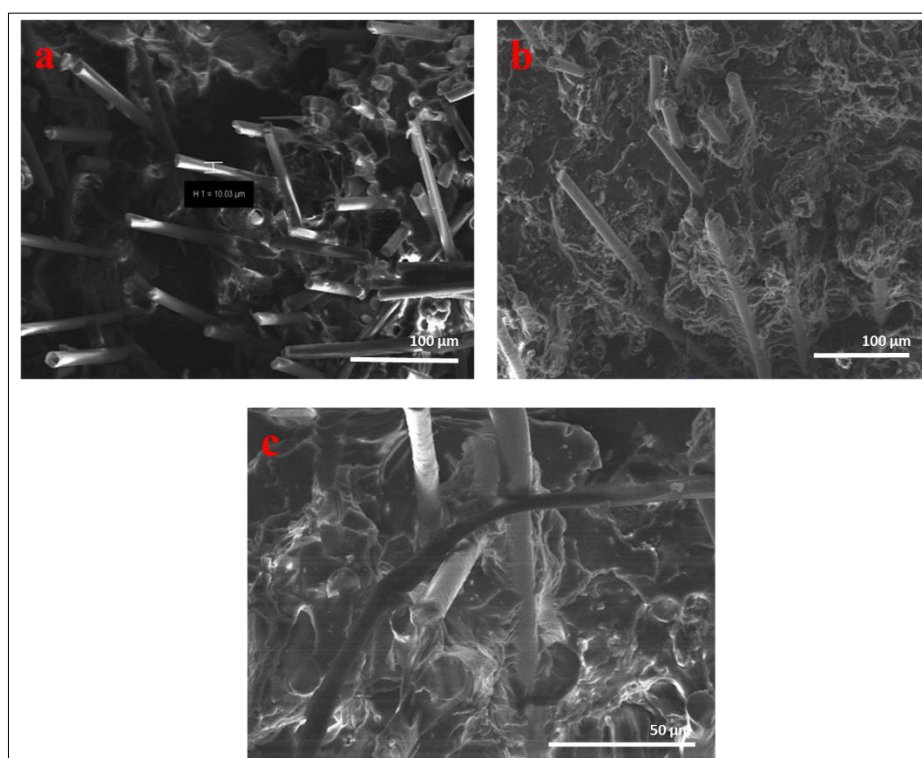

Figure 4. SEM images of PP/34GF (a), PP/34GF/2MA (b),
PP/24GF/10rPET/2MA (c)

3.4. FTIR analysis

The chemical interaction between MA-g-PP with glass fibers and rPET flakes was evaluated by FTIR spectroscopy. Figure-5 shows the FTIR spectra of neat PP, rPET, MA-g-PP and rPET/GF/PP MFCs in the zone of 400 cm^{-1} - 3200 cm^{-1}. The FTIR spectrum of MA-g-PP has two absorption peaks located at 1714 cm^{-1} and 1780 cm^{-1} for the cyclic anhydride groups of the MA-g-PP. The symmetric and asymetric C=O stretching vibration of the maleic anhydride group was assigned to peak at 1780 cm^{-1} [23]. The peak at 1714 cm^{-1} was assigned to carboxylic acid C=O stretching vibration by the self-hydrogen bonding within the carbonyl groups [24, 25]. The assigned carbonyl peaks were absent in the spectra of the neat PP. The absorption peak at 1720 cm^{-1} in the FTIR spectra of rPET was assigned to ester carbonyl C=O stretching, and the same peak was found in the FTIR spectra of PP/GF/rPET MFCs. Disappearance of the carbonyl stretch peak at 1780 cm^{-1} on the PP/GF/rPET/MA MFCs indicated the possible chemical reactions between the maleic anhydride groups with the silane coating of the GF and the terminal -OH and -COOH end groups of rPET [14].
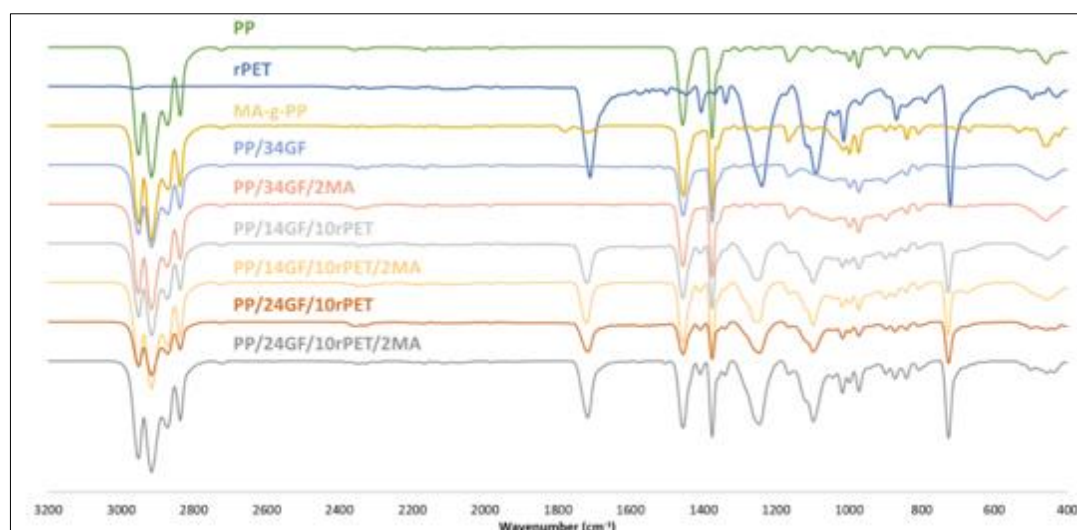
Figure 5. FTIR spectra of PP, rPET, MA-g-PP and rPET/GF/PP MFCs

4. Conclusions

34% GF reinforced PP is being used by the home appliance industry to produce washing machine tubs. To reduce the overall cost of the composites and to make the composites more sustainable and environmentally friendly, microfibrillar rPETs were introduced into the PP/GF. The effect of microfibrillar rPET on the mechanical and viscoelastic properties of PP/GF/rPET hybrid composites was investigated. SEM results showed that rPET flakes are transformed into PET fibers during the compounding process, and MA-g-PP is crucial for the adhesion of GFs into the PP matrix. Tensile, flexural, and DMA test results showed that 10% of the glass fibers could be replaced with 10% microfibrillar PETs without sacrificing the mechanical properties. By replacing 10% glass fiber content with rPET from waste PET bottles, overall cost of the composites is significantly reduced in an eco-friendly way.

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