EVALUATION OF DIFFERENT CELLULOSIC FILLERS AS REINFORCEMENT IN POLYPROPYLENE AND THEIR DIE-DRAWING BEHAVIOUR

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Abstract
In the present study microcrystalline cellulose (MCC), regenerated cellulose fiber (Tencel SF) and ethyl cellulose (EC) have been used as potential reinforcements in polypropylene (PP). MCC, Tencel SF increase the stiffness and reduce the strength. EC maintains both stiffness and strength. Addition of maleic anhydride grafted PP as compatibilizer increases strength of the composites, except for composites with EC. Scanning electron microscopy (SEM) analysis corroborates the improvement in interface between filler and matrix. Die drawing studies were done on composites with 20% filler loading and tensile properties of drawn samples were measured. Both stiffness and strength of drawn composites increase significantly.

1 Introduction

Many natural fibers have been explored in the past as reinforcements in thermoplastics and thermosets [1-7]. The advantages of using natural fibers as reinforcing agents in different polymers are to reduce weight, gain relatively good stiffness and strength, as well as ease of recycle and disposal. There have been intensive research and product development of composite materials using polypropylene and polyethylene reinforced with various natural fibers. However there are limited studies on the effect of solid-state drawing of these composites.

Anhydride functional materials are commonly used as compatibilizers in the area of natural-fiber composites, with anhydride-grafted polyolefins in commercial PE and PP natural fiber composites as the prime example [8]. The polar anhydride groups can form covalent and/or hydrogen bonds with the hydroxyl groups on the natural fiber surface, whereas the non-polar backbone is more compatible with the matrix polymer.

In the present study microcrystalline cellulose powder, regenerated cellulose fiber and ethylated cellulose have been used as reinforcements in PP. The properties are compared with that of talc filled composites as talc is widely used as filler in PP. Maleic anhydride grafted PP (PP-g-MA) has been used as compatibilizer as it can be used directly during compounding. Mechanical properties like tensile, flexural and impact have been studied to understand the

degree of reinforcement. Thermal characterization has been done to understand the effect of these fillers on crystallization behavior. Interface of these composites has been studied using scanning electron microscopy technique. These composites have also been subjected to die drawing to understand their die drawing behavior and to see whether die drawing can be used to overcome the limitations of these natural fillers.

2 Materials

Isotactic polypropylene (PP) Repol® H050MN grade manufactured by Reliance Industries, India was used as the base resin for all formulations. Polypropylene grafted with maleic anhydride (PP-g-MA) produced by Exxon Mobil Chemicals was used as a compatibilizer to enhance interfacial bonding between the resin and the filler. Talc was received from Luzenac. The JetFine® talc grade used was E3CA. Microcrystalline cellulose was obtained from Asahi Kasei, Japan. The exact grade used was CEOLUS KG-802. Lyocell fibers are commercially supplied by Lenzing Fibers under the trade names Tencel® (Tencel SF). Ethyl cellulose (EC) obtained from Fecheng Ruitia fine chemicals from China was used in all formulations.

3 Experimental

3.1 Compounding & Injection Molding

Filler loading has been kept at 20% by weight and samples were prepared with and without the addition of 5% PPgMA as a compatibilizer. Compounding was carried out between 150-180°C using an intermeshing, twin screw extruder of Coperion make (Model ZSK-25). Screw speed was maintained at 300 RPM during the melt extrusion to maintain through put rate of 8kg/hour. Screw and barrel configuration was chosen to minimize the thermal degradation of natural fillers used in the present study. Compounded pellets were dried at 100°C for a minimum of 6 hours in a hot air circulated oven as cellulosic fibres are hygroscopic in nature. Compounded pellets then, were injection molded between 130-210°C into standard test specimens using LT Demag 60 injection molding machine of L&T Make.

3.2 Die Drawing

It is well known that the mechanical properties of a polymer can be significantly improved by orientation. Oriented samples were prepared by the die-drawing process [9]. Schematic set up used in die drawing is as shown in Figure 1. The entire set up along with the sample is heated to 140°C and maintained at that temperature for 1 hour so as to allow the sample to attain the set temperature. Then after this the samples were pulled at constant speed of 10 mm/minute. Tapered dies with nominal draw ratio of 4, 2.6 and 1.6 were used. Once sufficient sample length of constant cross sectional area was formed, moving frame of the machine is stopped. Heater was switched off and sample was cooled under tension.
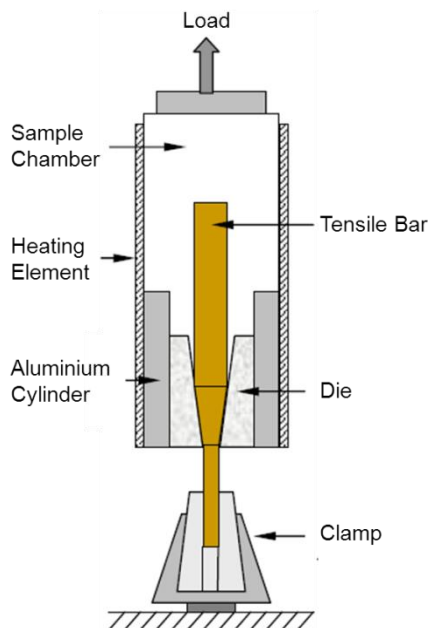
Figure 1. Schematic of set up used for die drawing.

3.3 Testing

All the test specimens were conditioned at 23°C & 50 % relative humidity for a minimum of 48 hours before testing. For impact testing, specimens were conditioned for a minimum of 24 hrs, after the notch cutting.

Uni-axial tensile testing was done using Zwick universal testing machine (Model No. Z010, motor driven test frame) as per ISO 527 test method. Flexural testing was done on the same machine with flexural testing fixture as per ISO 178 test standard. NII was determined as per ISO 180/1A test protocol. Heat distortion temperature (HDT) was done as per ISO 75 test standard. Melt flow index (MFI) was measured as per ASTM D1238 test protocol, using a Gotfert make melt volumetric flow rate/melt flow rate Testing Machine. All the formulations were dried for a minimum of 3 hours at 100°C in a hot air circulated oven. The exact test conditions were 230°C as temperature of the barrel, 2.16 kg as load and the total pre-heating time was 360 seconds. Strands were cut at an interval of 15 seconds and weighed. MFI has been reported in grams per 10 minutes.

Thermo-mechanical analysis was done to measure the co-efficient of linear thermal expansion (CTE) as a function of temperature. This was done using TMA analyzer supplied by TA instruments (model TMA 2940). Thermo gravimetric analysis (TGA) was done using thermo gravimetric analyzer from TA instruments (model hiRES TGA 2950). All the formulations were heated from room temperature to 800°C at a rate of 20°C per minute in air atmosphere and in nitrogen for just fillers. All microscopy studies have been performed on a FEI QUANTA 400 ESEM operated at 30 kV.

4 Results and discussions

TGA of fillers was done in nitrogen atmosphere to understand their intrinsic thermal stability. From Figure 2 we can make out that the onset of degradation for all the cellulosic fillers used

in the present study are well above 200°C. Since PP can be processed around 200°C, we could comfortably use PP as matrix resin without causing too much of degradation of cellulosic fillers used. Thermal stability of Talc > Ethyl Cellulose > MCC > Tencel Fibre. Also from Figure 3 it is clear that addition of talc does not decrease the thermal stability of formulations and whereas addition of cellulosic fillers decreases the thermal stability of formulations.
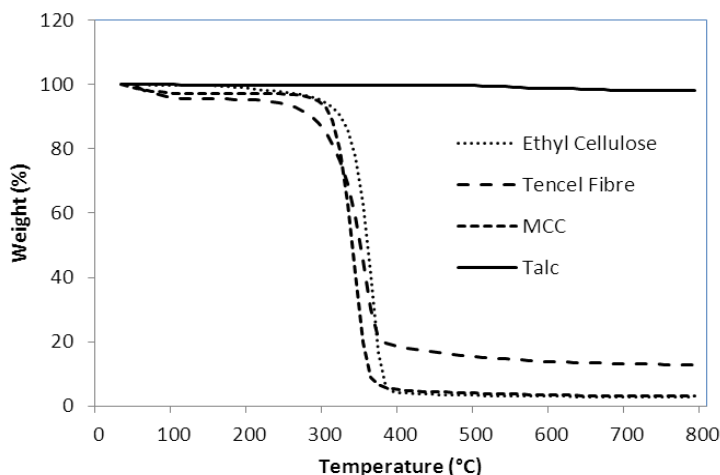
Figure 2. TGA curves of MCC, Tencel fiber and ethyl cellulose.
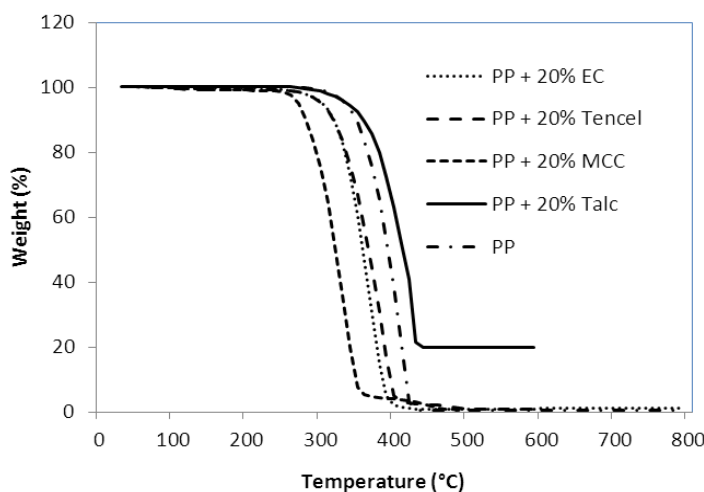
Figure 3. TGA curves of PP and PP compounds with 20% Talc, MCC, Tencel fiber and ethyl cellulose.

Mechanical and thermal properties of unfilled and filled polypropylene with and without PPgMA are given in Table 1. When we add talc only the modulus of corresponding formulations increase indicating a typical reinforcement behavior of short and stiff filler. MCC also increases the modulus of PP but not to the same extent as talc and tensile strength decreases with MCC addition. This could be because of poor dispersion of polar MCC in a non-polar matrix like PP. With Tencel fiber increase in modulus is lower than that of MCC, which

|	Unfilled	20% Talc	20% Talc + 5% PPgMA	20% MCC	20% MCC + 5% PPgMA	20% Tencel	20% Tencel + 5% PPgMA	20% EC	EC + 5% PPgMA
Tensile Modulus (MPa)	1962	3038	3200	2507	2681	2273	1840	1823	1690
Tensile Strength (MPa)	29.9	26.4	36.3	26.6	36.1	27.8	31.9	31.6	30.0
% Elongation	12.9	15.5	_	10.0	_	9.2	_	6.9	_
Flex Modulus (MPa)	1834	3034.0	3023.0	2484.0	2312.0	2213.0	2041.0	1679.0	1519
Flex Strength (MPa)	50.5	52.4	55.9	45.3	53.1	42.9	52.4	44.2	44.4
Nothched Impact kJ/m^2	2.3	3.3	3.9	2.0	3.3	3.3	4.3	2.3	2.4
HDT (^{o}C)	90	114.0	_	118.0	_	99.0	_	87.0	_
MFI (gm/10min)	6.1	5.9	_	5.6	_	2.2	_	27.7	_
CTE in flow (μm/m ^{o}C)	98	97	_	89.5	_	95	_	132	_
CTE cross flow (μm/m ^{o}C)	151	146.0	_	146.0	_	133.0	_	143.0	_

Table 1. Mechanical and thermal properties of filled and unfilled polypropylene

could be due to non-fibrillation of Tencel fiber bundles. In case of ethyl cellulose tensile strength is more or less maintained with a slight drop in modulus. This is expected as ethyl cellulose is amorphous in nature. On replacing neat PP resin with 5 weight % of PP-g-MA in 20% filled formulations, we see that for formulations with talc, MCC and Tencel SF fibre tensile strength increases. In ethyl cellulose formulations, since there is no interaction between anhydride groups of PP-g-MA and ethyl cellulose, the tensile strength is 30 MPa which is equivalent to the effect of diluting just PP with PP-g-MA. Improvement in tensile strengths of formulations with talc, MCC and Tencel SF fiber indicate a positive interaction between PP-g-MA and corresponding fillers. From Table 1, it is clear that ethyl cellulose improves the flow, talc maintains the flow. MCC reduces the flow marginally; whereas Tencel SF reduces flow drastically, because of its high aspect ratio. The most interesting observation here is ethyl cellulose because of its amorphous nature increases the flow drastically, not affecting other enabling mechanical properties. As we can make out from Table 1, talc maintains the CTE value of PP, whereas MCC and Tencel SF reduce the CTE values. Ethyl cellulose whose Tg is around 100°C increase the CTE of PP in the temperature region of interest. We do observe improvements in the NII of compositions. This could be due to increase in stiffness because of the addition of fillers. We can infer that addition of these fillers does not adversely affect the NII value of PP.

Scanning electron microscopy analysis was done on formulations with and without PP-g-MA to understand dispersion of these fillers, qualitative understanding of PP/filler interface and to corroborate the observations made in tensile property measurements. Figure 4 shows the SEM images of all 20% fillers compositions which indicate good dispersion of filler in the matrix. Figures 5 show SEM images of the same compositions with 5 weight % of PP-g-MA. From Figures 4 and 5 it is clear that addition of PP-g-MA does not change dispersion of fillers in PP to any significant extent. It can be seen that in the case of MCC and Tencel fibre addition of PPgMA seem to improve interface between these fillers and PP. In case of ethyl cellulose there is no improvement at the interface. This poor interaction between ethyl cellulose is expected as there are no or reduced hydroxyl groups in ethyl cellulose to react with PP-g-MA.
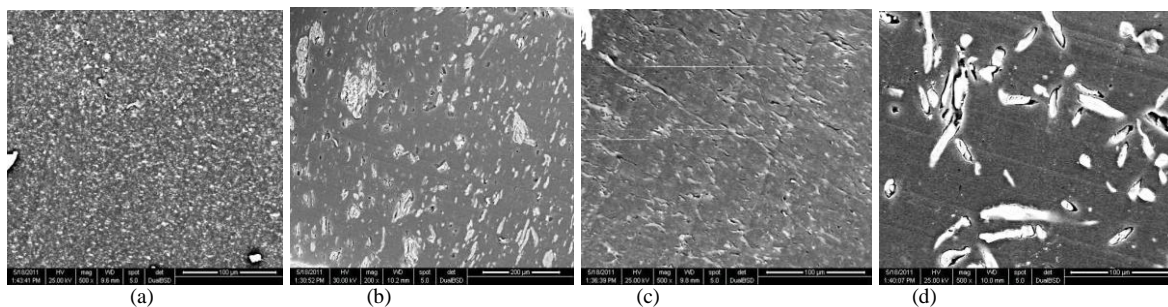
Figure 4. SEM images of PP with 20% loadings of (a) Talc, (b) MCC, (c) Tencel fibre and (d) Ethyl Cellulose.
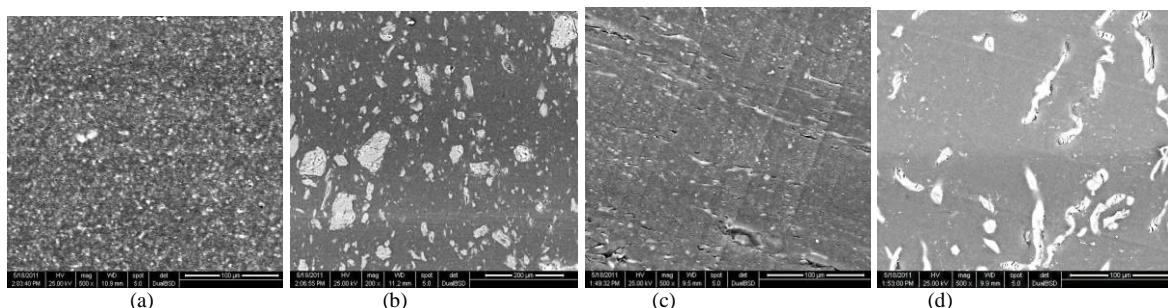
Figure 5. SEM images of PP with 5% PPgMA and 20% loadings of (a) Talc, (b) MCC, (c) Tencel fibre and (d) Ethyl Cellulose.

DSC studies were done to understand whether addition of fillers aids or hinders crystallization process of PP. Most of the inorganic fillers act as nucleating agents which help in accelerating the crystallization process. There is no change in overall crystallinity levels of neat PP resin and those with 20% filler in it. In terms of crystallization behavior talc acts as a nucleating agent and hence shifts peak crystallization temperature (T_c) by 2°C, whereas all other organic fillers like MCC, Tencel SF and ethyl cellulose decrease the T_c and hence slow down the process of crystallization. MCC and Tencel SF decrease T_c by 3°C and 6°C respectively. Ethyl cellulose in particular decreases T_c by almost 16°C and this could be due to its amorphous nature with a glass transition temperature (T_g) of around 120°C. It seems like segmental movements of ethyl cellulose above its T_g, disturbs arrangement of PP chains into neatly packed crystals. DSC exotherms are shown in Figure 6.
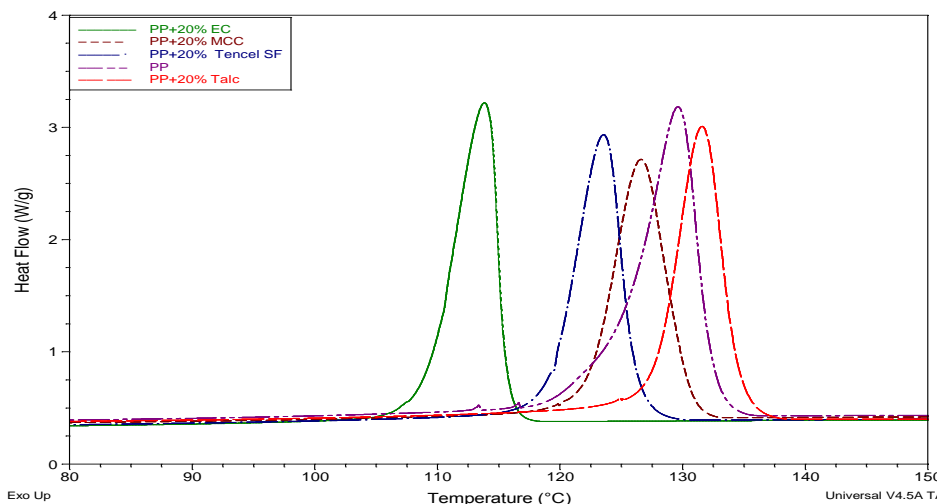
Figure 6. DSC exothermic curves of PP and its composites with 20% filler loading in DSC.

4.1 Die drawing studies

All samples were drawn at a constant draw temperature of 140°C, through dies of R_N 1.6, 2.6 and 4. Drawing was carried out at 10mm/minute. As the material leaves the die exit it draws down further and hence actual draw ratios are much higher than nominal draw ratios. Actual draw ratios of these samples is are shown in Table 2. It can also be observed that ethyl cellulose samples draws significantly more when compared to samples with other fillers. This might be because of lubricating effect of amorphous ethyl cellulose, which helps in drawing polypropylene chains to higher extent.

R_N	Actual draw ratio (R_A)				
	PP	PP+ 20% talc	PP+ 20%MCC	PP+20% Tencel SF	PP+20% Ethyl cellulose
4	5.2	5.0	4.9	4.9	7.3
2.6	4.3	4.1	3.8	3.7	5.2
1.6	3.2	2.3	3.6	3.4	4.8

Table 2. Actual draw ratios at 10mm/minute and 140°C.

Tensile modulus and strength were measured on all drawn samples. Tensile modulus and tensile strength increases with increase in draw ratio as shown in Table 3 and Table 4. From the results it is clear polymer orientation is more dominant than the type of filler used for these properties. Please note that R_N =1 corresponds to values of isotropic samples.

R_N	Tensile modulus in MPa				
	PP	PP+ 20% talc	PP+ 20%MCC	PP+20% Tencel SF	PP+20% Ethyl cellulose
4	5359	6206	4479	4655	7049
2.6	3508	5526	3978	3300	4436
1.6	2665	5780	2842	2933	4526
1	1962	3038	2507	2272	1762

Table 3. Tensile modulus for samples drawn at 10 mm/minute at 140°C.

R_N	Tensile strength MPa				
	PP	PP+ 20% talc	PP+ 20%MCC	PP+20% Tencel SF	PP+20% Ethyl cellulose
4	192	123	154	136	171
2.6	120	126	78	102	90
1.6	140	105	94	66	95
1	36	36	30	29	35

Table 4. Tensile strength for samples drawn at 10 mm/minute at 140°C.

5 Summary and Conclusions

Microcrystalline cellulose, regenerated cellulose fiber and ethyl cellulose have been used as reinforcements in polypropylene matrix. Talc has been used as standard filler for comparison purpose. MCC and Tencel SF have been found to increase the stiffness of the composites, while dropping the strength marginally. EC maintains the strength and stiffness and hence could be used as a bio diluent. Addition of maleated PP increases the strength of composites having MCC and Tencel SF and does not affect the strength of composites having EC. The positive interaction between MCC and Tencel with maleated PP has been corroborated using scanning electron microscopy (SEM). Thermal analysis like differential scanning calorimetry shows that overall crystallinity of composites is not affected because of the addition of these fillers. Talc increases peak crystallization temperature (T_c) by 2°C, which shows that it acts as a nucleating agent. MCC and Tencel SF have been found to reduce T_c by 3-6°C hindering the crystallization process. EC reduces T_c by 16°C and this issue needs to be addressed by using nucleating agents. Flow as measured using MFI shows that drastic reduction is observed for composites with Tencel SF, which could be attributed to the high aspect ratio of these fibers. EC increases the flow to a significant extent and maintaining all other enabling properties, which indicates this could be used as plasticizer in PP. TMA data shows that CTE is not affected because fo the addition of these fillers, except for EC, which increase CTE in flow direction. Talc, MCC and Tencel SF increase HDT, whereas EC reduces it by 4-5°C. Die drawing studies was done using 20% filler loading composites. Tensile modulus and strength of drawn samples increase with increasing draw ratio.

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