MULTILAYER CONTAINERS FEATURING NANO-NYLON MXD6 BARRIER LAYERS WITH SUPERIOR PERFORMANCE AND CLARITY

MITSUBISHI GAS CHEMICAL CO., INC.

Nanocor

INTRODUCTION

This presentation addresses the subject of PET bottles designed for applications requiring high levels of gas barrier to oxygen and carbon dioxide. This category is commonly referred to as sensitive beverages, which include beer, flavored alcoholic beverages, 100% juices, specialty waters, and sports drinks.

Bottles appropriate for these beverage types carry the moniker of "barrier bottles."

A handful of barrier technologies have been proposed to create barrier bottles. Multilayer technology is by far the most common in use today and it is growing in popularity.[1] Multilayer co-injection has advanced rapidly over the past few years. It features the following advantages:

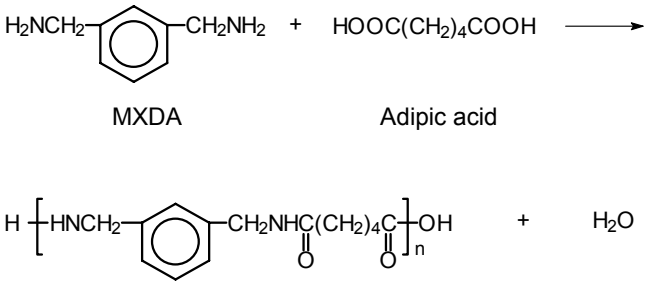
- Moderate capital investment
- Predictable process variables based on monolayer experience
- Preform cycle times equal to monolayer
- Flexibility to use multilayer equipment for monolayer
- Flexibility to incorporate a variety of barrier materials
- Lower unit bottle costs

At least 80% of all barrier bottles in use today are multilayer bottles.

NYLON-MXD6 BARRIER RESIN

The critical component of barrier bottles is the barrier resin itself. Barrier resin is typically incorporated at the preform stage as an inner layer with PET on both sides, making PET the beverage contact layer as well as the layer gripped by the consumer.

N-MXD6 resin is a product of Mitsubishi Gas Chemical Company, Inc. It is produced by polymerization of MXDA and adipic acid. The resulting resin contains meta-xylylene groups of the following formula:



Due to this unique chemical composition and crystalline structure, N-MXD6 has excellent gas barrier properties, especially in high humidity conditions. In addition, it offers important processing benefits for multilayer bottle manufacture. Among them are:

- ♣ Temperature processing window overlapping PET
- ♣ Adhesion without the need for tie layers
- ♣ Close rheology match to PET
- ♣ Fast crystallization time
- ♣ Superior recyclability and good retortability

In the common vernacular N-MXD6 is known as a passive barrier. This is a misnomer. N-MXD6 is more appropriately a static barrier, meaning it creates gas barrier which does require "activation" and does not change or deplete over time. Because N-MXD6 is static, it provides barrier to all gases, even hydrocarbon fuel vapor. It follows that N-MXD6 is a multi-gas barrier resin, contributing both oxygen and CO_2 barrier in PET bottles.

NANO-N-MXD6 (GRADE M9)

Nano-N-MXD6, available as grade M9™, is an improved N-MXD6 multi-gas barrier resin. M9 incorporates nanocomposite technology*, which creates a barrier resin with extraordinary performance. In PET bottles M9 improves carbon dioxide barrier by 50% and oxygen barrier by a factor of 4X compared to standard N-MXD6.

* US Patents # 6,232,388; 6,376,591; 6,387,996; 6,391,449

Much has been published about plastic nanocomposites and Nova Pak has sponsored three presentations over the past 4 years.[2,3,4] In its simplest form, plastic nanocomposite technology consists of dispersing nanoclays in polymer matrices. Nanoclays are platelet sheets with extraordinarily high aspect ratios. When properly dispersed, nanoclay platelets enhance barrier by creating a tortuous path to gas permeation.[5] The hydrophilic nature of nylons makes them particularly suited to nanocompositing.

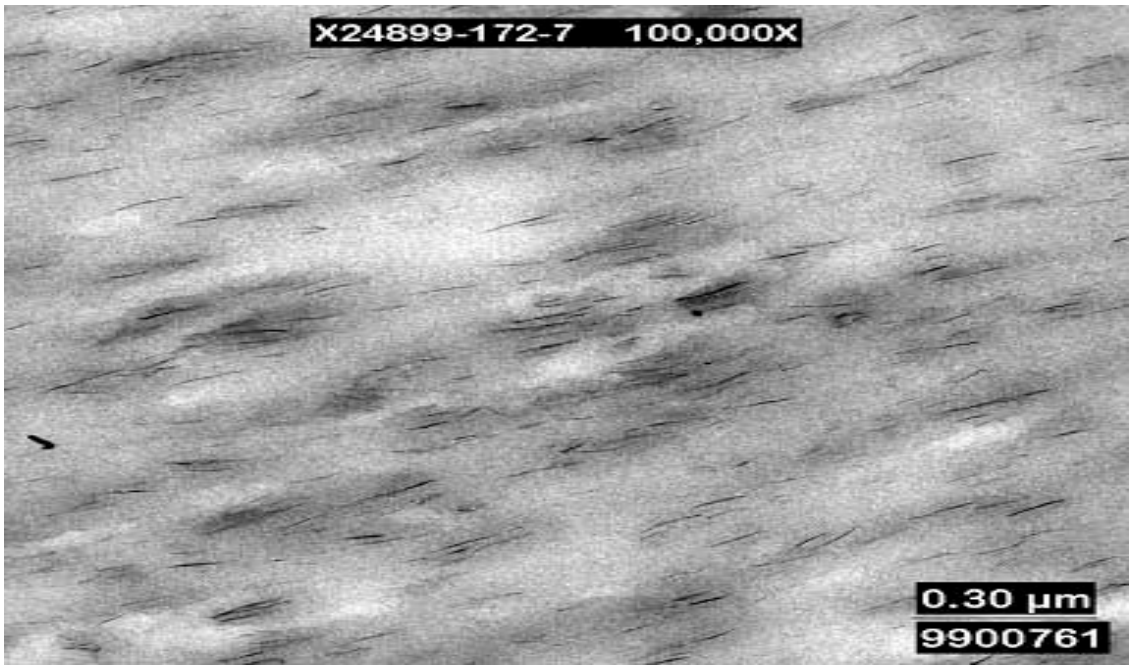


Figure 1. TEM of grade M9 from a barrier PET bottle

Nanocor has developed and patented both a nanoclay and a process for creating N-MXD6-based nanocomposites. Figure 1 shows a transmission electron micrograph of this nanocomposite. The dark lines in the TEM are the edges of dispersed nanoclay platelets, oriented parallel to the specimen surface. Because the platelets are about one nanometer in thickness, only the reflection of the edge can be detected by the microscope.

In conjunction with Mitsubishi Gas Chemical, the technology has been further refined into commercially available M9.

MATERIAL CHARACTERISTICS

Although M9 is an improved N-MXD6 from a gas barrier perspective, other key material properties remain quite similar. Table 1 lists typical properties. Most notable is haze. M9's superior nanoclay dispersion keeps haze at a level equal to standard N-MXD6. This creates clear barrier bottles with very good transparency.

Table 1. Material properties of N-MXD6 and M9 (cast film)

Property	Units	N-MXD6	M9
Density (non-crystallized)		1.19	1.22
(crystallized)		1.22	1.24
Glass transition temperature	°C	85	85
Melting point	°C	237	237
Semi-crystallization time	sec	100	50
Haze	%	1.4	1.5
Tensile strength	MPa	85	83
Tensile elongation	%	3.3	2.9
Tensile modulus	GPa	3.1	3.5
OTR/23°C 60%RH	cc·mm/m^2·day·atm	0.09	0.02
CO2TR/23°C 60%RH	cc·mm/m^2·day·atm	0.30	0.15
WVTR/40°C 90%RH	g·mm/m2·day	1.36	0.58

Nanoclay is a UV absorber. It should not be surprising that M9's UV protection exceeds PET (Figure 2). Because barrier layers rarely exceed 10% of bottle thickness the contribution to UV permeation will be small, but it is comforting to know that M9 will not cause deterioration of the UV package.

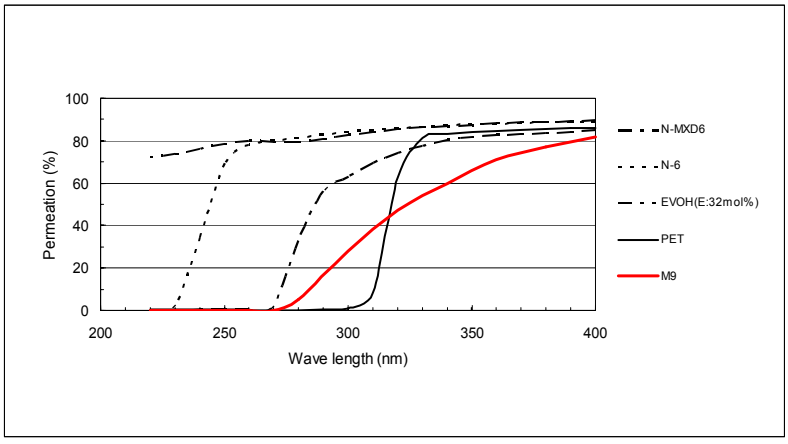


Figure 2. UV permeation for cast films

GAS BARRIER PERFORMANCE

M9 is a potent oxygen barrier across the entire effective relative humidity range. This is illustrated in Figure 3. M9 is superior to N-MXD6 and EVOH (44 mole %) in the 50-100% relative humidity range. Above 70% rh it is also superior to EVOH (32 mole %). The M9 curve virtually parallels that of standard N-MXD6, but does so at far lower permeation. Parallel behavior is consistent with the theory of torturous path impedance.

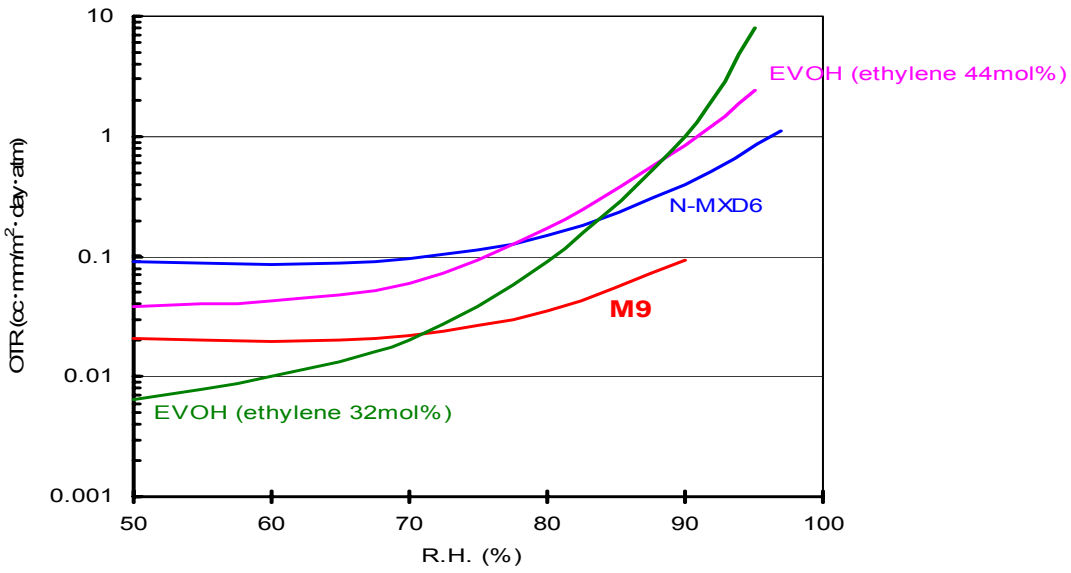


Figure 3. OTR for barrier resins (23˚C)

M9's OTR is improved 4X over standard N-MXD6 and at high relative humidity its OTR is far superior to EVOH. Many barrier applications also require enhanced CO_2 and water vapor barrier. M9 provides it, delivering performance twice as good as standard N-MXD6 under non-pressurized conditions.

PROCESSING CHARACTERISTICS FOR BOTTLES

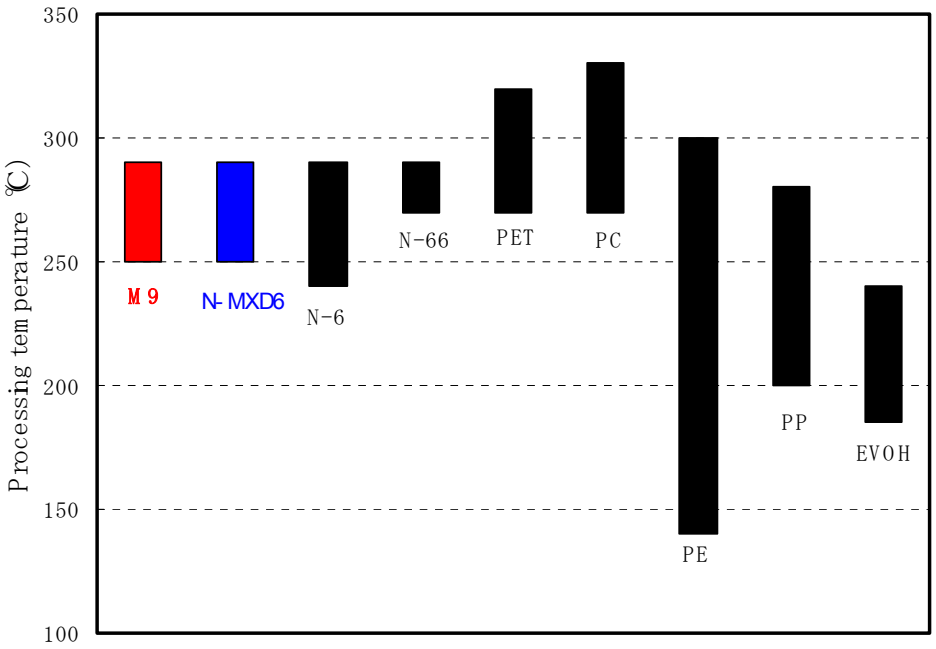
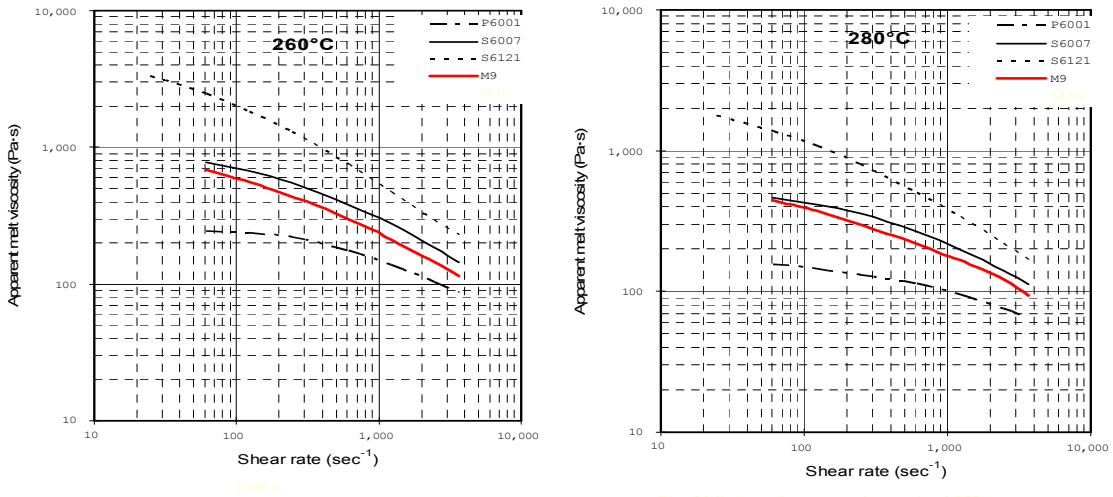


Figure 4. Processing windows for M9 and typical resins

Processing behavior mirrors that of standard N-MXD6. Figure 4 demonstrates that M9's process window remains ideal for multilayer PET construction with a window of at least 20°C. Rheology is also matched to PET as demonstrated in Figure 5A and 5B. Preform manufacture and bottle blowing can be done with considerable flexibility. Companies with experience using N-MXD6 can incorporate M9 with little or no learning curve.



Figures 5A and 5B. Melt viscosity at different temperatures and shear rates
P6001, S6007 and S6121 are standard grades of N-MXD6

BOTTLE PERFORMANCE

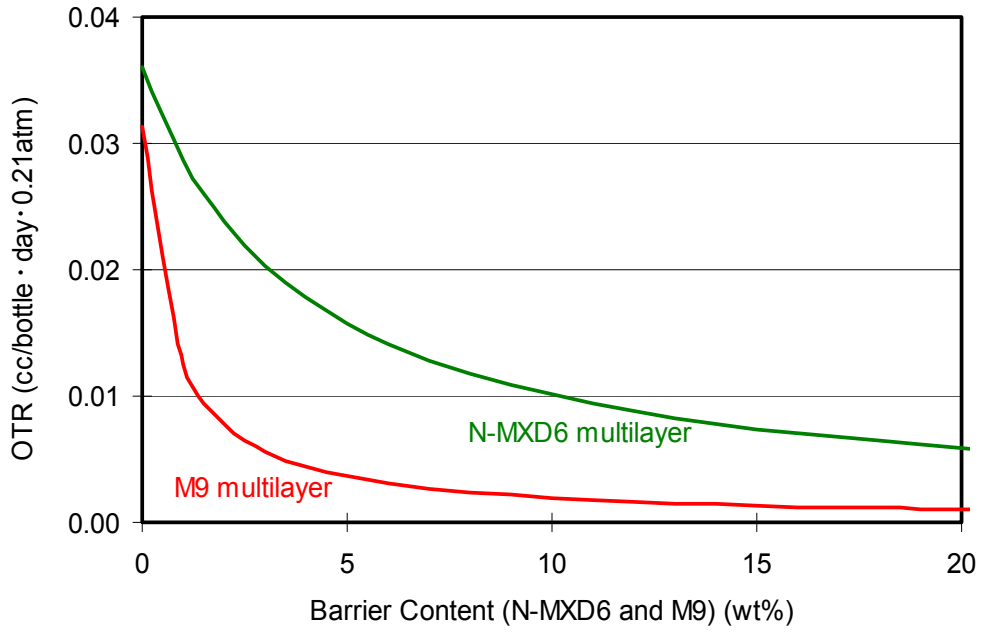


Figure 6. OTR of PET multilayer bottles

Bottle construction:	500 ml, 30 gram weight, 400 micron thickness
Testing conditions:	Air, 100% RH inside, 50% RH outside
Temperature:	23°C
Test method:	Mocon

Barrier performance carries through for bottles, as Figure 6 shows. An important feature of M9 is its ability to deliver high levels of static oxygen barrier at layer thicknesses around 3-5% wt/wt in line with recent advances in co-injection technology. PET bottles with a 5% layer thickness are suitable for beer. Figure 7 provides estimated oxygen ingress into different structured bottles. Table 2 compares multilayer performance with monolayer PET. The Barrier Improvement Factor (BIF) for M9 at 5% layer thickness is double that of N-MXD6 at 10% thickness, indicating that a thin M9 barrier layer will suffice for most PET bottle applications.

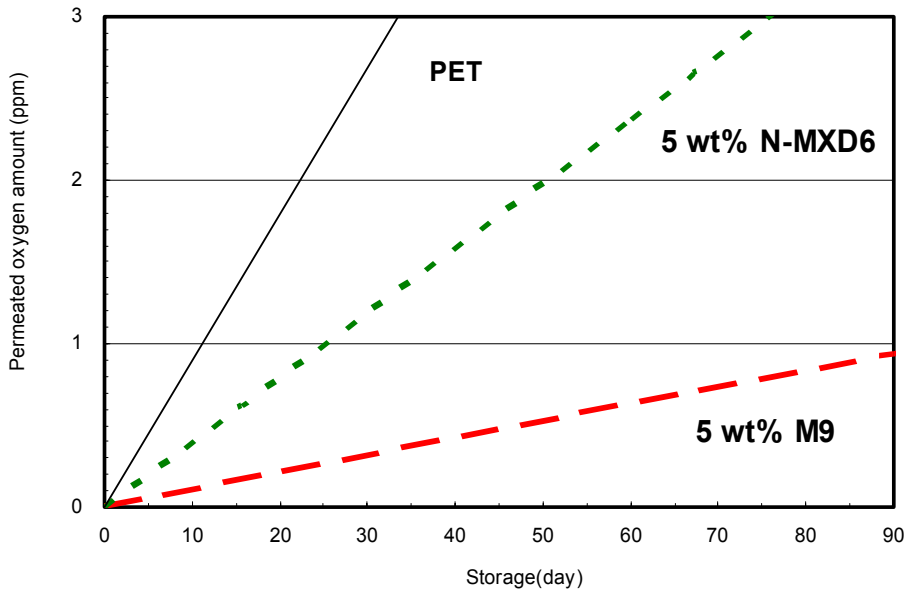


Figure 7. Oxygen ingress into multilayer PET bottles

Bottle construction:	500 ml, 30 gram weight, 400 micron thickness
Testing conditions:	Air, 100% RH inside, 50% RH outside
Temperature:	23°C
Test method:	Mocon

	cc/pkg.day	5% Barrier	BIF	10% Barrier	BIF
MONOLAYER					
PET	0.035		n/a		n/a
N-MXD6		0.016	2.2	0.01	3.5
M9		0.005	7.0	0.003	11.6

Table 2. Oxygen ingress for multilayer bottles of specific barrier layer thickness

M9 also delivers a higher level of carbon dioxide barrier. For bottles of 28 gram weight, a 5 % barrier layer of M9 extends shelflife from 14 weeks for standard N-MXD6 to 21 weeks, using 90% CO_2 retention as the cut-off.

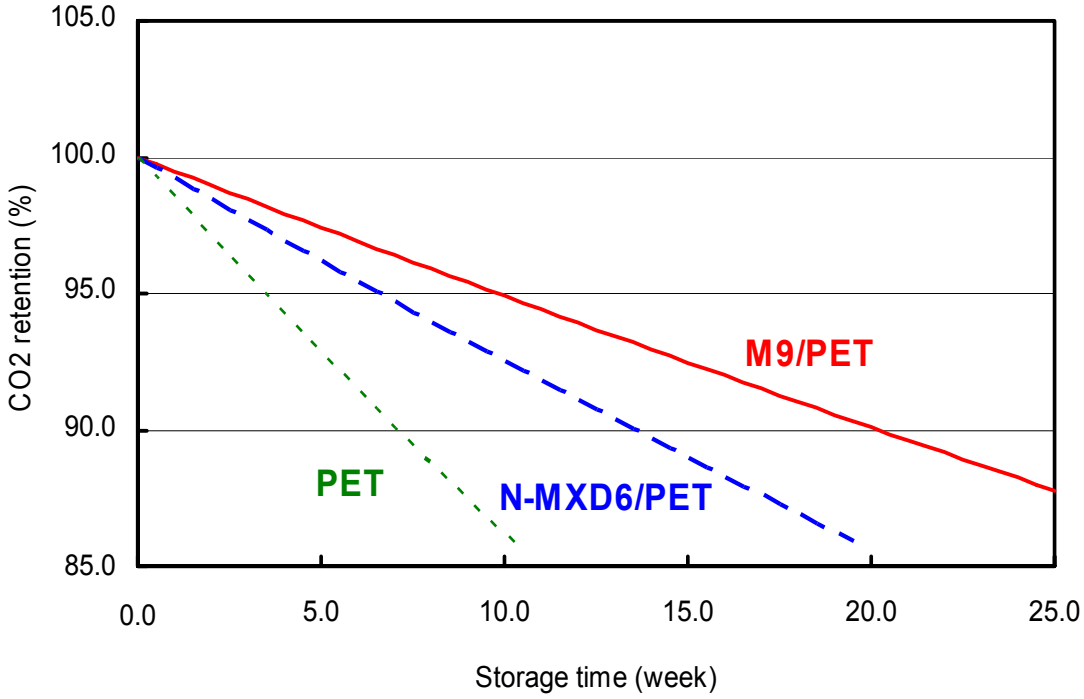
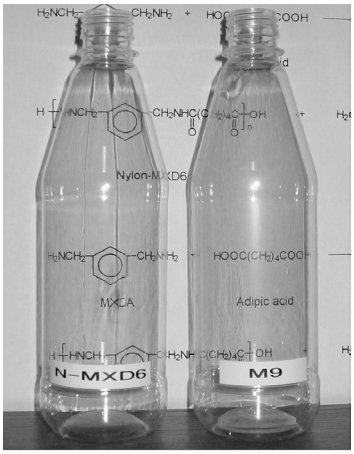


Figure 8. CO_2 retention of multilayer bottles

Bottle construction:	500 ml, 28 gram weight, 390 micron thickness
Barrier content:	5 wt%
Testing conditions:	100% RH inside, 50% RH outside
Temperature:	23°C

Bottle haze is 3-4 %, suitable for virtually all applications.



N-MXD6 M9

RECYCLABILITY

M9's superior gas barrier provides flexibility in designing bottles with a range of layer thickness to meet specific shelf life needs. Layer adhesion is virtually the same as standard N-MXD6, so it can be separated from PET by normal recycle methods. Because M9 is miscible with PET at layer thickness of 5% or lower, recyclers have the option of reprocessing thin-layer bottles in-total, eliminating the separation step.

REGULATORY STATUS

M9 is approved for PET bottles when used as a non-contact layer in conjunction with an inner PET contact layer of 2.0 mils thickness or greater. Keller and Heckman Opinion Letters have been obtained covering both FDA and EU jurisdictions.

SUMMARY

Nano-N-MXD6 grade M9 is a high gas barrier resin commercially available from Mitsubishi Gas Chemical Company. It delivers enhanced barrier to oxygen and carbon dioxide, while maintaining the processing advantages of N-MXD6. M9 is suitable for all PET bottles where shelf life and transparency are requirements.

M9 is a product of the Mitsubishi Gas Chemical/Nanocor strategic alliance. For more information visit our websites at www.mgc-a.com and www.nanocor.com.

REFERENCES

1. **"Beer in PET – A Global Baseline Review"**, Business Development Associates, Inc. Bethesda, MD, USA in cooperation with Packaging Strategies, West Chester, PA, USA, 2001 page 14.

2. **"Emerging Nanocomposite Technologies For Barrier and Thermal Improvements in PET Containers",** Nanocor, Inc., Arlington Heights, IL, USA, Nova Pak Americas 1999 Proceedings, pages 1-6.

3. **"Nylon-Nanocomposite Formulations For Improved Barrier PET Container Applications",** Eastman Chemical Company, Kingsport, TN, USA, Nova Pak Americas 2000 Proceedings, pages 243-260.

4. **"New High Barrier, Oxygen Scavenging Polyamides For PET Co-injection Stretch Blow Molded Bottle Applications",** Honeywell International, Inc. Morristown, NJ, USA, Nova Pak Europe 2001 Proceedings, pages 75-84.

5. **Journal of Polymer Science, Part A, 31 2493**, Yano, K., Usuki, A., Okada, A., Kurauchi, O., Kamigaito, O., 1993

6. **"Recycling of Coated and Multilayer PET Bottles",** Visy Plastics, Nova Pak Europe 2000, pages 317-340.