

Reversible Plasticization of Nylons 6 and 11 with Anhydrous Ammonia and Their Deformation by Solid-State Coextrusion

ANAGNOSTIS E. ZACHARIADES and ROGER S. PORTER, *Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

Reversible plasticization of nylons with anhydrous ammonia is a new concept. In the present studies, nylons 6 and 11 have been plasticized with anhydrous ammonia and subsequently were solid-state coextruded below the melting point. The plasticization is attained by a temporary disruption of the strong hydrogen bonding between amide groups of adjacent nylon chains. Thermogravimetric and infrared analysis show that for the nylons 6 and 11 the amount of ammonia absorbed is 18% and 10% of the weight of the dry samples, respectively. The ammonia incorporation to preformed nylon ribbons prior to extrusion alleviated significantly the processing difficulties encountered with untreated nylons and aided the rapid extrusion of highly oriented states (EDR 12). The extent of orientation is documented by the high total birefringence values (8.25×10^{-2} for nylon 6 and 5.8×10^{-2} for nylon 11), by the significant increase in crystallinity (23.5%–53% for nylon 6 and 25.7%–40% for nylon 11), and by the enhanced tensile moduli (13 GPa for nylon 6 and 4 GPa for nylon 11).

INTRODUCTION

The range of physical properties of thermoplastic polymers may be extended by the addition of reinforcing agents and orientation. The deformation of thermoplastics, and in particular in the solid state, has provided oriented states of exceptional modulus and tensile strength.¹⁻⁵ The deformation of thermoplastics with strong intermolecular secondary bonding attracts attention because such bonding results in higher crystalline melting points. However, the presence of such bonding makes the deformation in the solid state feasible at low rates and only at low molecular weights and temperatures near the melting point. This difficulty may be alleviated considerably by the use of plasticizers that "dissolve" in the polymer and thus aid deformation. The choice of plasticizer depends on many variables. A disadvantage in their use is that after the processing the plasticizer remains in the thermoplastic, affecting its properties, e.g., lower modulus and melting point. In principle, therefore, it would be desirable to remove the plasticizer after processing or have it be self-reinforcing.

Nylons are a family of thermoplastics with wide industrial application, and plasticizers have been used extensively in their processing. The crystalline-state deformation by extrusion was initiated in our laboratory with emphasis to the higher nylons 11 and 12.⁶ These nylons have longer olefinic segments and therefore a smaller concentration of interchain hydrogen bonds involving adjacent amide and carbonyl groups.⁷

Volatile plasticizers can aid in processing yet be subsequently removed for enhanced final properties. In this report we communicate results on the plas-

ticizing effects of anhydrous ammonia, a volatile plasticizer, utilized for the solid-state deformation of nylons 6 and 11. The latter was achieved by the recently developed technique of solid-state coextrusion.⁸

Ammonia has been previously used effectively for the plasticization of wood.^{9,10} It now appears to be a likely candidate for the plasticization of nylons since it may be potentially removed from the deformed state by volatilization. Under the conditions of our studies, incorporation of NH_3 in preformed nylon films alleviates significantly the processing difficulties for untreated nylons and aids considerably the preparation of oriented nylon 6 and 11 films.

EXPERIMENTAL

Materials and Methods

It has long been known that nylons absorb water. Experiments carried out at the University of Massachusetts recently have shown that anhydrous ammonia can similarly be readily absorbed by nylons. In these early experiments, nylon 6 ($M_w = 16,000$) and 11 ($M_w = 34,000$) films of thicknesses 0.15–1.5 mm were prepared by compressing pellets in a mold using a hydraulic press (PHI, California) thermostated at 250 and 210°C, respectively. After heating for 20 min, the pellets were gradually compressed at 12 MPa and subsequently cooled to ambient. The pellets used for the preparation of the films were dried in a vacuum oven at 150°C for one week and the films stored in a desiccator over CaCl_2 . Subsequently, ribbons 5–9.5 mm wide were cut from the films and exposed to anhydrous ammonia at ambient temperature in a stainless steel pressure vessel in which the vapor pressure of ammonia at ambient temperature was 1 MPa.¹¹ The ammonia was introduced to the pressure vessel by submerging the latter in a CO_2 /isopropanol cooling mixture (-78°C) and condensing in the ammonia from a storage cylinder as shown in Figure 1. Subsequently, the valve (A) was turned off and the vessel was brought to ambient temperature by removing the cooling bath. The pressure in the vessel rose to ~ 1 MPa, and the system was then under these conditions for ~ 5 –10 hr. At the end of treatment, the pressure vessel was again chilled at -78°C , whereas the feed in the NH_3 line was connected to a water aspirator. When the vessel pressure dropped to 0.1 MPa, the cooling bath was removed and the aspirator and valve (A) were turned on. Simultaneously, the threaded sealed plug (B) of the vessel was removed to retrieve the nylon ribbons.

The ribbon was quickly inserted in a longitudinally split billet of high-density polyethylene (HDPE, Alathon 7050, $M_w = 59,500$) which had been precooled in liquid nitrogen ($\sim -193^\circ\text{C}$). The HDPE–nylon ribbon assembly was snug-fit in the 0.95-cm-diameter barrel of an Instron capillary rheometer maintained at the desired extrusion temperature. Upon loading, the temperature dropped by ~ 4 –5°C, and the HDPE–nylon film assembly was pressurized to ≤ 0.23 GPa and extruded through a die of nominal extrusion draw ratio (EDR) of 12. Extrusion conditions and the thickness of extruded ribbons are summarized in Table III. After extrusion, the ammonia was liberated from the deformed sample at the die exit.

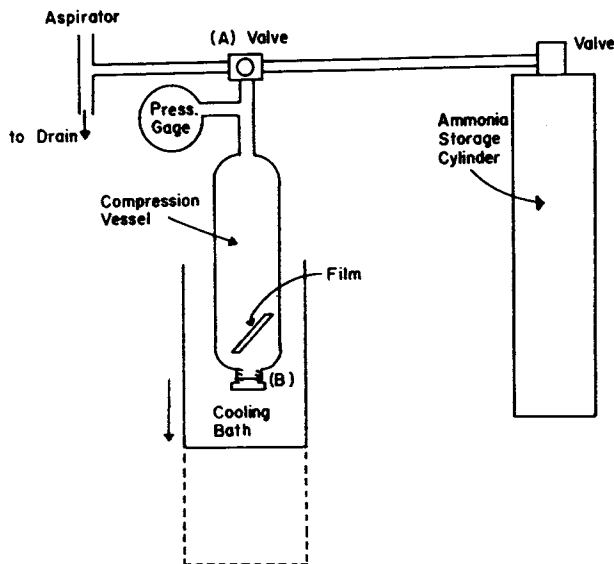


Fig. 1. Apparatus for ammonia treatment of nylon film.

Physical Property Measurements

Thermal analysis of samples before and after extrusion was performed with a Perkin-Elmer differential scanning calorimeter (DSC) Model 1B calibrated by the melt transition of indium and at a heating rate of $10^{\circ}\text{C}/\text{min}$. The fraction crystallinity was determined from transition heats assuming the values of 46.2 cal/g and 53 cal/g for the heat of fusion of perfect crystals of nylon 6 and nylon 11, respectively.^{7,12} The total birefringence was measured with a Zeiss polarizing microscope equipped with an Ehringhaus compensator. Infrared spectra were obtained with a Perkin-Elmer spectrophotometer, Model 283.

The tensile modulus of the nylon coextrudates was performed at room temperature on an Instron testing instrument, Model TTM, using a strain gauge extensometer (10 mm gauge length) at a strain rate $6.6 \times 10^{-4} \text{ sec}^{-1}$. The tensile modulus was determined from the tangent to the stress-strain curve at 0.1% strain.

The amount of ammonia absorbed was determined from the weight recovery of treated nylons 6 and 11 upon its desorption from samples respectively 0.15 and 1.50 mm thick using a DuPont 950 thermogravimetric analysis balance. The rate of weight recovery was measured at three different temperatures.

RESULTS

Anhydrous NH_3 is a suitable candidate for hydrogen bond interruption and our recent results indicate that it is an effective plasticizer. Figure 2 shows the plasticization effect with unoriented ribbons of nylon 6 and 11. Nylon ribbons (1.50 mm thick) after they were treated with ammonia in the pressure vessel were removed and deformed rapidly by bending, twisting, or rolling. When the samples were released from their deforming stresses after the ammonia had

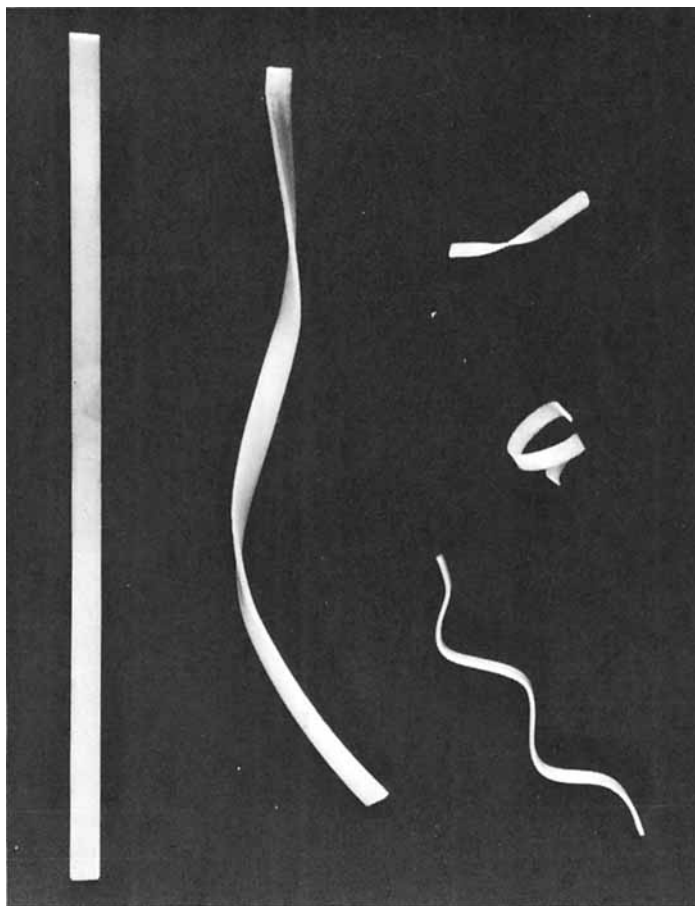


Fig. 2. Illustration of plasticization of nylons 6 and 11 by ammonia. Treated ribbons have relaxed under the deforming stress.

volatilized, they preserved their deformed shape. This indicates that relaxation of deforming stresses is complete as it is not exhibited by untreated nylon samples.

The results of thermogravimetric analysis for NH_3 -treated nylons 6 and 11 are shown in Figures 3 through 5. Figure 3 shows that the rate of ammonia absorption depends on the vapor pressure of the ammonia at which the nylon samples were subjected. These results were obtained with nylon 6 ribbons which were treated with ammonia at different vapor pressures and at room temperature for 1 hr. The weight recovery of the treated samples represents the amount of ammonia that was absorbed during 1 hr at the vapor pressures indicated. Figures 4 and 5 show the weight recovery of treated samples of nylons 6 and 11, respectively, as the ammonia was desorbed from the ribbons at the temperatures shown. Furthermore, they indicate that the rate of desorption increases with temperature. Anhydrous ammonia is highly volatile, bp -35°C at standard pressure, and therefore, if ammonia were only absorbed at the surface of the ribbons, the time for complete desorption would have been short at room temperature. The results in Figures 4 and 5 show that ammonia is absorbed, and as discussed below

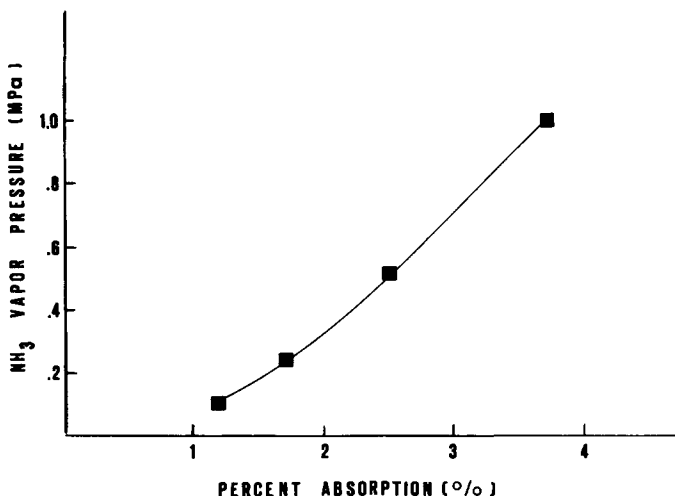


Fig. 3. Extent of ammonia absorption by nylon 6 samples at different ammonia vapor pressures. Treatment duration 1 hr. Film thickness 0.15 mm.

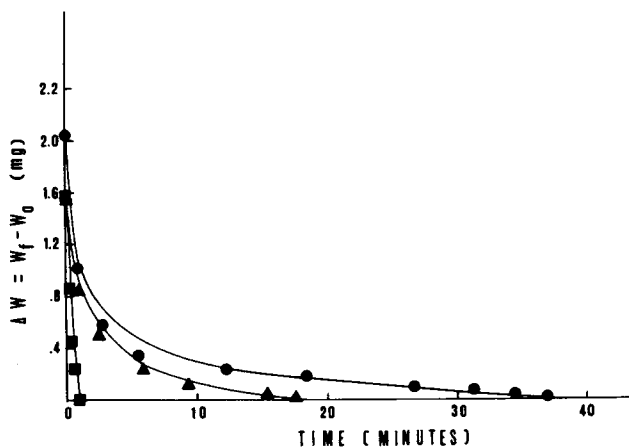


Fig. 4. Desorption of ammonia as a function of time at 27 (●), 50 (▲), and 100°C (■) expressed by the weight loss (mg) of a nylon 6 sample. W_f is the weight of sample during desorption and W_0 , the weight of sample after desorption. Film thickness 0.15 mm.

the extent of absorption is considerable. The amount of ammonia that was absorbed by the nylons 6 and 11 was determined from the thermogravimetric analysis data and was 18% and 10%, respectively, of the weight of the dry samples. These values were obtained and confirmed with nylon ribbons of different thickness (0.18 and 1.50 mm) and were in very good agreement with evaluated values. The latter were obtained by assuming that (a) each ammonia molecule is incorporated with one hydrogen bonding; (b) there is one hydrogen bond per repeat unit; and (c) the densities of nylons 6 and 11 are 1.145 and 1.05 g/cm³, respectively. These density values were calculated by considering that the crystallinity of the original material was ~25% for both and were in good agreement with those obtained by flotation.^{13,14}

On the basis of these assumptions, the theoretical and experimental amounts

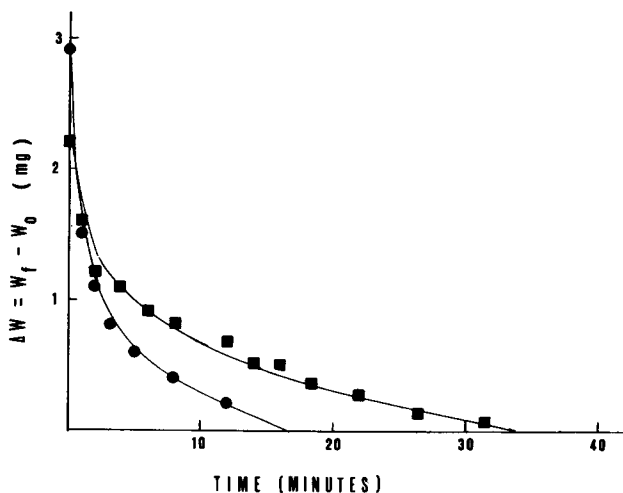


Fig. 5. Desorption of ammonia as a function of time at 50 (■) and 100°C (●) expressed by the weight loss (mg) of a nylon 11 sample. W_f is the weight of sample during desorption and W_0 , the weight of sample after desorption. Film thickness 0.15 mm.

of ammonia absorbed were evaluated from the relations (1) and (2), respectively, and are summarized in Table I:

$$\frac{\rho}{MW_{\text{repeat unit}}} \quad (1)$$

$$\frac{(\% \text{ weight recovery}) \times \rho}{MW_{\text{NH}_3}} \quad (2)$$

where ρ and $MW_{\text{repeat unit}}$ is the density and the molecular weight of the repeat unit of the nylon examined; the % weight recovery term indicates the recovery of the sample weight after the ammonia was liberated and hence represents the amount of ammonia absorbed by the sample during the ammoniation process; and MW_{NH_3} is the molecular weights of ammonia. Furthermore, these results may be cross-checked by comparing the ratios of the experimental (M_e) and calculated (M_c) amounts of ammonia absorbed in nylons 6 and 11. Thus, (M_c nylon 6)/(M_c nylon 11) = 1.77; and (%NH₃ in nylon 6)/(%NH₃ in nylon 11) = 2.25. Under our experimental conditions, these ratios are in very close proximity.

On the basis of the present results, therefore, we may imply that ammonia is absorbed selectively and that the extent of absorption is governed by the total number of hydrogen bonds in the polymer and apparently irrespective to whether they are in the amorphous or crystalline phase. The results also confirm¹⁵ that ammonia neither reacts, dissolves, nor swells significantly the nylons despite

TABLE I
Absorption of Ammonia by Nylons 6 and 11

	Amount of NH ₃ (moles)	
	Nylon 6	Nylon 11
Experimental ($M_e \times 10^2$)	1.27	0.56
Calculated ($M_c \times 10^2$)	1.01	0.57

the prolonged treatment periods (two to three days) at vapor pressure of ~ 1 MPa. Further evidence for the absorption of ammonia was obtained from infrared spectra of ammoniated nylon 6 films scanned as a function of time. Polyamides exhibit an NH stretching vibration band at 3290 cm^{-1} and an NH out-of-plane deformation vibration at $\sim 690\text{ cm}^{-1}$ (the H-bond nonfree amide V band).¹⁶⁻¹⁸ The spectra obtained with ammoniated nylon 6 films show a broad absorption at $\sim 3300\text{ cm}^{-1}$ but with a new shoulder at $\sim 3450\text{ cm}^{-1}$ which disappears as ammonia is desorbed (see Fig. 6). At the same time a new absorption band at 785 cm^{-1} disappears, whereas the intensity of the H-bond nonfree amide V band at 690 cm^{-1} increases. Trifan and Terenzi¹⁹ have studied the free nonhydrogen-bonded NH stretching absorption for a series of polyamides in detail and observed it at 3448 cm^{-1} and adjacent to the hydrogen-bonded NH absorption at 3300 cm^{-1} only at elevated temperatures. No free NH absorption is observable at room temperature, indicating that no more than 1% of nonbonded NH is present. Arimoto¹⁷ reports that upon adsorption of iodine the NH stretching band at 3290 cm^{-1} and the amide V band at 690 cm^{-1} shift to 3400 cm^{-1} and away from the NaCl region, respectively.

Free gaseous ammonia exhibits a stretching vibration at 3336 cm^{-1} which shifts to lower frequencies when coordinated. In conjunction with the above information, the present results suggest that the bands at 3450 and 785 cm^{-1} are associated with free nonhydrogen-bonded amidic vibrations which upon NH_3 desorption shift to 3300 and 690 cm^{-1} , respectively. The frequencies of the studied infrared bands for NH_3 -treated and nontreated nylon 6 samples are summarized in Table II. Having measured the ammonia absorption for the two nylons, we examined the effectiveness of such plasticization by solid-state coextruding NH_3 -treated and untreated nylons 6 and 11 ribbons with HDPE. Coextrusion of the untreated nylons at 100°C and 0.23 GPa proceeded only at $\text{EDR} < 4$. However, the NH_3 -treated nylon 6 and 11 ribbons deformed readily in the temperature range from 65 to 95°C and under applied pressures of $\leq 0.23\text{ GPa}$. The rate of coextrusion was controlled mainly by the extrudability of the HDPE substrates. Table III summarizes the extrusion conditions for the solid-state deformation of treated and untreated nylons.

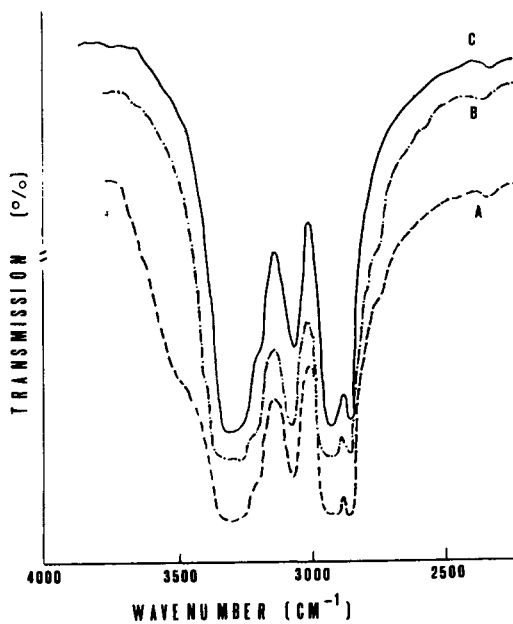
The extrusion draw ratio of the deformed ribbons was calculated as a function of the extrudate length and assuming constant volume deformation²⁰:

$$\text{DR} = \frac{R^2}{r} \geq \left[1 + \frac{3L \tan(\theta/2)}{r} \right]^{2/3} \quad (3)$$

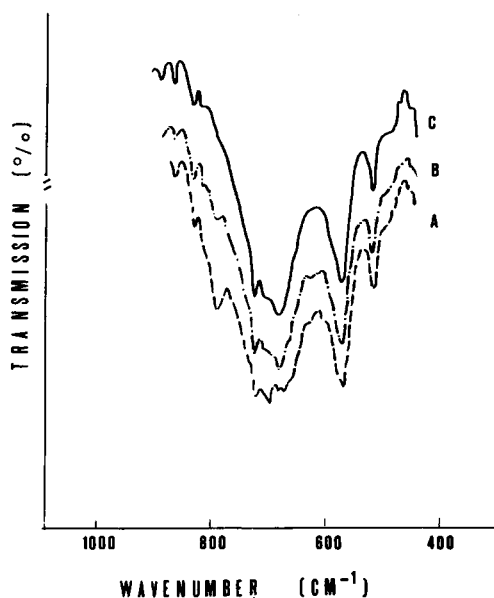
where θ is the entrance angle of the conical die, R is the radius of the die at the entrance, and L and r are the length and radius of the unlaminated composite extrudate. Table IV shows the physical and mechanical properties of nylon 11 extrudates prepared by conventional solid-state extrusion⁶ and the coextrusion technique using the new NH_3 -plasticization approach.

DSC analysis performed on starting nylon 6 and 11 samples and their (treated) extrudates shows a concurrent increase in crystallinity and melting point. Upon extrusion at $\text{EDR} = 12$ the crystalline content of nylon 6 increased from 23.5% to 53% and for nylon 11, from 25.7% to 40%. Similarly, the melting point of the undeformed nylon 6 increased at $\text{EDR} 12$ from 219 to 223°C and of nylon 11 for the same draw, from 183 to 185.2°C .

Although there is a similar increase in percent crystallinity for nylon 11 ex-



(a)



(b)

Fig. 6. Infrared spectra of nylon 6 obtained prior to (A), during (B), and after (C) ammonia desorption at: (a) $4000\text{--}2500\text{ cm}^{-1}$ and (b) $900\text{--}500\text{ cm}^{-1}$

trudates prepared by the conventional extrusion technique and the new approach, there is a large difference in melting point increase for the conventionally extruded fibers at the same draw ($\text{EDR} = 12$). Perkins⁶ suggests that the sharp increase in melting point probably arises from polymorphism at elevated temperatures and/or the processing conditions. The total birefringence for the

TABLE II
Variation of the Infrared Frequencies (cm^{-1}) of NH Stretching and Amide V Bands of Nylon 6 on Absorption of Ammonia

	NH Stretch	Amide V
Untreated nylon 6	3290	690
Treated nylon 6 (NH_3 absorbed)	3290, 3336, 3450	690, 785
Treated nylon 6 (NH_3 desorbed)	3290	690
Free gaseous ammonia	3336	—

optically transparent nylon 6 and 11 extrudates ($\text{EDR} = 12$) was 8.25×10^{-2} and 5.8×10^{-2} , respectively. The high values are attributed to the draw efficiency under the extrusion conditions of the present studies. The latter is further documented by tensile modulus measurements. As shown in Table III, the moduli for nylon 11 extrudates obtained by conventional extrusion and the new approach at $\text{EDR} = 12$ compare satisfactorily. Nylon 6 films at $\text{EDR} = 12$ display a modulus of 13 GPa.

DISCUSSION

Several factors affect the solid-state extrusion of nylons below their melting point. In addition to molecular weight, strain hardening, and initial morphology, nylon extrusion is also affected by the presence of intermolecular hydrogen bonding between amide groups. These bonds exist in both the crystalline and noncrystalline regions of nylons,²¹ have a dissociation energy of ~ 8 kcal/mole, and inhibit a sliding displacement along consecutive hydrogen-bonded planes which is the common deformation mode of nylons ascertained from x-ray diffraction patterns.²² The influence of hydrogen bonding on the flow of polymer melts has also been investigated with copolymers of ethylene and acrylic and methacrylic acids.^{23,24} The flow activation energy and viscosity increased significantly with the amount of hydrogen bonds which act as quasi-crosslinks between neighboring nylon molecules. Thus, lower nylons such as nylon 6, as expected, extrude with extreme difficulty in the solid state because of intermolecular hydrogen bonding. This difficulty may be partially alleviated by the use of plasticizers. Plasticizers for nylons are usually polar compounds of low volatility, capable of interrupting hydrogen bonding between neighboring chains and withstanding the processing conditions. Phenolic compounds, cyclic ketones, sulfonated esters, and amides are examples of compounds used as plasticizers for processing nylons.²⁵ Inorganic salts (LiCl , LiBr , KCl) and aqueous solutions of salts (KSCN , ZnCl_2 , alcohol-salt combinations) have also been used as plasticizers.^{26,27} Disruption of hydrogen bonds in this case results in part by forming metal complexes with the amide compounds. Water, alcohols, partially halogenated hydrocarbons, and in general solvents containing hydrogen atoms attached to electrophilic groups may swell or dissolve nylons by disrupting intermolecular hydrogen bonds.²⁶ Plasticizers, however, lower the mechanical performance and should generally be removed from the deformed state after processing. Thus, a temporary disruption of hydrogen bonds during our deformation process with ammonia followed by volatilization removal after deformation appears to potentially remedy the problem of difficult deformation of nylons in crystalline state extrusion.

TABLE III
Extrusion Conditions for the Preparation of Plasticized and Nonplasticized Nylon 6 and 11

Material	NH ₃ Plasticized	Applied pressure, GPa	Temperature, °C	EDR	Rate, cm/min	Extrudate thickness, mm
Nylon 6 (film) ^a	yes	~0.23	65-70	12	—	0.55
	yes	~0.16	65-70	12	—	0.12
	yes	~0.20	90-95	12	~2-3	0.2
Nylon 11 (film) ^a	no	0.23	100	<3	—	0.2
	yes	~0.21	65-70	12	~0.7	0.6
	yes	~0.12	90-95	12	~3.0	0.6
Nylon 11 (filaments) ^b	no	~0.23	90-95	<3-4	—	0.6
	no	0.23	186	5	<0.01	2.78
	no	0.49	194	12	~0.01	2.78

^a Films prepared by solid-state coextrusion.

^b Films prepared by conventional extrusion.

TABLE IV
Comparison of Properties of Plasticized and Nonplasticized Nylon 6 and 11 Extrudates of
EDR = 12

Property	Plasticized films		Nonplasticized filaments
	Nylon 6	Nylon 11	Nylon 11
Visual appearance	transparent	transparent	translucent
Melting point, °C ^a	223	185.2	205
Crystallinity, %	53	40	44
Birefringence	8.25×10^{-2}	5.8×10^{-2}	—
Tensile modulus, GPa	13	4	~5.5

^a Heating rate 10°C/min.

Plasticization of nylon with NH₃ is a new concept that is likely applicable to other thermoplastics with strong hydrogen intermolecular bonding. The use of ammonia over other plasticizers is advantageous for a number of reasons: (1) Ammonia is an effective hydrogen bonding agent; its penetration into the sample is achievable under practical conditions. (2) It has a relatively low critical pressure (11.13 MPa)¹¹ and can be readily preserved in the extruded sample under the applied pressure of the rheometer plunger (≤ 0.23 GPa). (3) It is readily removed by volatilization from the sample as it emerges deformed from the die exit. (4) It is effective in the gaseous phase and therefore is required in only small amounts.

Plasticizers are known to depress the transition temperature of nylons,²⁵ and this has a twofold implication for our new deformation process: (a) Solid-state deformation may be achieved at even lower temperatures. This suggestion can be made from the present work and furthermore from our current studies²⁸ on the conventional drawing of NH₃-plasticized nylons 6 and 11 to draw ratio ≤ 7 at room temperature and therefore substantially below the T_g of the untreated materials which are 54°C for nylon 6 and 42°C for nylon 11.¹² (b) A possible restriction of the critical temperature of ammonia ($\sim 133^\circ\text{C}$)¹¹ for the use of the latter as plasticizer at temperatures $> 133^\circ\text{C}$ may be bypassed by such temperature transition depression.

CONCLUSIONS

In the present study we have investigated the plasticization of nylons 6 and 11 with anhydrous ammonia. Ammonia plasticizes by the temporary disruption of hydrogen bonding interactions between amide groups of adjacent nylon chains. Thermogravimetric and infrared analyses show that it is absorbed selectively to an extent that is determined by (a) the vapor pressure of the NH₃ atmosphere, (b) treatment duration, and (c) the total number of hydrogen bonds in the polymer. Thus, for the nylons 6 and 11 the amounts absorbed are 18% and 10% of the weight of the dry samples, respectively.

The extent of plasticization is documented by (a) the feasibility to permanently deform the shape of nylons 6 and 11 at room temperature, i.e., below the T_g and T_m for either untreated polymer; and by (b) solid-state extrusion of nylons 6 and 11 to EDR = 12 at rates and conditions not attainable with the untreated nylon analogs.

The high total birefringence values and the significant increase in crystallinity

and tensile modulus for the two examined nylons document the effectiveness of the new plasticization approach. The use of ammonia as plasticizer appears to be advantageous over other agents for the solid-state deformation of nylons. Importantly, NH_3 can be removed by volatilization from the extruded sample after extrusion. Since it is effective in the gaseous phase, it is only required in small amounts and upon release from the deformed samples could be collected and recirculated.

Additional experiments on the plasticization of nylons are being undertaken to understand and optimize the process

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References

1. J. H. Southern and R. S. Porter, *J. Macromol. Sci., Phys.*, **B4**, 541 (1970).
2. N. J. Capiati and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1177 (1975).
3. P. Predecki and W. O. Statton, *J. Polym. Sci. Part B*, **10**, 87 (1972).
4. K. Imada, T. Yamamoto, K. Shigematsu, and M. Takayanagi, *J. Mater. Sci.*, **6**, 537 (1971).
5. A. G. Kolbeck and D. R. Uhlmann, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 27 (1977).
6. W. G. Perkins, Ph.D. Thesis, University of Massachusetts, 1978.
7. W. G. Perkins and R. S. Porter, *J. Mater. Sci.*, **12**, 2355 (1977).
8. P. D. Griswold, A. E. Zachariades, and R. S. Porter, presented at Symposium on Stress Induced Crystallization at Midland Macromolecular Institute, Midland, Michigan, August 1977.
9. C. Schuerch, *Forest Prod. J.*, **14**, 377 (1964).
10. C. Schuerch, private communication.
11. R. C. Weast, Ed., *CRC Handbook of Chemistry and Physics*, 50th ed., The Chemical Rubber Co., Cleveland, Ohio, 1969.
12. R. Grew and L. Nicolais, *Polymer*, **17**, 1049 (1976).
13. T. Kawaguchi, *J. Appl. Polym. Sci.*, **11**, 4, 56 (1959).
14. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1967.
15. Zytel nylon resins, *DuPont Design Handbook*, E. I. du Pont de Nemours & Co., Wilmington, Delaware.
16. N. M. Bikales, Ed., *Encyclopedia of Polymer Science and Technology*, Vol. 10, Interscience, New York, 1969.
17. H. Arimoto, *J. Polym. Sci.*, **2**, 2283 (1964).
18. A. Miyake, *J. Polym. Sci.*, **44**, 223 (1960).
19. D. S. Trifan and T. J. F. Terenzi, *J. Polym. Sci.*, **28**, 443 (1958).
20. N. Capiati, S. Kojima, W. G. Perkins, and R. S. Porter, *J. Mater. Sci.*, **12**, 334 (1977).
21. C. G. Cannon, *Spectrochim. Acta*, **16**, 302 (1960).
22. J. J. Point, M. Dosiere, M. Gillot, and A. Goffin-Gerin, *J. Mater. Sci.*, **6**, 479 (1971).
23. L. L. Blyer and J. W. Haas, *J. Appl. Polym. Sci.*, **13**, 2721 (1969).
24. K. Sacamoto, W. J. MacKnight, and R. S. Porter, *J. Polym. Sci. A-2*, **8**, 277 (1970).
25. M. J. Kohan, Ed., *Nylon Plastics*, Wiley, New York, 1973.
26. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1641 (1969).
27. D. Aciemo, E. Bianchi, A. Ciferri, B. DeCindio, C. Migliaresi, and L. Nicolais, *J. Polym. Sci.*, **54**, 259 (1976).
28. A. E. Zachariades, M. P. Watts, and R. S. Porter, to be published.

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