

Friction and Scratch Resistance of Polyamide 6 Modified with Ionomeric Ethylene/Methacrylic Acid Copolymer

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ABSTRACT: Ethylene/methacrylic acid copolymer Surlyn[®] 9020 (SU) was used to reduce the crystallinity of polyamide 6 (PA6). Differential scanning calorimetry was used to calculate the change in crystallinity of a modified polymer: four cases of SU weight fractions (5, 15, 20, and 30%) were considered. The fracture morphology was studied by use of scanning electron microscopy. With the increasing fraction of SU the structure transformed into a fine crystalline one. The effect of reduction in crystalline fraction on friction and scratch resistance of PA6 was investigated. The static and dynamic coefficients of friction decreased with respect to the increase in weight fraction of SU. With the

addition of SU, the scratch resistance was found to decrease as well, whereas the healing (i.e., recovery of material after a scratch was made) of the material was found to increase. SU hindered crystallization of PA6, and with higher content of SU plastification of material occurred. Results from thermomechanical tests confirmed that conclusion: the Young's modulus E decreases and the thermal expansion coefficient α_L increases with the addition of SU. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3866–3870, 2004

Key words: polyamides; blends; differential scanning calorimetry (DSC); modification; mechanical properties

INTRODUCTION

Blending entered the plastics industry half a century ago and became the most common method of producing new plastics. It is therefore not surprising that blends constitute (by various estimates) about half of the total polymeric market.^{1,2} The fundamental mixing behavior of polyamides has been widely studied. Polyamides form miscible or partially miscible blends with a variety of polymers^{3–8} and hybrid composites of polyamides have been widely discussed.^{9,10}

In particular, polyamide 6 (PA6), a highly crystalline polyamide, offers attractive mechanical properties with a useful temperature capability. The high crystallinity of PA6 contributes to its good wear characteristic. Furthermore, PA6 is a tough, resilient material having high tensile strength, good abrasive resistance, and good chemical and thermal resistance.^{11,12}

The copolymer Surlyn[®] 9020 (SU) is known to reduce PA6 crystallinity. SU is a thermoplastic resin, an advanced ethylene/methacrylic acid (E/MAA) copolymer, in which the MAA acid groups have been partially neutralized with zinc ions. The acid neutralization results in the formation of ion clusters within the resulting polymer matrix, and hence the general term "ionomer." SU resins incorporate many of the perfor-

mance features of the original ethylene-based copolymers, such as chemical resistance, melting range, density, and basic processing characteristics.^{13–17}

Tailoring of tribological properties is well developed for metals but tribology of polymers is a rapidly growing research field.^{18–23} Polymer technology offers economically attractive materials for numerous tribological applications. Polyamides are often used in mechanical junctions.^{24,25} Unfortunately, most polymers have low scratch resistance. The main purpose of this study was to decrease friction of PA6 without lowering its scratch resistance.

EXPERIMENTAL

PA6 [Tarnamid 27[®], Zaklady Azotowe, Poland; $\rho = 1.13 \text{ g/cm}^3$, melt flow index (MFI) = 5.4 g/10 min] was modified by addition of 5, 15, 20, and 30 wt % of SU (Surlyn[®] 9020, DuPont, Wilmington, DE; $\rho = 0.96 \text{ g/cm}^3$, MFI = 1 g/10 min). Samples were injected following ISO Standard 3167.²⁶ All investigated samples had the same thermal history.

To reveal structural details samples were cooled with liquid nitrogen and immediately broken. Fractures were coated with gold, by vapor deposition, using vacuum sputtering. The specimens were studied in a JEOL JSM-T300 scanning microscope (JEOL, Peabody, MA).

The differential scanning calorimetry (DSC) technique was used to characterize the change in PA6 crystallinity X_c . All the measurements were conducted

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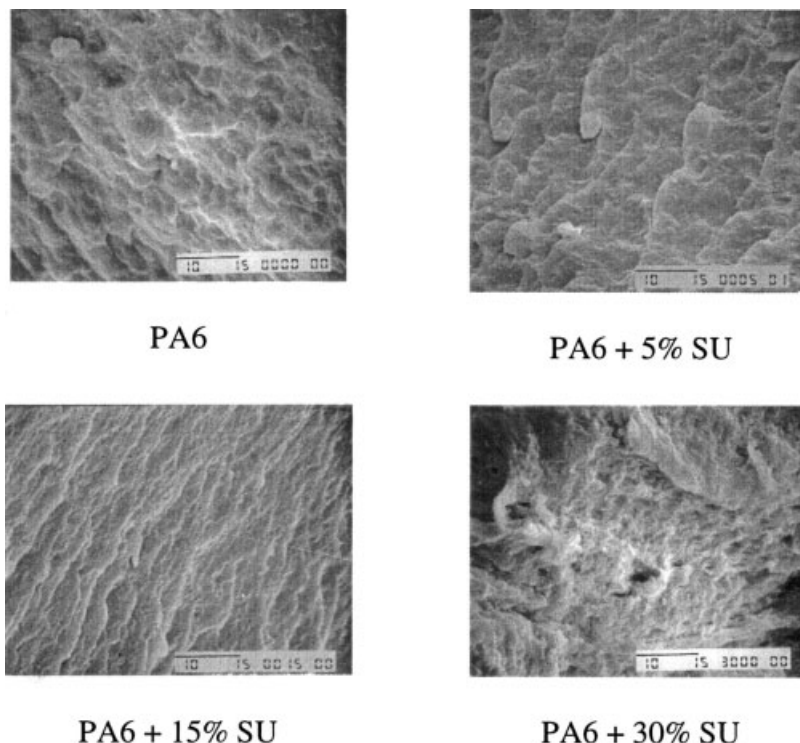


Figure 1 Microstructures of modified PA6 (magnification $\times 2000$).

using a Perkin–Elmer DSC-7 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) within the temperature range from 10 to 250°C at the heating rate of 15°/min. The purge gas was nitrogen (flow 20 mL/min).

Thermal mechanical analysis (TMA) was used (Perkin–Elmer TMA-7 apparatus) to evaluate the thermal resistance of modified PA6. The temperature range tested in each scan was between -140 and 120°C. The linear thermal expansivity α_L was measured as the slope of a temperature versus probe position curve,

within the temperature range of -140 and 100°C. The equipment conditions were set with nitrogen as a purge gas (feed: 20 mL/min; ramp: 5°C/min).

The Sintech universal testing machine was used to determine the friction characteristics at room temperature. A 44.5-N load cell and a sled with the nominal weight of 700 g were used. The testing speed was 150 mm/min. A Teflon cospecimen was used. The results reported below are the averages each of 10 tests.²⁷

To measure the scratch resistance, the scratch tester MST-CESEMEX was used (with Rockwell indenter).

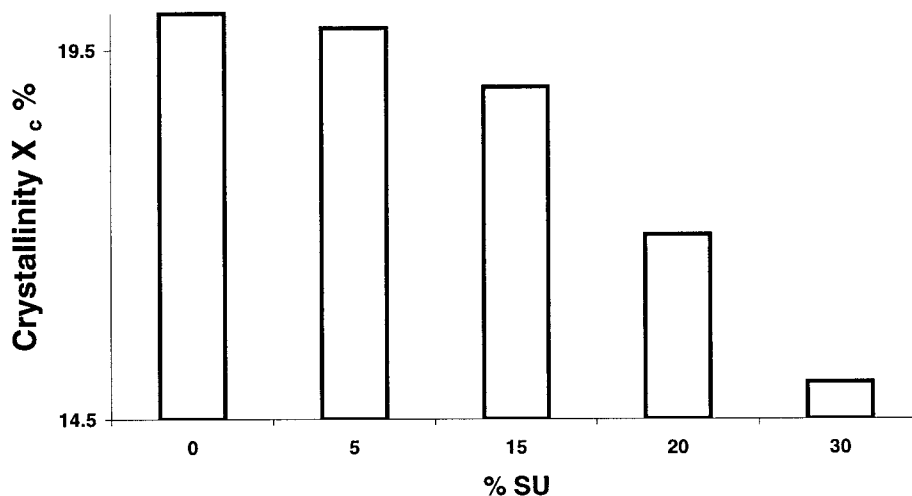


Figure 2 Crystallinity (X_c) of PA6 as a function of SU wt %.

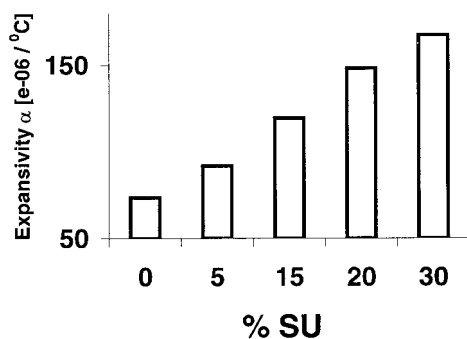


Figure 3 Thermal linear expansivity (α_L) of modified PA6 as a function of SU wt %.

The topology of the surface was obtained before the scratch and after the scratch (to determine the amount of depth recovery after a scratch) by scanning with a very small constant force (0.03 N). The accuracy of the depth determination was ± 7.5 nm. A minimum of 15 scratches was performed for each sample under the constant load of 15 N; all numbers reported below are averages. The velocity of scratching was 5 mm/min and the scan length was 3 mm.

Tensile tests were run with a DMA 7e Perkin–Elmer dynamic mechanical analyzer. The tests were carried out at 23°C. The Young's modulus E was determined in each case as the slope of the initial straight-line portion of the stress σ versus strain ϵ curve.

RESULTS AND DISCUSSION

Fractography

In Figure 1 the change in morphology of modified PA6 is presented. Scanning electron microscopy reveals the highly crystalline microstructure of PA6. With the increase of SU weight fraction the microstructure transforms into a semicrystalline one. SU bonds ionically to PA6, and no evidence of phase separation was detected even in samples modified with 30 wt % of SU.

Crystallinity

The normalized crystallinity X_c was calculated from the equation

$$X_c = \left(\frac{\Delta H_f}{\Delta H_f^0} \right) \times 100\%$$

where ΔH_f is the experimental enthalpy of melting and ΔH_f^0 is the enthalpy of fusion of the perfectly crystalline PA6, 230 J/g (55 cal/g).²⁸

In Figure 2 reduction of PA6 crystallinity X_c , calculated from a DSC curve using the above equation, is presented. DSC results are in good agreement with

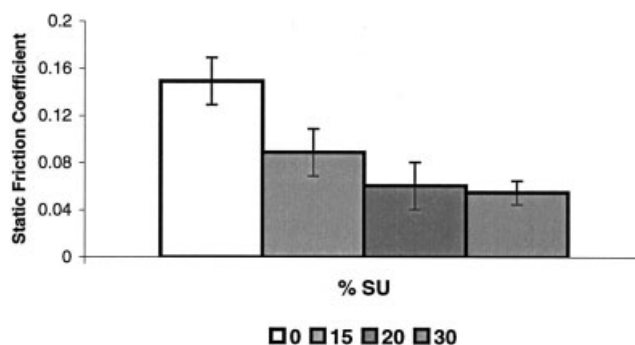


Figure 4 Static coefficient of friction measured for modified PA6.

SEM data and confirm that the presence of SU reduces PA6 crystallinity.

Thermal properties

In accordance with the results reported in Figures 1 and 2, thermal linear expansivity α_L was shown to increase significantly (Fig. 3) from 73.4930 e-06/°C for nonmodified material to 167.3746 e-06/°C for the material with the highest content of SU. This effect is clearly associated with the reduction of the crystalline part. Modified PA6 loses dimensional stability at lower temperatures.

Surface properties

The values of static and kinetic coefficients of friction vary with the content of SU. In particular, the static coefficient decreases from 0.15 for nonmodified PA6 to 0.05 for the sample modified with 30% of SU (Fig. 4). At the same time the value of the kinetic coefficient decreases from 0.11 for nonmodified PA6 to 0.04 for the sample modified with 30% of SU (Fig. 5). The modification results in strong reduction of friction.

In Figure 6 the average values of the penetration depth as a function of SU wt % are presented. The

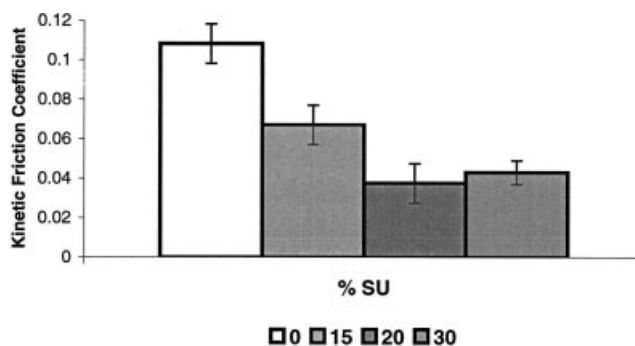


Figure 5 Kinetic coefficients of friction measured for modified PA6.

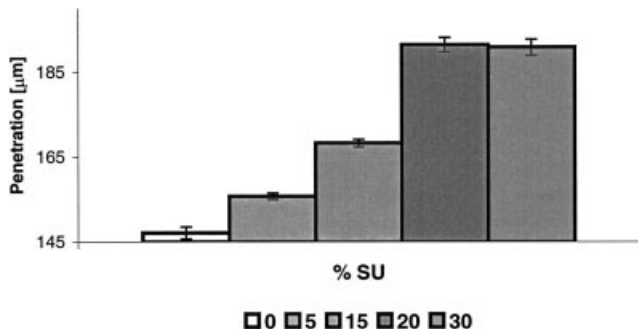


Figure 6 Average of penetration depth for compositions studied.

penetration depth has a minimum value of 147 μm for PA6 and varies for blends with different percentages of SU content. Because the crystallinity is subsequently reduced, the penetration depth increases to 190 μm for the blend with addition of 30% of SU.

In Figure 7 the average values of healing (recovery of material after a scratch was made) are presented. There was a time interval of 30 min between scratch and postscan. One could expect that with reduction of scratch resistance, attributed to reduction in crystallinity, healing should also decrease. A plausible explanation of the fact that healing increases for samples modified up to 20 wt % of SU might be a change in viscoelastic²⁹ behavior in the glassy state of modified PA6. Cancellation of the compression stress under an indenter leads to a recovery of some part of strain. The healing mechanism combines both elastic and viscoelastic recovery. At some point a saturation point is reached. Modification with 30 wt % of SU results in material with a lower healing value than that of material modified with 20 wt % of SU.

Mechanical resistance

Unfortunately, as a result of the plastification of PA6,²⁹ modification with SU is also accompanied by mechanical weakening of the material. As expected, the

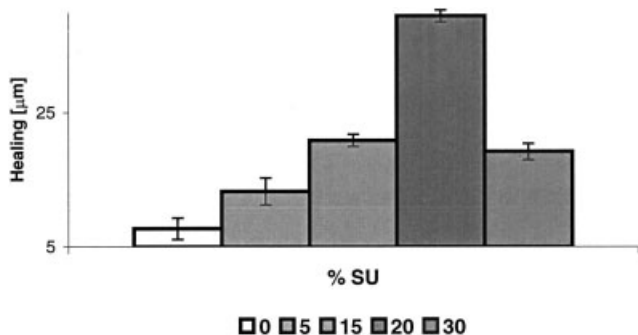


Figure 7 Healing values obtained for compositions studied.

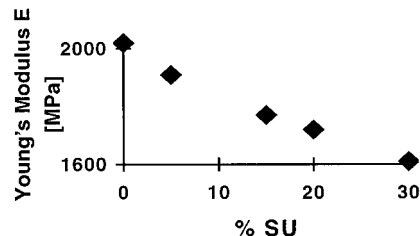


Figure 8 Young's modulus (E) of modified PA6.

Young's modulus (Fig. 8) for the modified material is significantly lower. PA6 modified with 30 wt % of SU had a Young's modulus that was approximately 20% lower.

CONCLUSIONS

The data collected showed that the modification of PA6 with SU results in different and somewhat competing trends. In general, lowering crystallinity causes a plastification of PA6, which in turn results in a strong improvement of friction properties and, up to some point, the healing values. Deterioration of thermomechanical properties were evident when the material was significantly weaker. Modified PA6 can serve as a plastic material for joints, although the work conditions should exclude an abrasive environment.

Constructive comments of the referees are appreciated.

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