

Ductile Transition in Nylon-Rubber Blends: Influence of Water

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Synopsis

On nylon 6 and nylon 6/EPDM blends the influence of water on the glass transition temperature, mechanical properties, and the ductile transition temperature was studied. Blends of 10% and 20% were prepared with a particle size of $0.3\ \mu\text{m}$ and the tensile properties, flexural moduli, torsion moduli, and notched izod impact strength were studied as functions of water concentration. The ductile transition temperature in polyamides can be lowered by plasticizing the nylon and by a rubber particle-induced process; both processes show some synergistic effects.

INTRODUCTION

Polyamides are semiductile materials at room temperature (RT) in the dry state and above their glass transition temperature (T_g) they are ductile.¹⁻³ By passing the glass transition, the yield strength of the nylon is lowered by a factor two⁴ to four¹ while the tensile strength changes some 30%, and above the T_g , excessive yielding can take place.¹⁻³ Thus at the T_g a semiductile to ductile transition takes place.

There are two ways to lower this ductile transition temperature, one is by plasticizing the polyamide¹⁻³ and the other is by blending with rubber.⁵⁻¹¹ On wetting the nylon, the T_g is lowered and the toughness at RT increases.

With rubber modification the impact properties of the nylons can greatly be improved. These blends show a ductile transition at a much lower temperature than the neat nylon.⁷ The ductile transition temperature of the blend depends on a number of factors such as rubber concentration, rubber particle size, and rubber modulus.⁷⁻¹¹ The mechanism by which the blend deforms in the ductile region seems to be cavitation of the rubber and shear yielding between the cavities.⁸

Both methods of improving the impact behavior of the nylon seem to be based on quite different deformation mechanisms and the question arises whether these two mechanisms have synergistic effects.

EXPERIMENTAL

Materials

Nylon 6, type Akulon M258 was obtained from Akzo Plastics it had an η_{rel} in 96% H_2SO_4 of 5.8. EPDM rubber, type Keltan 740, was obtained from DSM Maleic Anhydride (MAh) was obtained from BDH Diisopropyl isobutyl peroxide (Perkadox 14) from Akzo Chemie.

EPDM modification with maleic anhydride. A mixture of 100 parts EPDM, 2 parts MAh, and 0.025 parts Perkadox 14 was fed three times to a 19-mm Brabender single screw extruder, first with the barrel temperatures at 50°C, the second time at 170°C, and the third time at 250°C. The MAh concentration as determined by endgroup titration was found to be 0.4%.

Blend Preparation. The nylon-rubber blends were prepared on a 40-mm Kautex single screw extruder which was fitted with a cavity transfer mixing head, zone temperatures of the barrel were 225°, 225°, 225°, and 230°C. Test samples were prepared with an Arburg injection-molding machine, type 221-55-250, zone temperatures of the barrel were 260°, 260°, 260°, and 260°C.

Conditioning. The samples were conditioned in four ways:⁶

1. Drying in a vacuum oven at 110°C for one day (dry)
2. Boiling in a saturated potassium acetate solution for one day (~ 50% relative humidity, RH)
3. Boiling in a saturated sodium phosphate solution for one day (~ 65% RH)
4. Boiling in water for one day (~ 100% RH)

Tensile tests were carried out on dumbbell-shaped samples (DIN 53455, specimen type 4) with a deformation speed of 250%/min.

The flexural moduli were determined according to ISO 178. The torsion moduli were determined at a frequency of 1 Hz and a heating rate of 0.5°C/min with a Myrenne ATM3. The notched izod impact test was carried out according to ISO 180, specimen type 1, notch type A. The particle size of the dispersed rubber in the blend was measured on cut surfaces with a scanning electron microscope. For this the cutted injection-molding bars were treated 16 h with boiling xylene, dried overnight in a vacuum oven at 110°C, and coated with gold.

RESULTS AND DISCUSSION

Water Absorption

The water absorption data of the materials are given in Table I. The blends absorb somewhat less water than the nylon. If assumed that the EPDM

TABLE I
Water Absorption Data

		Water (%)	Water in nylon (%)
Sat. potassium acetate	nylon	2.3	2.3
	B10	2.2	2.4
	B20	1.8	2.2
Sat. sodium phosphate	nylon	7.8	7.8
	B10	6.8	7.6
	B20	6.2	7.7
Water	nylon	11.6	11.6
	B10	10.4	11.6
	B20	9.4	11.8

rubber absorbs little water, the water concentration in the nylon phase can be calculated and found to be as high as in the neat nylon. From this it is expected that the dimensional stability of the blends improves with the volume fraction of the rubber.

Structure

The rubber in the blends is in the form of dispersed particles with a weight-average particle size of $0.3 \mu\text{m}$ for both blends. This size compares well to the particle sizes in industrial nylon rubber blends.

Tensile Properties

The tensile strength of all these materials decreases as they absorb water (Fig. 1). Blends have a lower tensile strength than nylon both dry and wet.

Elongation at break increases on wetting, and blends were found to have a lower elongation at break than nylon. The high elongations at break of the dry materials is due to the high molecular weight of the nylon.

Flexural Modulus

The flexural modulus decreases strongly on wetting. As the nylon is wetted the T_g is lowered from above to below room temperature. The tailing off of the moduli at the highest water concentrations suggest that the glass transition temperature has been exceeded.

Torsion Moduli

In Figure 2, the G' of the nylon and both dry and wetted blends are given. The behavior of nylon is well known.¹ Water increases the low temperature moduli and shifts the T_g to a lower temperature. The difference between the 7.7% and 11.7% water content samples is small and the moduli above the T_g are only slightly affected by its presence.

The blends have an extra transition at -55°C , related to the T_g of the EPDM rubber. On wetting the blends, the T_g of the rubber seem to increase slightly, possibly due to the approaching nylon transition.

Impact Behavior

Dry nylon has a ductile transition at 80°C and a semiductile behavior at RT and -40°C (Fig. 3). On wetting, the ductile transition shifts to lower temperatures (for the 11.7% water sample to -30°C), the notched Izod at RT increases to very high values and the Izod at -40°C increases from 2.9 to 5.7 kJ/m^2 .

In its dry state, B10 material has a ductile transition at 17°C , and below that temperature is still quite tough (Izod at -40°C is 9.3 kJ/m^2). On wetting, the ductile transition is shifted to lower temperatures but the low temperature impact value changes are minor.

Ductile transition of dry-state B20 is -17°C , and its notched impact strength at -40°C is 13 kJ/m^2 . Wetting this material changes the impact behavior slightly at the highest water concentrations.

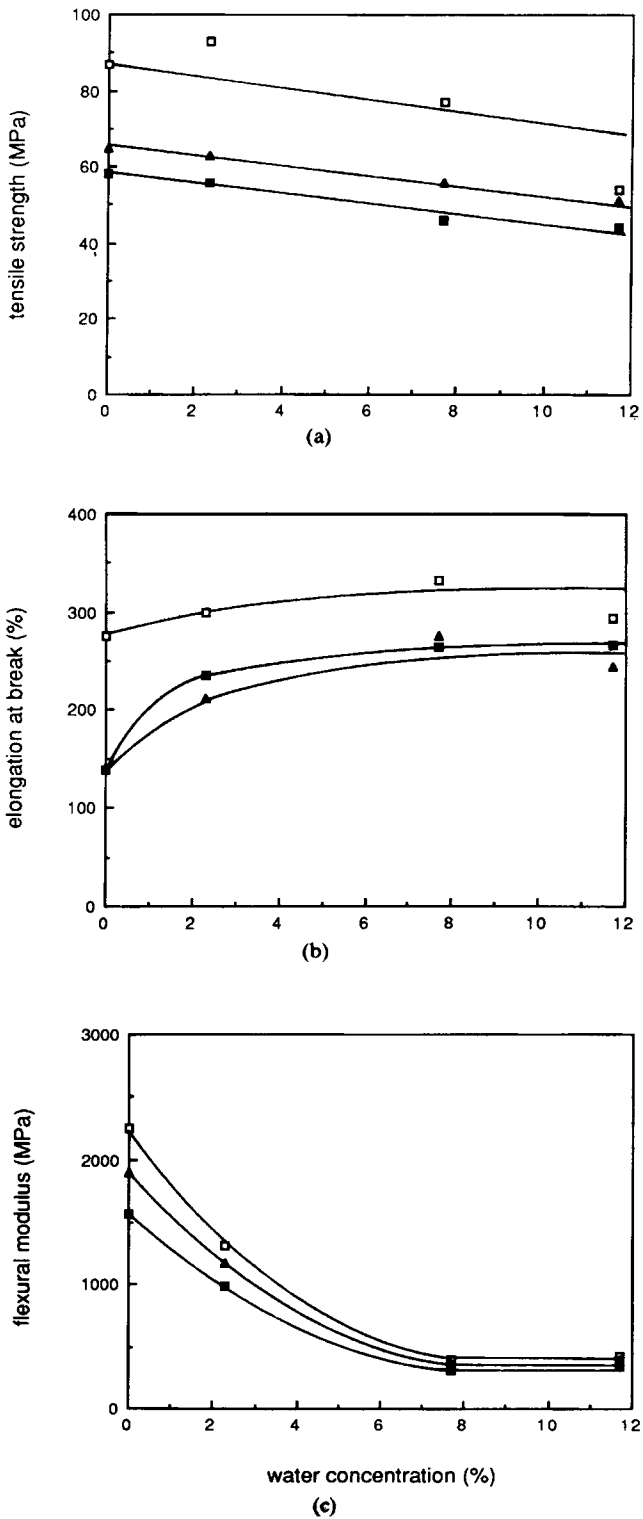


Fig. 1. Tensile strength, elongation at break and flexural modulus as function of water concentration in the nylon phase: □, Nylon 6; ▲, B10; ■, B20.

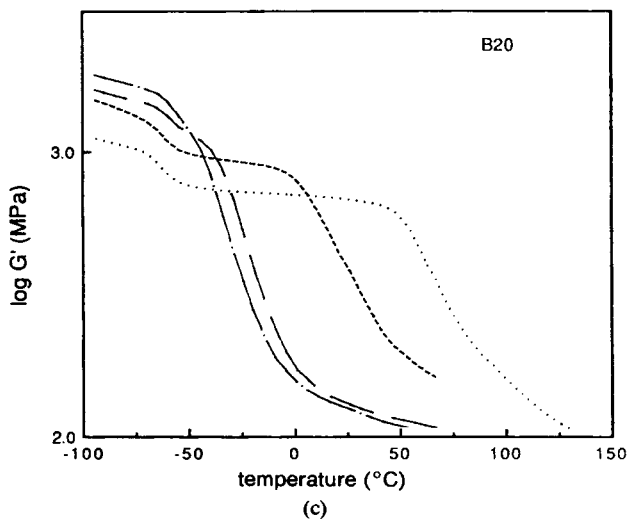
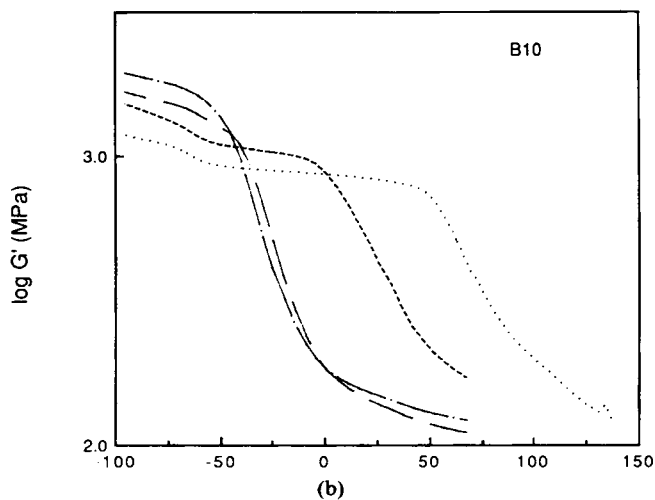
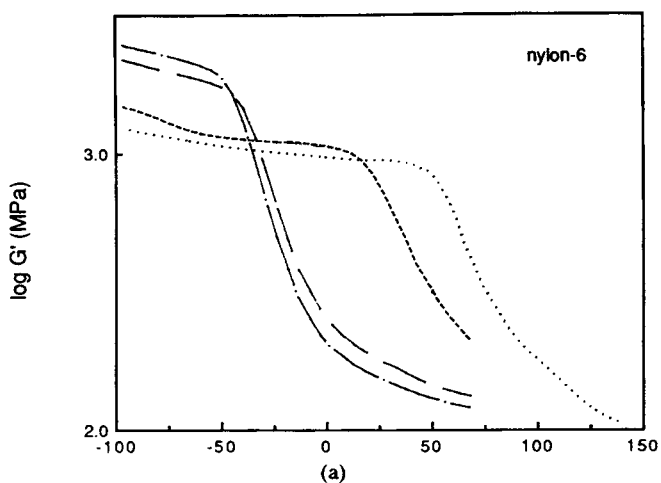


Fig. 2. Torsion moduli (G') as function of temperature at the water concentrations: \cdots , dry; $-\cdot-$, 2.3%; $- -$, 7.6%; $- - -$, 11.6%.

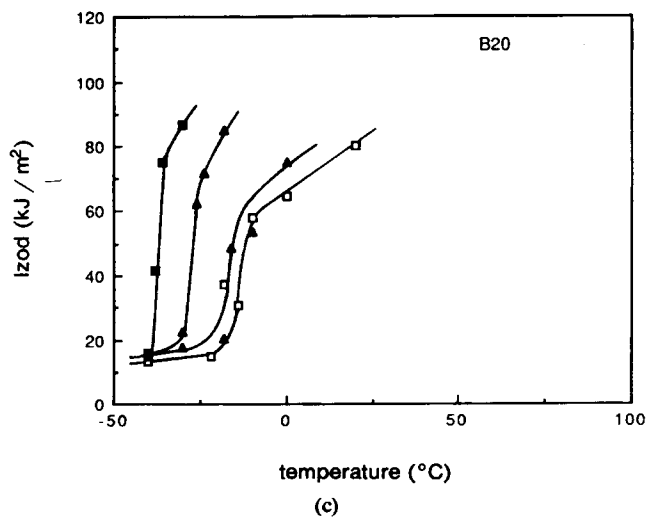
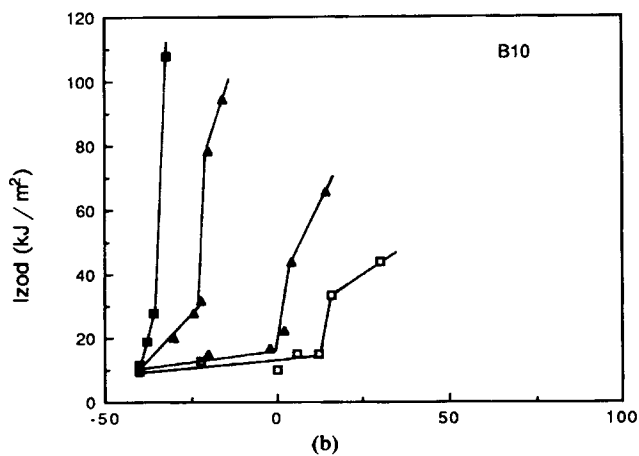
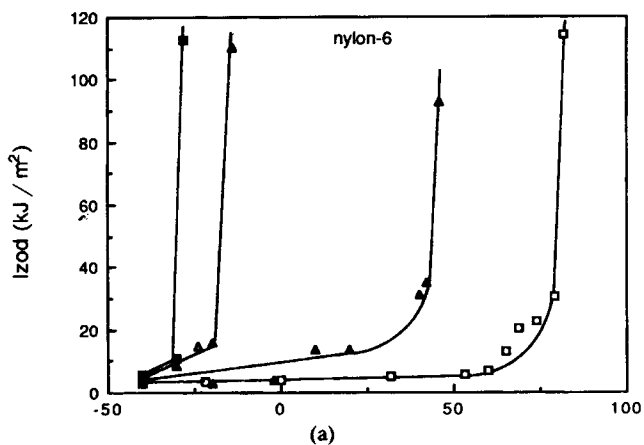


Fig. 3. Notched Izod impact strength as function of temperature at the water concentrations in the nylon phase of: □, dry; ▲, 2.3%; △, 7.6%; ■, 11.6%.

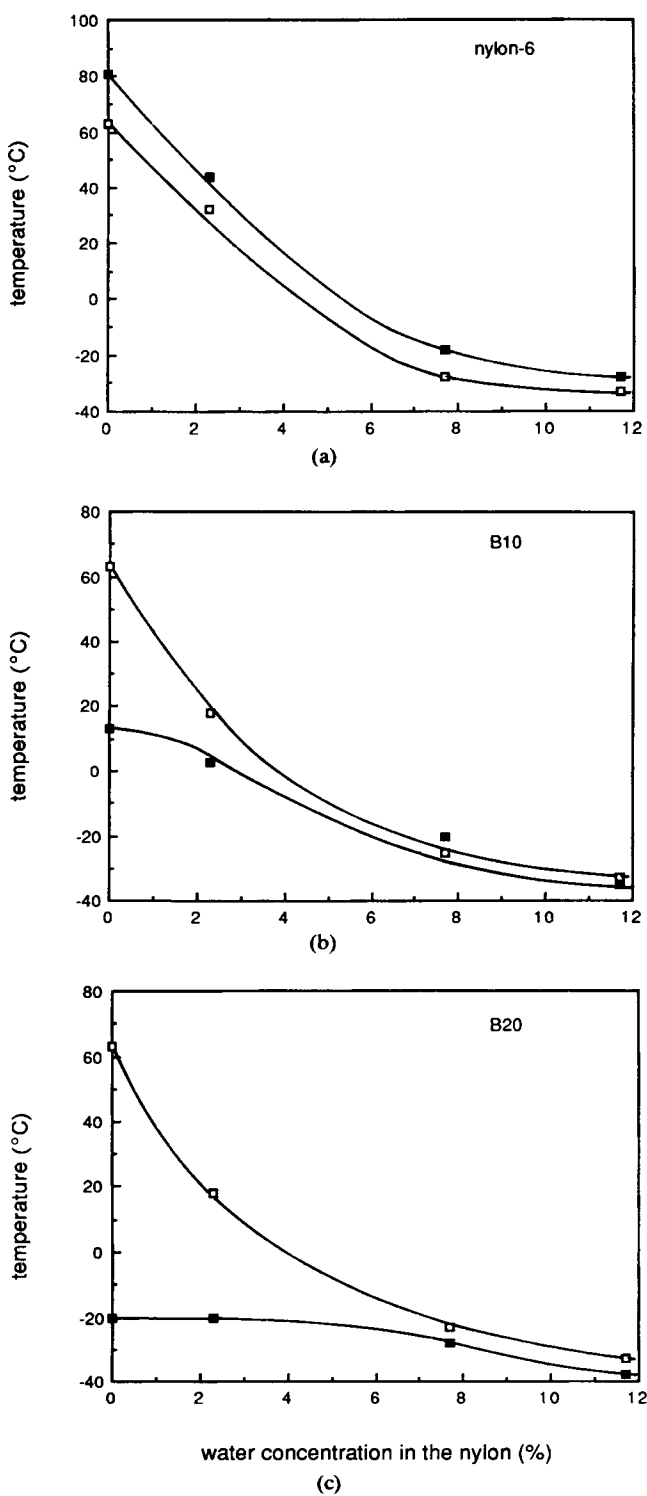


Fig. 4. Influence of water concentration on the transition temperatures (□, T_g), (■) ductile transition.

Both the glass and ductile transitions are dependent on water concentration. Figure 4 plots both as a function of water concentration. In the neat nylon, the ductile transition is 10–15°C higher than the glass transition temperature range. In the neat nylon, both processes are clearly coupled.

Dry-state ductile transition of 10% and 20% blends occurs at a much lower temperature than the glass transition. On wetting these blends, the T_g is lowered and the ductile transition is influenced gradually. There are clearly two processes involved for blends: one well below the T_g of the blend and one coupled to the T_g . Compared to the dry blends, the wetted blends have a higher impact strength in the ductile region, and compared to the neat nylon, a slightly lower ductile transition and a higher impact strength in the semi-ductile region.

Clearly both types of mechanisms which induce the ductile transition in polyamides have some synergistic effects.

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