

New Materials from Polyamide 6

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Polyamide 6 was first synthesized in 1920's and today is one of the most widely used thermoplastics¹⁾. Figure 1 shows the common way of preparation of this polymer. It has an overall combination of properties like high moisture absorbability, elasticity, dyeability, etc., which are highly desirable for synthetic fibers used in the textile clothing industry²⁾. For a long time it was also used as a technical polymer. However some deficiencies for technical applications had appeared. These are: brittleness, poor dimensional stability, marginal heat deflection temperatures, etc., which can be improved. Improvement of the properties is attractive since the production of polyamide 6 is relatively simple and inexpensive.



Figure 1 Preparation of polyamide 6 from ϵ -caprolactam¹⁾.

Great palette of possibilities for blending of polyamide 6 with other polymers represents the base for development of synthetic materials with new features. On the other hand, materials based on polyamide 6 containing various inorganic additives are also very competitive. There are also a number of possibilities for involving polyamide 6 as a second component in the copolymers in order to make use of some specific features that primary polymer does not have. Four examples of

recent research on the new materials from polyamide 6 will be briefly presented below.

EVOH/copolyamide-6/6.9 blends

Development of new useful blends is sometimes limited by the incompatibility of many polymer pairs of interest, unless they are chemically similar or possess specific interactions. The general challenge of polymer blending is to overcome low entropy of mixing and unfavorable enthalpy of mixing of most high molecular weight polymers. One of the potential miscible blends appeared to be the ethylene vinyl alcohol (EVOH) and copolyamide 6/6.9 (COPA).

Nir et al.³⁾ studied the improvement of technical characteristics of the fibers made from EVOH/COPA blend. COPA is unique for its relative low degree of crystallinity and low melting temperature, while EVOH exhibits a high degree of crystallinity and high crystallization rate. When copolymer is made so that COPA constitutes the main phase, amide group content is much higher than the amount of available hydroxyl groups of EVOH. Therefore the probability of forming hydrogen bonds with the OH groups of EVOH and amide groups of COPA increases the miscibility of the components in copolymer.

It was observed that crystallinity of the COPA as the main phase increases, as well as the melting point consequently. A strong interaction was found between the blend components and the chain mobility was decreased due to blending.

This is the reason for the increasing in the glass transition temperature with EVOH content (Figure 2).

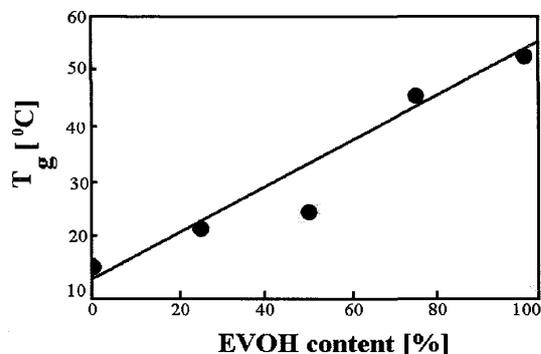


Figure 2 Glass transition temperature of EVOH/Polyamide 6 blends against EVOH content³.

On the other hand, the shear viscosity of the blend decreases with increase in COPA amount (Figure 3) and consequently the processability of the melt is also improved.

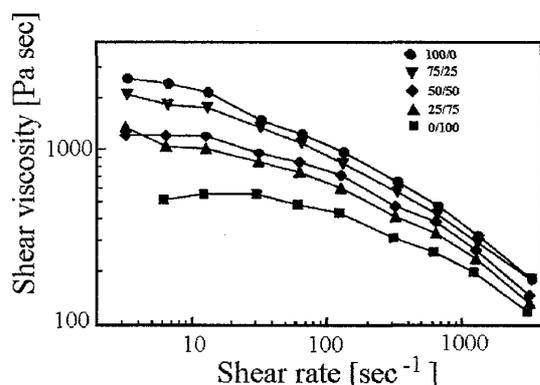


Figure 3 Shear viscosity of EVOH/Polyamide 6 blends at 210°C³.

From the optimized combination of crystallinity and viscosity, which can be controlled by presented parameters, application of this material as the technical thermoplastic could be directly projected, owing to the miscibility of the components.

ABS/polyamide 6 blends

Another example of the polymer blend interesting for the engineering

application is the one made from ABS (acrylonitrile butadiene styrene) and polyamide 6. In particular, the chemical functionality of polyamide 6 through its amide and carboxyl groups allows dispersion of ABS if a proper compatibilizer is used⁴. Widely used compatibilizing agents are polymers containing maleic anhydride. These can react with amine end group of polyamide and are miscible with the ABS. emulsification curves are followed in order to control the mixing process. Emulsification curves represent plot of average diameter of the particles of the dispersed phase (ABS) as a volume average diameter d_v , and the number average diameter d_n .

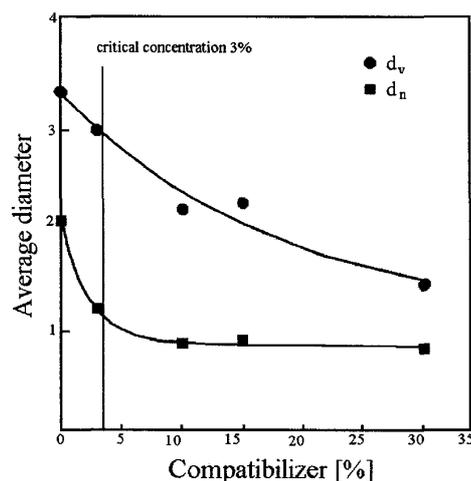


Figure 4 Emulsification curve (d_v and d_n given in μm) for blend of polyamide 6 and ABS (70/30)⁴.

In the Figure 4, it can be observed that with the percent of added compatibilizer the diameter of dispersed ABS in polyamide 6 decreases. Such trend is desirable in the purpose of mixing, but on the other hand, impact strength of the blend material decreases.

In the case of blend containing 70% of polyamide 6 and 30% ABS that the critical concentration of compatibilizer occurs at about 3%. The blend containing 15 % of compatibilizer

has nearly three folds of the impact strength of the uncompatibilized blend. Beyond the value of 15 %, the impact strength decrease is significant (Figure 5).

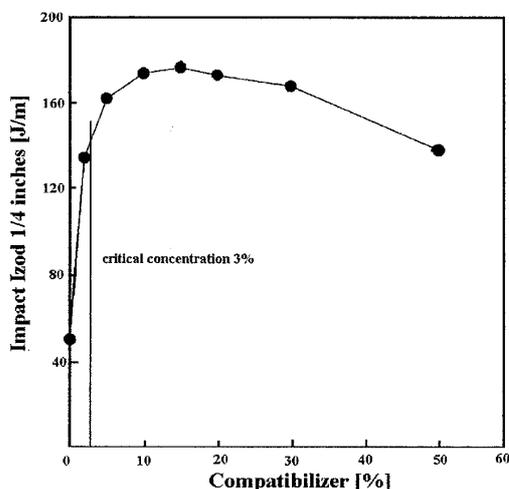


Figure 5 Izod Impact as a function of percentage compatibilizing agent (based on the weight of dispersed phase⁴).

These results obtained by Lacasse et al.³) show that emulsification curves are able to distinguish the point of optimum mixing. Hence, highly homogenous blends of the ABS, which is heat resistant and polyamide 6 with satisfying mechanical quality are applicable in the automotive and electronic industry for high performance parts.

Polyamide 6 containing phosphorus oxynitride

Phosphorus oxynitride (PON) was known about 150 years, but its role as fire retardant additive for polymers was observed relatively recently⁵). However, there was still an open question about a possibility that inside the burning polymer, phosphorus content could be mobilized in an active form. Levchic et al.⁶) showed there is no such effect if PON is used as a fire retardant for polyamide 6. They studied combusting performance and made thermal analyses of polyamide 6 containing PON and

various additives. Oxygen indexes (OI), shown in Table 1 were compared to thermogravimetric curves at Figure 6.

Table 1 Oxygen indexes for polyamide 6 formulations with PON⁵.

Additives		Oxygen index	Char Wt. %
Name and ratio	Wt. %		
No additives	-	21.7	2
PON	20	28.3	42
PON	30	32.0	53
PON+Melem (1:1)	20	27.3	18
PON+Fe ₂ O ₃	30	37.3	40

It was observed that addition of PON increases OI and involves polyamide 6 in charring. Especially increased is the char yield value. Combination of PON with other additives such as Fe₂O₃ and melem (condensation product of melamine⁵), showed less increased values for char yield. Increase of OI for PON+Fe₂O₃ is significant.

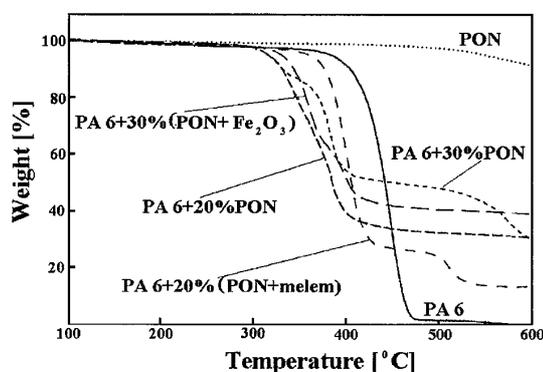


Figure 6 Thermogravimetry curves of the pure polyamide 6, pure PON and polyamide 6 fire retarded with various additives⁶.

However, thermogravimetry indicated that the solid residue amount was highest for polyamide 6 containing 30wt. % of PON, though the degradation temperature is shifted somewhat lower. Results showed that PON is an efficient fire retardant for polyamide 6 what opens many possibilities for application of polyamide 6 as a 'safety fiber'¹).

Copolymerization of polyethylene with polyamide 6

In the automotive and agrochemical industry widely used polyethylene (PE) plastic fuel tanks and agrochemical bottles were suffering from significant permeation of hydrocarbon solvents. The solution of this problem was found in the "laminar blending" with polyamide 6. Polar barrier properties of polyamide 6 are inducing the formation of a layered structure containing dozens of overlapping and discontinuous plates in PE. Since PE and polyamide 6 are thermodynamically immiscible, and the compatibilizers have to be used to improve interfacial properties between PE and polyamide 6.

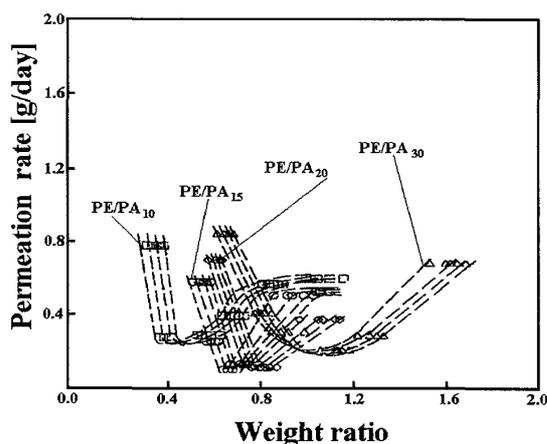


Figure 7 Xylene permeation rates of bottles produced from the blends with various weight ratio of PE/polyamide 6⁷⁾.

Recently Yeh et al.⁷⁾ studied series of polyethylene blend with polyamide 6 compatibilized by zinc-neutralized ethylene/acrylic acid copolymer. The grafted polyamide 6 containing different weight percentage of compatibilizer (e.g. 10, 15, 20, 30) was mixed with polyethylene in various ratios, and blow-molded in bottles of 1-liter volume. They measured the permeation barrier properties of these bottles relating

to xylene. The results are shown in Figure 7, as the weight loss of xylene against the weight ratio of polyamide/polyethylene.

The obtained results are exclusive since the xylene permeation decreased 10-100 folds comparing to the values of 9-12 g/day for the bottles from pure polyethylene. Moreover, the minimums of permeation could be observed on the curve what gives the possibility for the evaluation of optimum ratio of the polyethylene and polyamide 6/compatibilizer copolymer.

Conclusion

Some concrete examples of the engineering applications of polyamide 6 were presented here through the newest research reports respectively. From these examples it can be observed that the development of polymer blending technologies of old very well known polymers, such like polyamide 6 may led to the materials of highly desirable properties which can be farther improved by process controlling.

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