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Reprocessing of Polypropylene/Cellulose Composites: Effects on Thermal Properties

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Abstract:
The reprocessing and the effects maleic-anhydride grafted polypropylene (MAPP) coupling agent on the thermal properties of recycled polypropylene (rPP)/microcrystalline cellulose (MCC) composites were investigated. rPP composites with MCC loading of 5wt% and 20wt% were prepared by injection molding up to five cycles. The change in the chemical composition of the composites was monitored with Fourier transform infrared spectroscopy (FTIR). Differential scanning calorimetry (DSC) and Thermogravimetric (TGA) tests were performed to compare thermal behavior of the rPP/MCC composites at different processing cycles. Analysis of thermal behavior showed a slight increase in the melting temperature of reprocessing composites with increasing number of cycles; associated to the higher percentage of crystallinity. The thermal stability of composites is affected by the number of reprocessing cycle, temperature and MCC loadings. It is noticed that the reprocessing did not disrupt the interaction between MAPP, MCC fibers and rPP matrix.

Index Terms: thermal, FTIR, cellulose, PP, recycle, crystallization

I. INTRODUCTION

The application of polypropylene (PP) in several industries such as automotive, packaging and construction has made PP as one of the most used thermoplastics. As a result, its solid waste generation increases. Thus, the recycling of plastic waste such as PP provides an alternative to reduce the burden of conventional waste management approach. The common methods in handling these solid wastes are incineration and landfill. In many countries including Malaysia, the concept of 3R (reduce, reuse and recycling) has been introduced to overcome the solid waste problem, particularly the non-biodegradable plastic. According to Moh and Abd Manaf [1], this 3R concept is essential to prolong the landfills lifespan such as in Malaysia, and it is cheaper than incinerators,

Nevertheless, the recycled PP (rPP) tends to have inferior property as compared to virgin materials which associated with the recycling process, thereby limited the application of the rPP. This issue can be resolved by blending the rPP with other polyolefin [2-3] or adding it with renewable fillers such as microcrystalline cellulose (MCC) [4]. The resultant composites usually exhibit the desirable properties and some properties even better than virgin materials [5-6]. The filler based natural fiber is preferred due to their biodegradability, low cost and low density.

Neither virgin nor recycled PP composites, the improvement of their properties are highly depending on the interfaces between the filler and the PP matrix. Several previous works have reported the miscibility or compatibility of PP [7-9] and recycled PP [5,10] composites enhanced by adding the maleic anhydride PP (MAPP) coupling agent or compatibilizer.

The feasibility of reprocessing PP composite based natural fiber is very important to promote the recycling rate. Indeed the recyclable properties of PP based natural filler composites are still not fully explored and only few previous studies have been reported. Lila et. al [11] and, Bourmaud and Baley [12] have studied the effect of recyclability on the mechanical and thermal properties of PP/bagasse fiber, and PP/hemp and PP/sisal fiber composites, respectively. However, these works have used long fibers which are above 1.5 mm in length. As a result, the effects of reprocessing or recycling's cycle of rPP reinforced with cellulose on their properties have not been fully studied.

Hence, the objective of the present research is to evaluate the recyclability of polypropylene (PP) reinforced with MCC composites fabricated via repeated injection molding process up to 5 cycles. The effect of number of reprocessing on the rPP composite's performance was observed by determining its thermal properties with differential scanning microscopy (DSC) and thermal gravimetric analysis (TGA). The Fourier transform infrared (FTIR) was also used to monitor any chemical changes.

II. EXPERIMENTAL

A. Materials

The recycled polypropylene (rPP) resin has flow index of 1.34 g/10 min and density of 1.07 g/cm^3 was obtained from Top Flow Industry Sdn Bhd. Microcrystalline cellulose (MCC) fibre with an average diameter of 20 µm and maleic anhydride grafted polypropylene (MAPP) was used as reinforcement and coupling agent, respectively. Both MCC fibre and MAPP were purchased from Sigma–Aldrich Company.

B. Sample Preparation

The initial rPP/MCC composite sample was fabricated in our previous reported study [5]. In this work, the rPP, MCC and MAPP were compounded with an extrusion and injection molded to obtain the standard samples and these samples were used in this study. The fabricated rPP composites with 5 and 20 wt% MCC content samples were crushed and dried in an oven at 80 ^{O}C for 24 hours to minimize the moisture content. Then the crushed composites were injection moulded using a Battenfield HM 600/850 injection moulding machine. The temperature profile was maintained between 180 ^{O}C and 190 ^{O}C. The final samples were prepared in the form of dumbbell type IV and rectangular shapes according to ASTM: D638 and ASTM: D790, respectively. After that the samples were characterized and a similar samples preparation and characterizing procedure were repeated another four times. The reprocessing cycle is shown in Fig. 1.

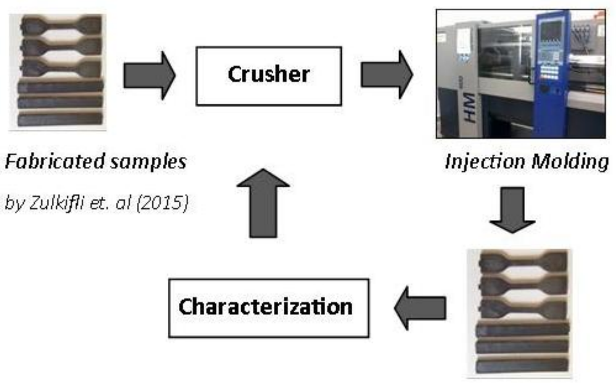

Fig. 1: Reprocessing cycle of rPP/MCC composites

C. Characterization

Differential scanning calorimetry (DSC) was performed under nitrogen gas with a 10 C min's heating rate from 30^{O} C to 300^{O}C, using a DSC 1/700 Mettler Toledo and the sample mass was approximately 10 mg for each sample. The percentage of crystallinity was calculated from equation (1)

$$X_c(\%) = \frac{\Delta H_m \, x100}{\Delta H_m^o x W} \tag{1}$$

Where,

ΔH_m = enthalpy of fusion

ΔH^O_m= enthalpy of fusion of 100% crystalline PP (209J/g)

W = the mass fraction of PP in the composites

Thermogravimetric analyses (TGA) were conducted using a TGA- Hitachi ST7300 (TA Instrument) from 25 to 600^{O}C. The heating rate was set at 10^{O}C min^{-1}.

Fourier transform infrared spectroscopy (FTIR), was used to detect the changes in chemical bond in the rPP and composite samples. The spectra were recorded using Nicolet iS50 FTIR machine with frequency range of 400-4000 cm^{-1}.

III. RESULT AND DISCUSSION

A. FTIR Analysis

Figures 2 and 3 show the FTIR spectrum of rPP composites added with 5wt% and 20t% MCC at different reprocessing or recycling cycles. Both composites exhibit the bands which represent the major characteristics of PP. The bands are the (1)stretching of CH in the range of 2950 - 2846cm^{-1}, (2)CH_2 in the range of 1460-1450cm^{-1} and (3)CH_3 1380 – 1370 cm^{-1} [6]. The stretching peak of CO, CH and CH_2 of the MCC fibre are between 1000cm^{-1} to 1400cm^{-1}. Regardless to the composition of the composites (Figure 2-3) and the reprocessing number, no major change was observed. This observation suggests that the rPP/MCC composites may retain its properties even after 5 recycling cycles.

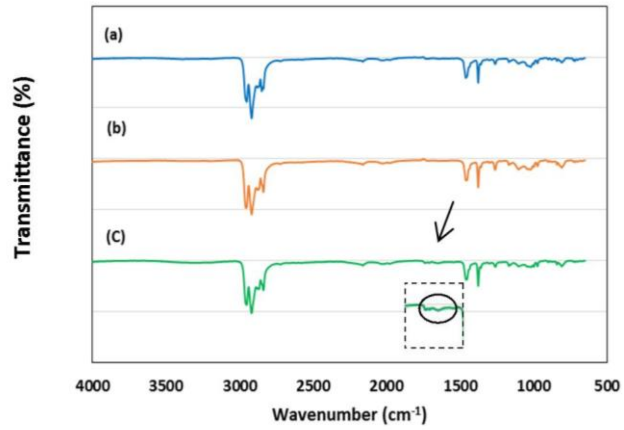

Fig. 2: FTIR spectra of rPP/5MCC composites at reprocessing cycle of (a)1, (b) 3 and (c) 5

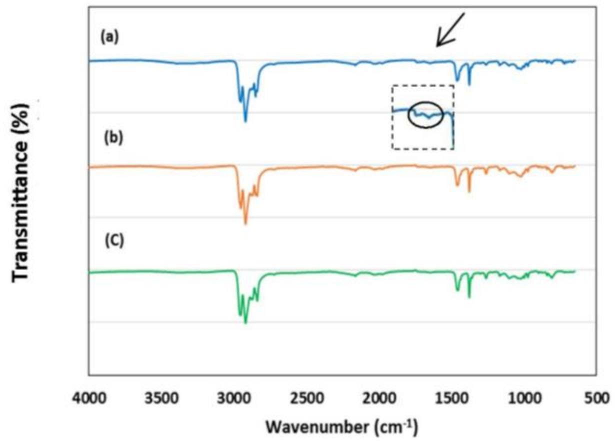

Fig. 3: FTIR spectra of rPP/20MCC composites at reprocessing at cycle of (a)1, (b)3 and (c)5

Interestingly the presence of peak indicating esterification reaction between the cellulose and MAPP coupling agent at around 1,600 – 1730 cm-1 is evident at all cycles. A closer view clearly (dotted square box) shows these bands. This indicates that the reprocessing did not deteriorate the function of MAPP coupling agent in enhancing the adhesion between MCC fiber and rPP matrix.

March – April 2020
ISSN: 0193-4120 Page No. 25906- 25909

B. DSC Analysis

The DSC results for rPP/MCC composites as a function of different recycling cycles and MCC content are shown in Figure 4. The existence of two melting peaks verified that the recycled PP also consists of high density polyethylene (HDPE). The first and second peak refers to melting temperature of HDPE and PP, respectively [13].

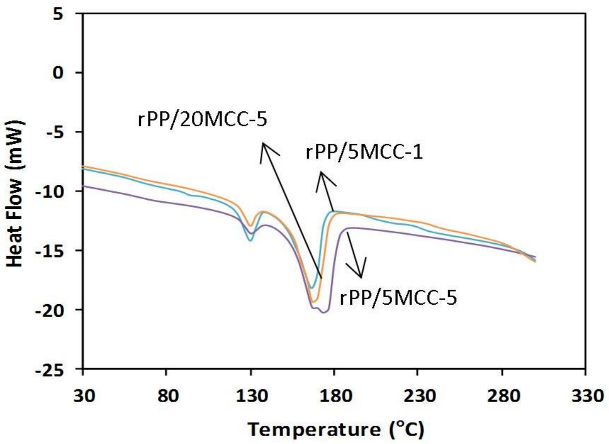

Fig. 4: DSC curves of rPP/MCC composites at different reprocessing cycles.

Table 1 summarizes the melting temperature (T_m), heat of fusion (ΔH_m) and degree of crystallinity (X_c) of the composites. It is observed that the T_m of rPP/5MCC composites at 5 cycles is higher than that at 1 cycle; 174^{O}C and 166^{O}C, respectively. This implies that the reprocessing cycles and the presence of MAPP coupling agent have significant effect on the T_m of PP composite reinforced with cellulose fiber.

Table 1: DSC data of rPP/MCC composites at different reprocessing cycles.

Sample	T_{onset} (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
rPP/5MCC-1	154.73	166.38	39.03	20.30
rPP/5MCC-5	172.25	173.93	52.15	27.12
rPP/20MCC-5	156.58	167.66	42.97	26.70

As seen in Table 1, the ΔH_m and X_c values of rPP/5MCC composites were also increased with increasing number of reprocessing process. The increment of ΔH_m and X_c values of rPP/5MCC composites in the current study are in accordance with previous works by [11-12,14]. Dungou et. al [14] suggested that the occurrence of degradation during the recycling had produced shorter chains. Subsequently, the chain mobility increased and induced the crystallization process.

Apparently the presence of higher MCC loadings (20wt%) had caused improvement to the T_m, ΔH_m and X_c values of rPP composites. According to Lazim and Samat [6], the increase in the X_c percentage was associated to the higher loading of MCC, in which the cellulose act as nucleating agent. In addition, it is presumed that the repeated cycling process along with the existence of coupling agent had promoted a better dispersion of higher MCC loadings. Hence, the occurrence of this phenomenon could also have assisted the nucleation process of shorter rPP chains and led to enhance the level of crystallinity.

C. TGA Analysis

The thermal stability of the rPP/MCC composite at different recycling cycle was measured by TGA in nitrogen from 30^{O}C to 600^{O}C and result is shown in Figure. 5. In this study, the thermal degradation is discussed based on the weight loss of sample which occurred at 10% (T_{10}) and 50% (T_{50}). Irrespectively to the number of recycling cycles, at low MCC content, the samples exhibits a single mass-loss step of thermal decomposition. On the other hand, as the MCC was increased to 20wt%; double mass-loss step thermal was observed instead.

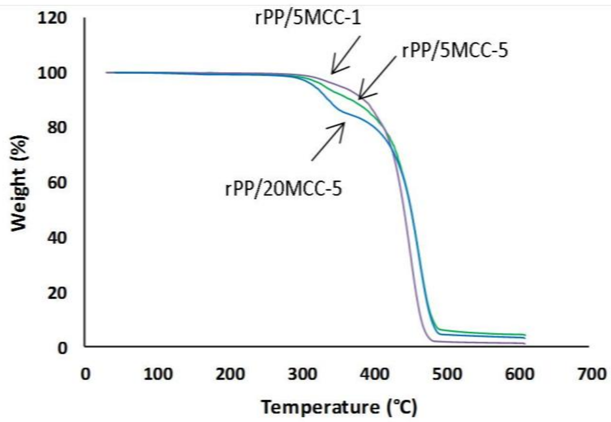

Fig. 5: FTIR spectra of rPP/MCC composites at different reprocessing cycles.

From Figure 5, generally the repeating recycling process improves the thermal stability of rPP/MCC composites. For sample rPP/5MCC composites, the degradation temperature at onset and T_{10} after 5 cycles is higher than that at 1 cycle. This observation is consistent with the DSC's result. As mentioned in earlier discussion, a slightly better thermal stability of rPP/5MCC composite could be related to an even dispersion of MCC fiber.

Table 2: TGA data of rPP/MCC composites at different reprocessing cycles

Sample	Degradation temperature (^{O}C)			Char at 600^{O}C (%)
	T_{onset}	T_{10}	T_{50}	
rPP/5MCC-1	302	370	453	4.64
rPP/5MCC-5	322	388	442	1.46
rPP/20MCC-5	294	338	452	3.54

It is interesting to note that as the testing temperature was increased (>500^{O}C), the thermal stability behaviour of this rPP/5MCC composite showed an opposite effect. At T_{50}, the thermal decomposition at 5 cycles occurred at temperature lower (442^{O}C) than that at 1 cycle (453^{O}C). As a result, the residual mass (char) value at 600^{O}C at 1st cycle is higher than that at 5th cycles; 4.64% and 1.46% respectively.

As suggested in the DSC analysis, although the reprocessing of the rPP/MCC composites may improve the MCC dispersion but repeated process also could cause degradation to the PP matrix. Bourmaud and Baley [12] found that the reprocessing of PP/hemp and PP/sisal composites had resulted in declined of the Newtonian viscosity value. This incident was attributed to the decrease of molecular weight as a consequence of chain scissions. For the rPP/20MCC, higher mass residue at 600^{O}C is due to the higher content of MCC.

IV. CONCLUSION

The effect of reprocessing cycle of rPP/MCC composites and the presence of MAPP coupling agent on their thermal properties was investigated. The use of MAPP coupling agent in promoting an improvement of the adhesion between MCC fibre and PP was exhibited by FTIR analysis. Higher reprocessing cycles along with the presence of MAPP enhanced the dispersion of MCC fiber in the rPP matrix. The occurrence of this incident was evident with higher value of crystallization percentage, melting temperature, heat of fusion and thermal stability. This effect was also seen in rPP composites with higher MCC loadings. Although higher reprocessing cycles deteriorated the rPP matrix, but the thermal decomposition behavior exhibits no significant effect, except at temperatures above 500^{O}C.

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Dr. Noorasikin, is an Assistant Professor at Department of Manufacturing and Materials Engineering, International Islamic University Malaysia (IIUM), Kuala Lumpur. She received her PhD in Materials Science and Engineering from The University of New South Wales (UNSW), Sydney, Australia, in 2010. Her Doctoral study was in the field of polymer nanocomposites. She obtained her MSc in Materials Science and Engineering from Universiti Sains Malaysia (USM), in 2001, and BSc(Hons.) in Material Science from Universiti Kebangsaan Malaysia (UKM) in 1999. Dr. Noorasikin research interest includes green composites/nanocomposites, recycling waste material for polymer composites application and flame retardant materials. She has involved in teaching, research, publication and supervising postgraduate students.

Second Author personal profile which contains their education details, their publications, research work, membership, achievements, with photo that will be maximum 200-400 words.

Muhd Izzudin Shafiee received his B.Eng degree in Materials engineering from International Islamic University of Malaysia in 2019. His final year project involves in the behaviour of composites during recycling process. He also involves in innovation competition at international level, which his project involves in the concept of precession**s.**