Polymer Bulletin 49, 465–472 (2003)

Polymer Bulletin

Effect of Inorganic Filler Phase on Mechanical and Morphological Properties of Binary Immiscible Polymer Blends

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Received: 19 June 2002/Accepted: 19 January 2003

Summary

A ternary composite composed of two immiscible organic phases, polypropylene (PP) and polyamide-6 (PA), and talc as inorganic filler is studied in terms of mechanical properties and microstructure. Effect of different filler levels (10-30 % by weight) on tensile and flexural properties of each polymeric phase is examined while special attention is paid to immiscible PPPA blend. Mutual effect of compatibilizer and filler on properties is searched by selecting maleic anhydride grafted polypropylene (MA-g-PP) as compatibilizer. It is observed from SEM studies that inhomogeneous, course and elongated morphology of uncompatibilized composites is changed to well dispersed, fine and more homogeneous particle-in-matrix morphology via additional compatibilization effect. This unique microstructure is believed to be responsible for the improved tensile and flexural properties in blend composites.

Introduction

Blending of two polymers has become an increasingly important industrial technique, because blends meet performance demands that cannot be satisfied by currently available commodity polymers. By blending polypropylene (PP) and polyamide (PA), superior thermal or mechanical properties of polyamide, and advantageous characteristics of polypropylene; like insensitivity to moisture, high chemical resistance, low density, and low cost, can be combined. However, blending of such immiscible polymers without compatibilizer which achieve satisfactory interfacial adhesion and stress transfer between phases, leads to coalescence of break–up phases at the molten state, heterogeneous phase dispersion and worsen overall properties [1-2]. Such blends can be compatibilized by reactive extrusion, where block or graft copolymers containing functional groups complementary to functionality of components are used to improve miscibility between two components. Binary blends of PP and PA have been studied previously [2-8]. Well-known compatibilizer for PPPA system is maleic anhydride grafted polypropylene (MA-g-PP) as studied by Ide et al [8]. In situ chemical compatibilization reaction at the melt mixing process takes place between the anhydride or carboxyl groups of the functionalised polyolefin;

namely MA-g-PP, and amine end group of the polyamide [3,7]. That reaction leads to grafted copolymer formation and preferentially resides at interface, which improves the interfacial adhesion, and resulting in a finer dispersion and more stable morphology. The studies concentrated on the effect of mixing process parameters (screw speed, throughput and barrel temperatures) on PPPA blends concluded that only efficient parameter controlling the final morphology is the compatibilizing agent amount [2,5].

Addition of fillers to a resin to form a composite material leads to reduce the cost of compound and extends the resin with minimal sacrifice in physical properties. One of the widely used fillers for thermoplastics is talc. Its plate-like structure or high aspect ratio improves the stiffness and creep resistance at both ambient and elevated temperatures, compared to other fillers such as calcium carbonate.

The aim of this study is to investigate the multiphase composites which have two immiscible organic phases, polypropylene and polyamide-6, in the presence of the inorganic filler, talc. Special attention is paid to examine the effect of selective wetting of filler surface by one of the polymer phases, compatibilizer, and amount of filler on morphology and mechanical properties of resultant composites.

Experimental

Materials

PA (Specialamid) with melt flow index of 22 gr/10 min. and density of 1.12 g/cc was obtained from Gruppo Bonazzi-Italy. PP (Moblen PM HP 502L) with melt flow index of 8 gr/10 min. and density of 0.89 g/cc was from Basell-Italy. MA-g-PP containing %1 maleic anhydride (MA) was Polybond 3200 from Uniroyal Chemical-USA, with the density of 0.91 g/cc, 157 ^{0}C melting point, 120 g/min melt flow rate. 10-micron mean diameter talc was supplied from DYO-Turkey.

Blend Preparation

PA and MA-g-PP were dried at 80^{0}C overnight to eliminate the hydrolysing effect of absorbed water. The filler talc and polymer (PP or PA) were fed separately into the extruder from the same inlet port with the help of volumetric feeders. The extruder was an intermeshing co-rotating modular twin-screw extruder with L/D of 28:1. The screw rotation speed was set to 100 rpm. Temperature profile was set to 70^{0}C for first feed port and 235^{0}C for the rest. It was previously shown [2] that back screw element following the kneading block would help to chemical compatibilization reaction. In this study, 30^0, 60^0 and 90^0 kneading element blocks were located at 12 L/D, followed by back mixing element and at 20 L/D, another 30^0, 60^0 and 90^0 kneading element blocks before venting port was located. The remaining elements were conveying elements. The extrudate was quenched in a water bath, pelletised and then dried. The samples were then injected into a specimen mould.

All blend composites were prepared by using PP/PA to give 75/25 (% by weight), respectively in the presence of 0-30 %, by weight of talc as filler. The following nomenclature is used: Compositions of polypropylene and polyamide composites having 0, 10, 20, 30 %, by weight talc are designated as PP, PP1, PP2, PP3, and PA, PA1, PA2, PA3, respectively. The blend composites without and with compatibilizer are designated as PPPA, PPPA1, PPPA2, PPPA3 and PPPAC, PPPAC1, PPPAC2, PPPAC3, respectively.

Measurements

Typical stress strain curves for determination of both tensile and flexural properties were obtained at ambient temperature using an Instron 4505 tensile testing machine according the ISO R565 and ISO 178 procedures, respectively. At least 5 specimens were tested with 50 mm / min crosshead speed for tensile test and 5 mm / min for flexural test. Tensile yield strength, elongation (strain), Young's modulus, flexural strength, flexural elongation (strain) and flexural modulus were all recorded.

A scanning electron microscope (Jeol JSM 35C) was used to examine the morphology of the blends. The specimens were notched and broken in liquid nitrogen, and the fractured surfaces were coated with gold.

Results and Discussion

Mechanical Properties

Some mechanical properties of the resultant composites are all summarized in Table 1. Tensile yield strength, Young's modulus, elongation at yield and corresponding trend lines are shown in Figures 1-3.

Table 1. Mechanical properties of samples

Sample name	Yield stress (MPa)	Yield strain (%)	Young's modulus (MPa)	Energy up to break (J)	Flexural stress (MPa)	Flexural strain (%)	Flexural modulus (MPa)
PP	34.654	10.354	1650.509	232.680	34.951	7.789	1013.876
PP1	33.907	6.905	2391.910	23.073	51.742	6.654	2147.745
PP2	33.052	5.903	2827.208	7.574	53.153	6.155	2516.276
PP3	32.695	4.579	3283.656	6.515	54.263	5.411	2873.319
PA	71.174	3.508	3002.691	117.950	86.800	6.638	2004.180
PA1	75.068	3.404	4678.693	21.617	80.526	6.780	2746.986
PA2	75.487	3.006	6307.150	7.229	92.223	6.346	4092.502
PA3	77.323	2.214	8809.185	3.494	94.471	4.816	5028.970
PPPA	31.120	4.012	2136.800	4.616	42.198	5.865	1067.909
PPPA1	27.404	3.645	2619.657	3.894	45.994	4.481	1922.428
PPPA2	24.659	3.238	2741.436	1.460	44.381	3.602	2495.365
PPPA3	22.798	2.094	3535.047	1.339	43.351	3.005	3021.733
PPPAC	37.760	5.360	2326.400	56.759	49.746	7.507	1488.230
PPPAC1	37.263	4.353	2881.219	5.436	56.767	6.160	2392.968
PPPAC2	36.331	3.589	3554.086	3.010	60.065	5.219	2533.505
PPPAC3	37.459	2.932	4500.546	2.433	63.395	3.878	3423.080

As it is seen from the Figure 1, tensile strength of PA is higher than that of PP due to its highly polar nature and large number of H-bonding interactions which then give rise to the resistance against external forces.

Increase in filler content to each system shows a different trend. As talc content increases, tensile strength of PA increases, while this effect is not well pronounced for PP. All talc filled PA composites break off without any neck formation and whitening, whereas they are observed for unfilled PA. On the other hand, up to %10 filler loading, neck formation is observed for PP. Beyond that point the deformation becomes more brittle since the triaxiality of the stresses in polymer phase is increased with filler content.

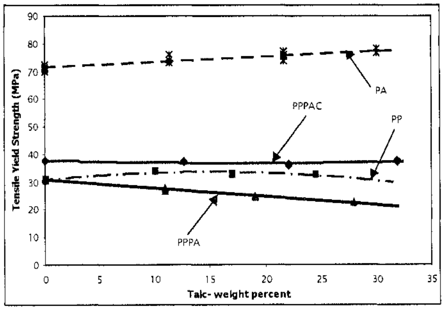

Figure 1. Tensile yield strength of PA, PP, PPPA, PPPAC composites

Morphology of binary polymer blends depends on the composition of the blend as well as viscosity of the two components. At high temperatures and high shear rates peculiar to extruders, the viscosity of PP is lower than that of PA [9]. Since PP is the major component in the selected composite (75/25) and has a lower viscosity than that of PA, the PPPA blend composites under current processing conditions (235°C and 100 rpm) must have a continuous PP phase in which PA phase is dispersed. Thus, since continuous phase determines the final properties, tensile strength of these blends without any compatibilizer and talc resembles to the behaviour of PP phase, as can be seen in Figure 1. Prominent whitening and crack formation on nearly all over the specimen outer surface are detected for PPPA and sudden failure is observed after certain level of stress is reached. This confirms that debonding of PP and PA phases is taking place during breaking.

It is worth noting that in the case of PPPA blends without any compatibilizer, addition of talc causes a decrease in tensile strength. In binary polymer mixtures, one of the phases may form a wetting-like layer at interface with solid particles. In reality, if the mixture components have different surface tensions, component having the higher surface tension should be transferred to the solid surface to minimize the interfacial tension [10]. There are many data concerning this type of selective adsorption from polymer mixtures that confirms this point of view. As a result only one phase is in direct contact with the solid particle surface. Since the surface tension of PA is higher than surface tension of PP, it seems reasonable to expect a selective wetting of talc surface by polar PA component, which then results in significant reinforcing effect on PA phases for all talc loadings. With the possibility of formation of adhesion joints between PA and talc, the resultant failure of material will be determined by strength of weaker layer, which may occur either at PA-talc interface or PP-PA interphase. Although PA-talc interaction increases in the matrix with talc amount, weak interactions of continuous PP phase with both PA and talc dominates the yield properties. As a result, an intrinsically tough PP matrix breaks at lower stress and lower elongation due to the existence of particles of disperse phase acting as stress concentrator. Prominent whitening and crack formation phenomena just before sudden failure for talc filled binary polymeric immiscible blends indicate that phase separation takes place most probably at PPPA interphase.

However, tensile strength of the blend composites can be remarkably improved with the addition of compatibilizer. For all filled and unfilled compatibilized blends there is no or so little whitening and also no neck formation just before breaking off. That indicates that at least PP and PA phases of composite adhere to each other and not separate even at high stress levels. Talc and polymeric matrix separation also cannot be claimed to be prominent. In this case, there is extra strong interaction between the anhydride or carboxyl groups of MA-g-PP and amine end groups of PA. The special interaction between surface hydroxides of talc and amine group of PA possibly throughout H- bonding also exists. Therefore, the adverse effect of weak interaction of continuous phase and PA is overcome. The resultant composite then gains almost constant tensile strength even at higher talc loadings as indicated in Figure 1.

For all type of polymeric matrices, increase in modulus - i.e. stiffening- can be observed as the most prominent physical effect of filler (Figure 2). Due to the possible agglomerates of talc and discrete PA phase that are not very well dispersed, the modulus of the resultant composites without compatibilizer are lower than that of compatibilized composites [10]. Modulus of unfilled uncompatibilized PPPA blend and unfilled but compatibilized one are close to each other. Whitening behaviour of uncompatibilized PPPA blend indicates that there is no interaction between polymeric phases. Both PP and PA chains most probably lie parallel to each other in the flow direction. They behave as parallel springs sharing the applied elastic stress. MA-g-PP forms a chemical linkage between PP and PA domains. Elastic stress is still shared, but chemical linkage between them facilitates elastic stress transfer among domains and leads to improved stiffness. As can be seen from Figure 2, addition of filler affects the moduli of uncompatibilized and compatibilized composites in the same manner. But for higher loading levels, compatibilized blend composites show higher values in modulus.

In Figure 3, a dramatic reduction in yield strain is observed in the PP matrix with talc loading, indicating the poor adhesion between the phases [11]. The favorable effect of compatibilization on the strain properties is also obvious. At all talc loading levels, the elongation values are higher for compatibilized composite compared to the uncompatibilized one. If the correlation between morphology and mechanical properties is conducted, the smaller dispersed phase morphology gained by the addition of compatibilizer seems to be very effective in increasing elongation values. In the case of compatibilized blend composites, the trend of elongation decrease with talc content is remarkable.

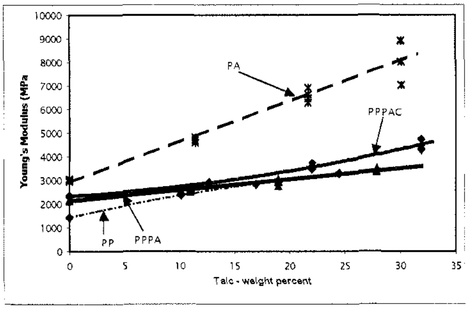

Figure 2. Young's Modulus of PA, PP, PPPA,PA, PP, PPPAC composites

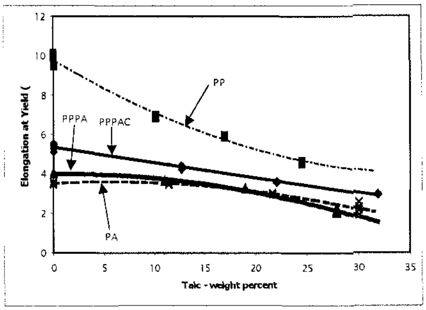

Figure 3. Tensile elongation of PPPA, PPPAC composites

The improvement in mechanical properties at all talc load levels, obtained by compatibilization can be better clarified by examining the stress-strain curves of compatibilized (PPPAC) and uncompatibilized (PPPA) composites in Figure 4.

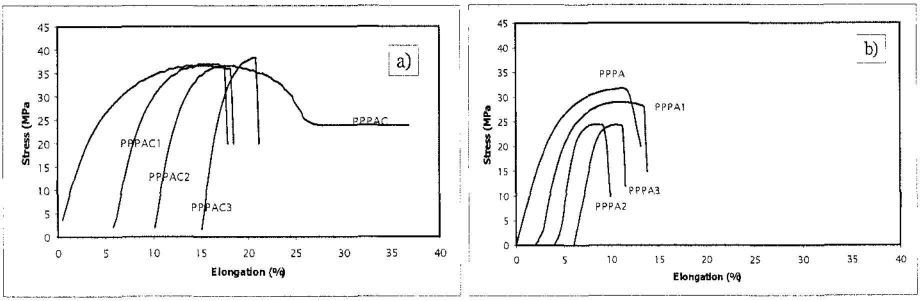

Figure 4. Stress-strain curves of a) PPPAC, PPPAC1, PPPAC2, PPPAC3 b) PPPA, PPPA1, PPPA2, PPPA3

The area under the stress - strain curve, that is given as energy to break in Table 1 is known to be proportional to the energy required to break the sample and corresponds to toughness. The toughness of resultant PPPAC composite is greatly increased compared to the uncompatibilized composites (PPPA). This result may be attributed to the better energy dissipation mechanism afforded by both reinforcing talc and maleic anhydride functional groups.

The flexural properties of the composites given in Table 1 vary with talc content in a similar way to that of the tensile properties.

Morphology

In order to provide evidence to the assertion that improved tensile and flexural properties can be related to the improvement in interfacial adhesion between the filler and polymeric matrix as well as between two polymeric phases, the fracture surfaces of the specimens are examined by SEM technique.

Figure 5 shows the topographic micrographs of cryogenically fractured surfaces of the

PP3 (a) and PA3 (b) composites. A two-phase morphology as a sign of poor adhesion between dark PP and bright talc regions is noted from the smoother fracture surface, in which the irregularly shaped inorganic fillers are dispersed in PP matrix (Figure 5 a). As far as PA is concerned (Figure 5 b), small talc particles are found more or less regularly distributed within the matrix and interconnected through stretched polymer threads. In other words filler particles are attached to the polymeric matrix through PA fibrils indicating the wetting of the filler surface by PA matrix.

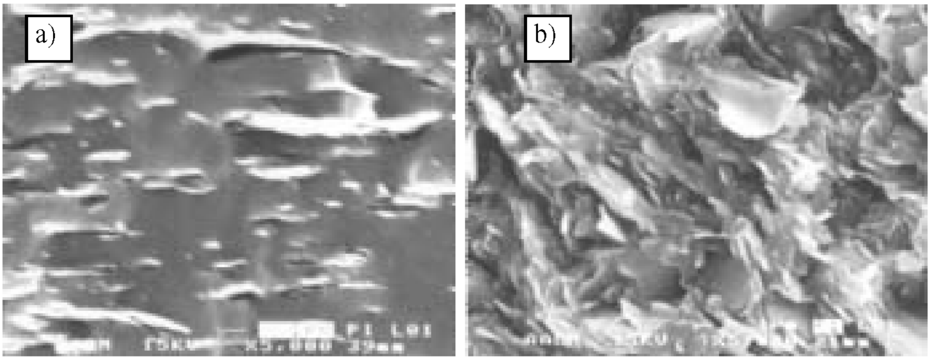

Figure 5. SEM micrographs of a) PP3, b) PA3 composites

The micrographs of PPPA1 blend composite and PA1 composite are given in Figure 6 (a) and (b), respectively. Similar topology of PA1 (Figure 6 b) exists also in the blend composites as light areas indicating overwhelming majority of the talc particles are selectively located in the dispersed PA phase of PPPA1 composites (Figure 6 a).

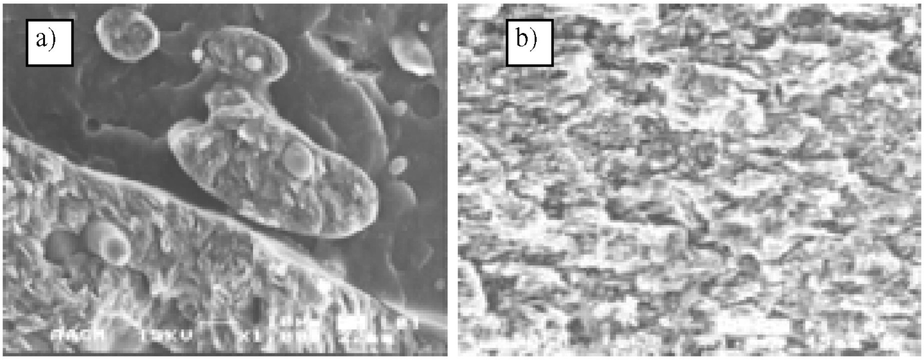

Figure 6. SEM micrographs of a) PPPA1 and b) PA1 composites

In Figure 7, on the other hand, PPPA3 composite (Figure 7 a) structure is completely different from those observed in the presence of compatibilizer, PPPAC3 (Figure 7 b). Addition of compatibilizer to the blend composite improves the homogeneity, which is attributable to a drastic reduction in the size of dispersed PA/talc phase from 15-30 to < 5 and better adhesion through the phases. It is observed that, inhomogeneous, course and elongated morphology of uncompatibilized composite is changed to well dispersed, fine and more homogeneous particle-in-matrix morphology via additional compatibilization effect.

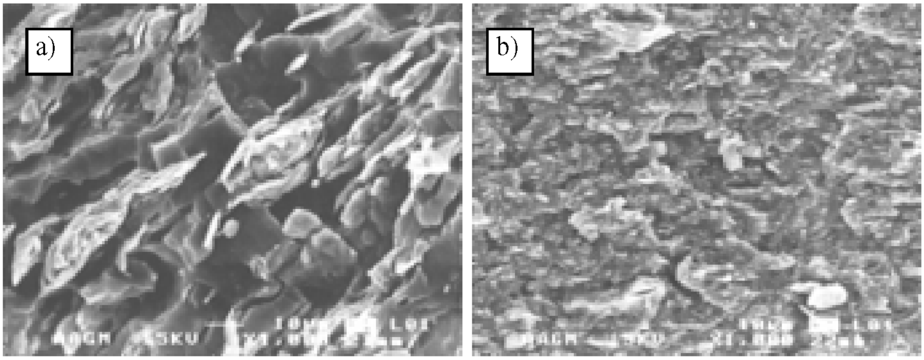

Figure 7. SEM micrographs of a) PPPA3 and b) PPPAC3 composites

Conclusions

PA has better mechanical properties than PP due to its polar nature and large number of H bonding interaction. As talc content increases, strength and modulus of PA rise rapidly than PP since there is an interaction between surface of filler and PA phase. Either breakage of PP matrix or debonding of PP and PA phase is the failure mechanism of unfilled and filled PPPA composites. Whitening and crack formation before breakage are the evidence of that failure mechanism. Addition of compatibilizer into unfilled and filled PPPA composites form chemical linkages which permit stress transfer between phases and improve mechanical properties. Morphology of the composites revealed using SEM shows that the majority of the talc is selectively dispersed in polar PA phase. It is observed that inhomogeneous, course and elongated morphology of uncompatibilized composites is changed to well dispersed, fine and more homogeneous particle-in-matrix morphology via additional compatibilization effect. This unique microstructure is believed to be responsible for the improved tensile and flexural properties in the blend compositions.

Acknowledgements.

The authors gratefully acknowledge the financial support given by Arcelik A.S. and Bogazici University as well as Turgay Gönül and Hatice Y lmaz for their helps in SEM studies and testing.

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