

EFFECT OF NYLON COPOLYMERIZATION IN FLEXIBLE THERMOFORMING

Tappi PLACE, Forth Worth, April 12 2016

Session 6 – Multi-layer Packaging Design and Evaluation

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In recent years, traditional packaging, like glass jars and metal cans, are steadily being replaced. While these containers have several benefits, drawbacks such as their higher weight and resulting high transportation costs, are causing producers to replace them with plastics.

In fact, plastics have taken the leading position in the packaging industry, and new plastic designs are combining functionality and efficiency.

The last step of this evolution is flexible plastic packaging, which is allowing for different shapes and technologies that can replace most existing rigid (glass, metal, rigid plastic) packaging while providing outstanding protection properties and efficiency through unbeatable weight reduction.

Among others, some of the current existing flexible packaging technologies are:

- Pouches:
 - o Standard
 - o Shrinkable
 - o Stand-up
- Vertical Form Film Seal (Flowpack)
- Horizontal Form Film Seal
- Flexible Thermoforming package

Focusing in the Flexible Thermoforming packaging, this technology shows a number of benefits that contributes to its success in the packaging market:

- Versatility: Many sizes, shapes, products can be produced and packed
- Efficiency: In the transport of raw material (film rolls) as the package is produced in the final user site, but also efficiency in the product volume/ film surface ratio, as the film is stretched to create enough volume to fit the product.
- Eco-friendly; Reducing the CO2 footprint in the transportation of the film, package and waste due to the weight reduction compared with other solutions, and also reducing the amount of raw materials necessities to pack the same article.

Flexible thermoforming is a well established packaging technology that has grown in importance, especially thanks to the developments of new extrusion equipment and raw materials that allows producing thinner films, with higher number of layers and additional safety and functionality.

Nylon has become one of the most used materials in this technology, because it's function as structural material, providing some of the required properties:

- Mechanical and puncture resistance (abuse)
- Barrier against gas and aroma
- Forming capacity
- Easy processing & possibility to co-extrude with other materials (Polyolefins, EVOH...)

Traditionally, PA6 based films have been used in this technology, being suitable for most of the common applications.

However, due to several factors, like:

- The pressure for finding new sizes and shapes of packaging
- The development of new extrusion technologies that allows to produce thinner films, with thinner and stable layers of structural materials
- And the necessity of increase the packaging productivity, reducing the number of defective/broken packages and ensuring the food safety

can move this technology in the direction of usage of advance materials with enhanced thermoforming properties.

In this paper a systematic and empirical comparison of the effect of copolymerization in the nylon 6-based films thermoforming properties is going to be presented, based on real, production conditions.

The chemical modification of PA6 by copolymerization of the caprolactam with other monomers, like nylon salt (PA6.6 monomer) or ADA (PA 12 monomer) have several effects in the crystalline structure of the resulting nylon, changing the processing behavior of the material as well as some basic properties.

This way, by INCREASING the copolymerization ratio, some properties like:

- Thermal properties (T_m , T_c , T_g)
- Tensile and flexural modulus
- Crystallization ratio
- Processing temperatures

Will significantly DECREASE, while others like:

- Transparency
- Gloss
- Stretchability (Inc. thermoforming)
- Elongation
- Flexibility
- Toughness
- Shrinkage

Will INCREASE.

Theoretically, based on the benefits of the copolymerization showed above, nylon copolymers should be the most suitable materials for the flexible thermoforming application.

However, there was a lack of a systematic study of the influence of the type of nylon in the thermoforming properties; this paper shows the results of this comparison based on empirical data, based on commercial or semi-commercial films with the aim to be as much applicable to the real process as possible.

In addition, the benefits of nylon copolymers are especially remarkable in the films produced by the '**air quenched blown film**' process, because of the lower cooling efficiency of this technology, compared with others have influence in the crystallinity of the films; however, the flexibility and versatility of sizes and structures, makes the airblown technology one of the most suitable production processes for thermoforming films; for this reason, all the results presented in this article are based on films produced by this technology.

At the end the question to be answered is: which UBE nylon will thermoform the best?

To answer this the following nylon resins from the UBE range have been used:

GRADE NAME	COMPOSITION	T _m		T _c		T _g	
		°C	°F	°C	°F	°C	°F
1030B	PA6 100 %	219	426	178	352	51	124
5032B	CoPA6/6.6 10%	205	401	162	324	50	122
5033B	CoPA6/6.6 15%	195	383	150	302	49	120
5034B	CoPA6/6.6 20%	191	376	146	295	48	118
6434B (Terpalex)	TerPA6/6.6/12	186	367	132	267	45	113

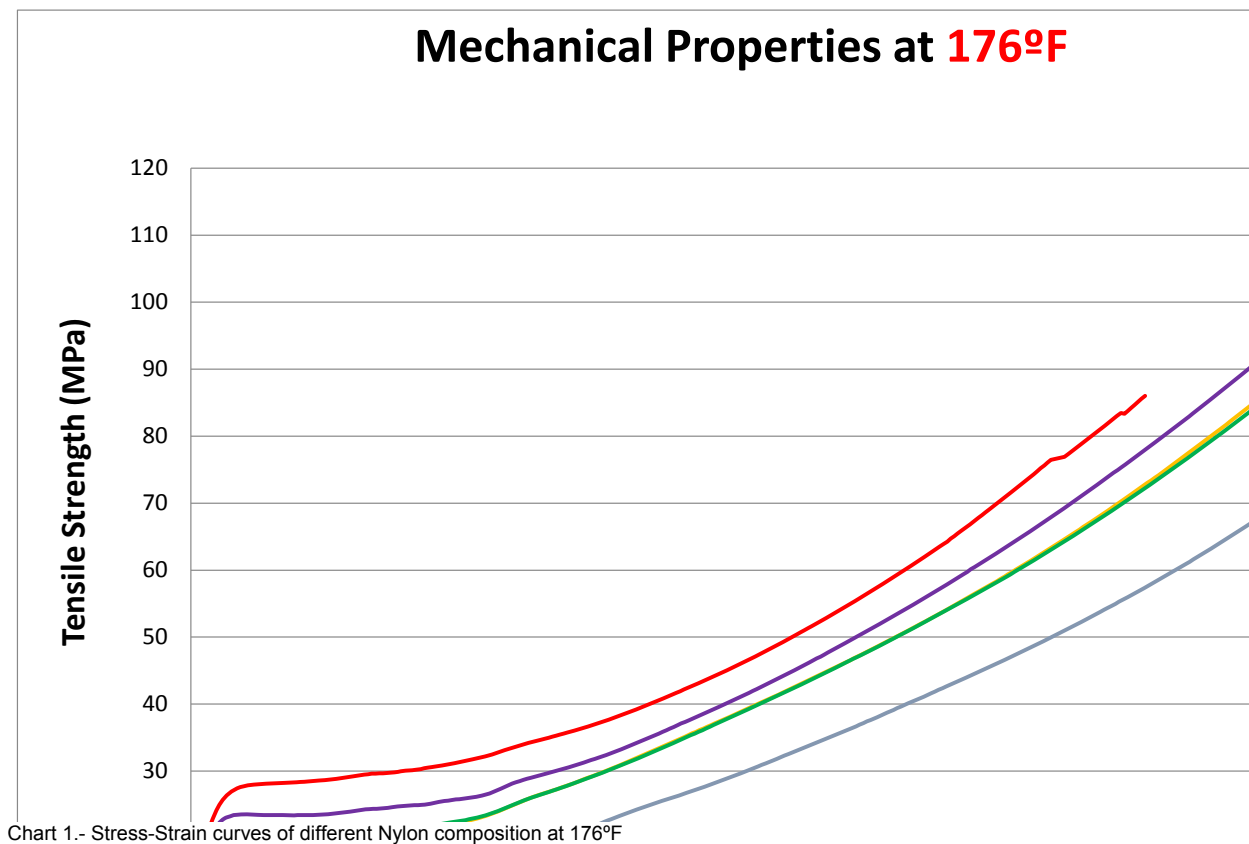
Table 1.- Properties of materials used in the research

PART 1: BASIC RESEARCH; AIR QUENCHED BLOWN FILM MONOLAYER NYLON

All these nylons have been processed to produce different types of film, in growing complexity, starting with **monolayer air quenched blown film** produced in R&D pilot line with a thickness of **50 microns**.

These films allow the study of the thermoforming behavior of the different nylons without the influence of other materials.

Before starting with the study of the film in real thermoforming equipment, the tensile strength necessary to achieve certain elongation at temperature above T_g was studied by obtaining the stress-strain curve of each material at 80°C (176°F).



This chart already provides information about the different force that need to be applied to achieve certain elongation (which can be simulate to the thermoforming depth) and how by increasing the copolymerization ratio less force it's necessary to be applied to achieve it.

As next step, using the same type of films, the thermoformability of all these films has been evaluated in real conditions using an industrial flexible thermoforming equipment available at the R&D Center focusing the research in two parameters:

1.1. Optimum thermoforming temperature

1.2. Maximum thermoforming depth until break.

These two parameters have been studied using the following mold and equipment conditions:

Mold :

Ø : 91 mm (3,6")

Depth : Adjusted until break

Heating :

Temp. : Adjusted to the optimal level for each grade

Time : 3s

Forming:

By pressure air



The used mold geometry is restrictive (high depth/diameter ratio) to evaluate better these properties.

1.1. Optimum thermoforming temperature

Based on the described methodology, the optimum forming temperature for different NYLON copolymers of the study was obtained, based on their maximum thermoforming depth, as follows:

Material	Optimum thermoforming temp	
	(°C)	(°F)
PA6	110	230
CoPA6/6.6 (10% AH ratio)	85	185
CoPA6/6.6 (15% AH ratio)	80	176
CoPA6/6.6 (20% AH ratio)	80	176
TerPA6/6.6/12	80	176

Table 2.- Optimum thermoforming temperature

The effect of the copolymerization can be observed in terms of significant reduction or the necessary temperature to properly thermoform it, from 230 °F for PA6, going down to 185 for CoPA with lower copolymerization ratio and 176 °C for CoPA with higher copolymerization ratio, or three different monomers.

This has an important effect in the industrial thermoforming process, because the possibility to use lower thermoforming temperatures, can allow higher productivities (packages/min), higher energetic efficiency, and possibility to co-extrude with thermal sensitive/low melting point materials.

1.2. Maximum thermoforming depth until break.

Using the optimum thermoforming temperatures determined in the first step of the study, the maximum thermoforming depth that can be achieved, without breakage, in a continuous and consistent way was determined, and these were the obtained results:

Material	Maximum thermoform depth	
	(mm)	(inch)
PA6 @ 230°F	70	2,76
CoPA6/6.6 (10% AH ratio) @ 185°F	70	2,76
CoPA6/6.6 (15% AH ratio) @ 176°F	85	3,35
CoPA6/6.6 (20% AH ratio) @ 176°F	85	3,35
TerPA6/6.6/12 @ 176°F	95	3,74

Table 3.- Maximum thermoforming depth monolayer films

Again, the influence of the copolymerization ratio is clear in the maximum thermoforming depth that can be achieved before break; The copolymer with low copolymerization ratio achieved the same maximum depth as the PA6, but requiring much lower temperature to achieve this depth.

Copolymers with 15% and 20% ratio, show significant higher depth, even when they don't show difference between them.

Finally the terpolymer 6/6.6/12 can go even deeper than the rest of copolymers.

PART 2: BEHAVIOUR OF BASIC MULTILAYER FILM STRUCTURE

Following the same procedure, basic multilayer film structures were produced in R&D pilot line as follows:

	Layer 1 Outer	Layer 2	Layer 3 Inner	Total
Material	PA	Tie	LDPE	
Thickness (μm)	50 μm (25 %)	10 μm (5%)	140 μm (70 %)	200 μm

Table 4: Basic multilayer film structure

In this case, and due to the presence of thick layer of LDPE that has influence in the heat transmission during the pre-heating for thermoforming, and also is limiting the maximum temperature that can be applied (it melts down if it's too high) the pre-heating temperature for these films has been fixed at **212°F (100°C)** for all different samples.

Following the same procedure and mold that in the first part of the study, the maximum thermoforming depth before breakage was determined as follows:

Material	Maximum thermoform depth	
	(mm)	(inch)
PA6 @ 212°F	60	2,36
CoPA6/6.6 (10% AH ratio) @ 212°F	65	2,55
CoPA6/6.6 (15% AH ratio) @ 212°F	75	2,95
CoPA6/6.6 (20% AH ratio) @ 212°F	75	2,95
TerPA6/6.6/12 @ 212°F	85	3,35

Table 5: Maximum thermoforming depth multilayer films

Same trend can be observed that with monolayer film; higher copolymerization ratio leads to the possibility of produce deeper thermoforming packaging, being the Terpolymer 6/6.6/12 the material that shows the best results.

The influence of LDPE in this case can be observed as a reduction in all the cases of the absolute values of thermoforming depth compared with the PA monolayer films, becoming the material that limits the thermoforming depth instead of supporting the PA.

PART 3: BEHAVIOUR OF INDUSTRIAL MULTILAYER FILM STRUCTURES

To complete this study, and check the validity of the obtained results and tendencies, several multilayer films were produced in a fully-commercial industrial airblown line in collaboration with one recognized extrusion systems producer, using the following film structure:

	Layer 1 Outer	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7	Layer 8	Layer 9 Inner	Total
Material	PA	Tie	PA	Tie	PA	Tie	PE	PE	PE	
Thickness (μm)	25 μm (16,7%)	15 μm (10%)	10 μm (6,7%)	15 μm (10%)	10 μm (6,7%)	12 μm (8%)	13 μm (8,7%)	20 μm (13,3%)	30 μm (20%)	150 μm

Table 6: Industrial multilayer structure

Following the same procedure that in the PART 2 of this study, the preheating temperature used in this study was **212°F** (100°C) and based on the same mold design, the maximum thermoforming depth before breakage was determined as follows:

Material	Maximum thermoform depth	
	(mm)	(inch)
CoPA6/6.6 (10% AH ratio) @ 212°F	65	2,55
CoPA6/6.6 (20% AH ratio) @ 212°F	70	2,75
TerPA6/6.6/12 @ 212°F	75	2,95

Table 7: Maximum thermoforming depth industrial films

Due to limitations in the extrusion equipment availability, only three different Nylons could be processed and studied in this part of the research. However, the observed trend in Part 1 and Part 2 can be also observed here; higher copolymerization ratio leads to the possibility of produce deeper thermoforming packaging, being the Terpolymer 6/6.6/12 the material that shows the best results.

Based on these data obtained from different films produced at different extrusion conditions, it has been observed that increasing the Copolymerization ratio of the Nylon has a beneficial impact in the thermoforming behavior, which has an impact in the design of films for flexible thermoforming packages, allowing:

- Design of deeper packages, with more complicated, sharp shapes.
- Reduce the number of re-pack and return goods by breakages in the film during the packaging and/or transport and handling
- Possibility of improve productivity by forming more packages/minute, due to less pre-heating time required
- Improve the shelf life of the product, due to the better film thickness distribution across the package.

Regarding shelf life of the product, it is necessary to consider that there are different barrier requirements, depending of the products:

- Products were the oxygen barrier is not necessary, were Nylon only provides the mechanical and thermoforming properties
- Products were medium barrier against oxygen or other gases is required; Nylon can provide this medium barrier.
- Products were high barrier against oxygen or other gases (MAP) is required; In this case, it is necessary the incorporation of EVOH to the Nylon structure.

EVOH is an excellent barrier material, but it shows a limited thermoformability, compared with other materials, like nylon.

Based on 50 microns monolayer film, following the same testing procedure that in the first PART 1.2 of the study, these are the comparative maximum thermoforming depth that can be achieve comparing EVOH, Nylon and LDPE:

Material	Maximum thermoform depth	
	(mm)	(inch)
CoPA6/6.6 (15% AH ratio) @ 212°F	85	3,35
EVOH (32% mol) @ 212°F	30	1,18
LDPE @ 212°F	45	1,77

Table 8: Maximum thermoforming depth of common material used in flexible packaging

Individually, Nylon Copolymer is the material showing the better thermoforming behavior; for this reason for thermoforming applications EVOH is placed in the structure protected by two layers of Nylon, which will ensure the integrity of the barrier layer and avoiding delamination at the same time thanks to the excellent compatibility between both materials.

To check this phenomena, two different films were produced in the R&D pilot line, with the following structure:

Medium barrier film:

	Layer 1 Outer	Layer 2	Layer 3	Layer 4	Layer 5 Inner	Total
Material	PA	Tie	PA	Tie	PE	
Thickness (μm)	25 μm (12,5%)	10 μm (5%)	25 μm (12,5%)	15 μm (7,5%)	125 μm (62,5%)	200 μm

Table 9: Medium barrier film structure

High barrier film:

	Layer 1 Outer	Layer 2	Layer 3	Layer 4	Layer 5 Inner	Total
Material	PA	EVOH	PA	Tie	PE	
Thickness (μm)	25 μm (12,5%)	10 μm (5%)	25 μm (12,5%)	15 μm (7,5%)	125 μm (62,5%)	200 μm

Table 10: High barrier film structure

Were the materials used are:

PA = CoPA 6/6.6. with 20%

EVOH = 32 % mol

PE = LDPE MFI 2,0

Tie = LLDPE anhidrid maleic acid modified LLDPE, MFI 1,7.

Comparing these thermoformability of these two films, using the same methodology and thermoforming conditions used in the previous study, the following results were obtained:

Maximum thermoforming depth:

Material	Maximum thermoform depth	
	(mm)	(inch)
Medium barrier film @ 212°F	70	2,76
High barrier film @ 212°F	70	2,76

Table 11: Maximum thermoforming depth of high barrier vs medium barrier films

Total thickness distribution comparison:

**200µm Film Medium vs High Barrier
5034B**

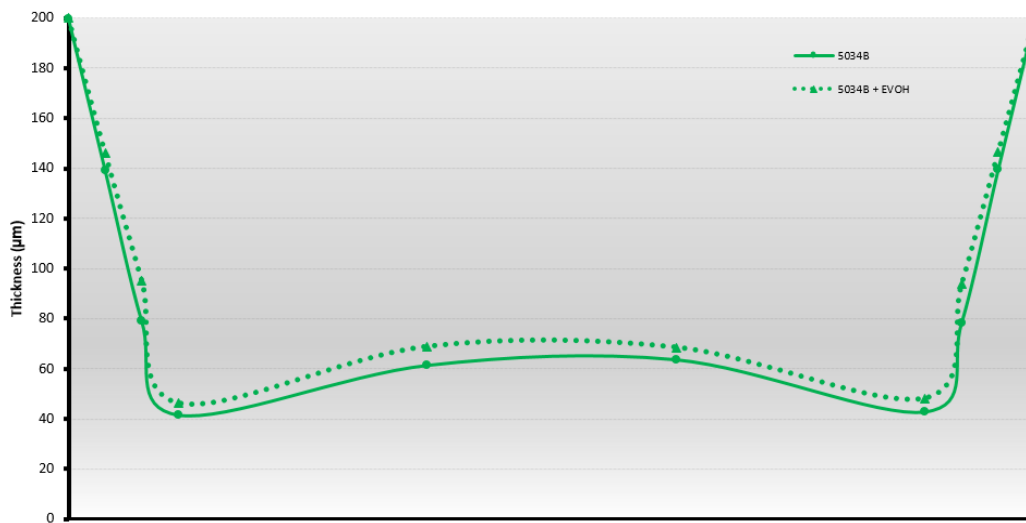


Chart 2: Comparison of total thickness distribution medium barrier vs high barrier films

This results shows that combining EVOH with nylon copolymer it's possible to overcome the thermoforming limitations of the coextruded materials and get a film with similar thermoforming behavior that with or without EVOH.

The obtained benefits in terms of thermoformability that nylon copolymers have shown during this study, can be used to provide better packaging, with enhance properties and protection to the packed article, or also can be used to DOWNGAUGE the multilayer film, providing the same benefits that standard PA6 film, but with much lower PA layer thickness.

As example of this possibility, if comparing a 50 microns monolayer film based on PA6 with different monolayer films of CoPA 6/6.6, with reduced film thickness:

Material	Film thickness (microns)	Maximum thermoform depth (mm) (inch)		Downgauging (%)
PA6 @ 230°F	50	70	2,76	---
CoPA6/6.6 (20% AH ratio) @ 176°F	50	85	3,35	---
CoPA6/6.6 (20% AH ratio) @ 176°F	40	80	3,15	---
CoPA6/6.6 (20% AH ratio) @ 176°F	35	75	2,95	---
CoPA6/6.6 (20% AH ratio) @ 176°F	30	70	2,76	40

Table 12: Downgauging possibilities of PA6 vs CoPA6/6.6

This example shows the great downgauging possibilities by using advanced materials like nylon copolymers, were the same maximum depth achieved with a 50 microns PA6 film can be achieve with a 30 microns CoPA6/6.6 film, and this difference is even higher by using terpolymer 6/6.6/12.

CONCLUSION

The reported study clearly shows how the chemical modification of nylon 6 by copolymerization with AH salt (CoPA 6/6.6), or in a more advance version by AH salt and ADA (TerPA 6/6.6/12) make possible to create materials more suitable for the flexible packaging industry:

- Better processing, lower melting point
- Higher flexibility, lower modulus
- Higher toughness, higher mechanical an puncture resistance

These advantages, applied to the flexible thermoforming packaging, show benefits in terms of:

- Possibility to achieve deeper packages
- Safer package, less breakages
- Higher design freedom
- Higher efficiency, lower weight and lower processing temperatures
- Cost down possibilities by downgauging of the film or Nylon layers thicknesses.

All the results are based on test done in airblown and thermoforming lines under commercial conditions which ensures the repeatability of the results, and are part of a deeper research carried out by our company; based on this research some materials specially designed for thermoforming are being launched to go even further in the thermoforming application.

For example, a modified version of the terpolyamide 6/6.6/12 that allows to achieve even deeper packaging as can be seen in the next table, carried out in multilayer film PA/Tie/PE, same as PART 2 of this study:

Material	Maximum thermoform depth	
	(mm)	(inch)
PA6 @ 212 - 230°F	60	2,36
CoPA6/6.6 (20% AH ratio) @ 212 - 230°F	75	2,95
TerPA6/6.6/12 @ 212 - 230°F	85	3,34
Special TerPA6/6.6/12 @ 212°F	110	4,33

Table 11: Maximum thermoforming depth of Special TerPA6/6,6/12 for thermoforming