



## PEN Resin Preparation from NDC

### Melt-Phase Polymerization

Producing PEN from NDC is analogous to producing PET from dimethyl terephthalate (DMT). The reactivity of NDC in a PEN polymerization process is similar to that of DMT in a PET polymerization and similar catalyst and conditions can be used. Because of this, PEN preparation can be typically accomplished in existing DMT based polymerization facilities with only minor modification. This modification is generally limited to the NDC feed system and changes required to handle the physical property differences of NDC versus DMT and of PEN versus PET.

In any PEN polymerization process the proper use and handling of NDC must be insured. The NDC physical property and handling bulletin describes recommended addition methods and safe handling procedures and should be consulted. Comparative physical properties of DMT and NDC are summarized in Table 1.

**Table 1: Properties of NDC and DMT**

	NDC	DMT
Molecular Weight	244.26	194.19
Melting Point (°C)	190	140
Specific Gravity	1.35	1.28

The primary differences between PEN and PET polymers from a preparation point of view are the glass transition temperature ( $T_g$ ) and the melt viscosity. Table 2 summarizes the  $T_g$  and  $T_m$  of PET and PEN.

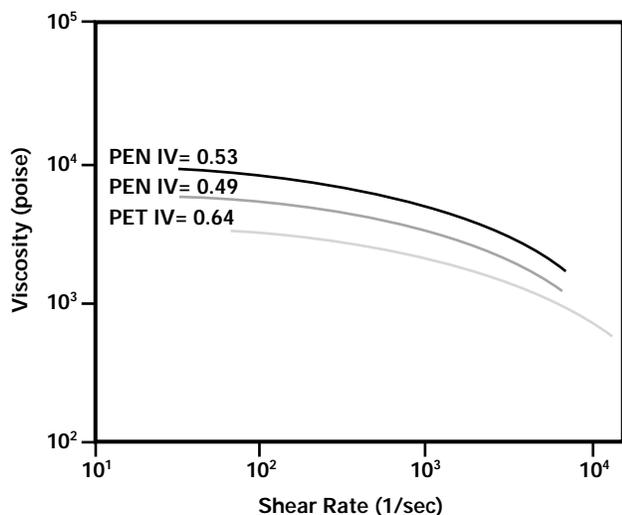
**Table 2:  $T_g$  and  $T_m$  of PET and PEN**

	$T_g$ (°C)	$T_m$ (°C)
PEN	125	268
PET	80	250

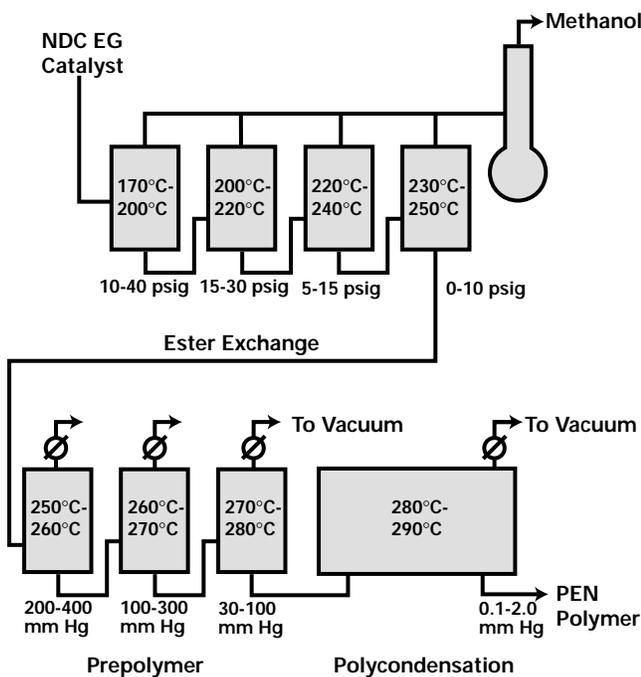
The melt rheology of PEN resin is significantly higher than PET even at lower IVs and/or higher temperatures. The rheology of PEN at inherent viscosity (IV) typically produced in a melt-phase polymerization (0.49-0.53) was measured at 295°C and compared to typical PET melt resin 1. As Figure 1 indicates both PEN IVs had higher viscosity than PET.



**Figure 1: PEN and PET @ 295°C  
Viscosity vs Shear Rate**



**Figure 2: Continuous PEN Polymerization**



PEN and copolyesters are readily prepared from NDC and ethylene glycol using either batch or continuous polymerization.<sup>1</sup> Solubility data for NDC in ethylene glycol is summarized in Table 3. An example of a typical continuous polymerization process is shown in Figure 2.

**Table 2: Solubility of NDC in EG**

Temperature	Solubility in g/100g EG
135°C	1.0
160°C	9.1
167°C	23.1
170°C	31.1
178°C	79.9

NDC, ethylene glycol (EG), and a suitable catalyst are metered into the first of a series of agitated back-mixed ester-exchange reactors. Normally, several ester exchange reactors provide control of the temperature profile and conversion to 2-hydroxyethyl terminated oligomers, while by-product methanol is removed and recovered. Glycol-to-ester feed mole ratios typically range from 1.5 to 3.0, while reactor temperatures range from 170°C in the initial reactor to 250°C in the final reactor. The initial reactor pressure can range from 10-40 psig, dropping to 0-10 psig in the final reactor.

The ester exchange reaction product, a mixture of oligomers, is subsequently metered into the first of a series of prepolymer reactors. Generally, several agitated reactors are used. Operating in a temperature range of 250 to 280°C, excess ethylene glycol is removed and the resulting prepolymer is metered into a final reactor to complete the polymerization. According to this process, PEN polymer is produced having an inherent viscosity (IV) of 0.4 to 0.6 dL/g. Examples of suitable final polymerization reactors include the horizontal types supplied by Zimmer AG (Germany) and Hitachi (Japan).

Catalysts, such as manganese, zinc, calcium, cobalt, and titanium, have been widely used as effective ester exchange catalysts. Polycondensation catalysts, such as those containing antimony, are commonly employed. Phosphorus compounds can be added to increase the thermal stability of the finished resin.

As in the case of PET, production of PEN polymer for

container or packaging applications will typically include a crystallization/solid-state polymerization step. Because PEN has a higher melt viscosity and gas barrier, the volatile byproducts of a solid stating process, such as water, ethylene glycol or acetaldehyde, are more easily trapped inside the amorphous pellet. This may result in a tendency of the pellets to undergo sudden expansion during crystallization or solid stating.

Several procedures have been recommended in the literature to crystallize/solid state PEN. These procedures include adding a devolatilization step,<sup>2</sup> or conducting the crystallization under elevated pressure,<sup>3</sup> or in the presence of a liquid.<sup>4</sup> Because of its higher  $T_g$  vs PET, the optimum crystallization temperature range for PEN (180–220°C) is higher than that of PET (150–190°C).<sup>2</sup> Similarly, because of its higher  $T_m$ , the typical SSP temperature of PEN (240–260°C) is higher than that of PET (210–240°C). On the other hand, PEN copolymers with 8–10 mole % PTA, which match the PET melting point, should be solid-stated at the same temperature conditions as PET. A typical solid-stated PEN resin has an IV in the range 0.55–0.70 dl/g.

## References

1. " Process for the Preparation of Polyalkylene Naphthalene dicarboxylate Polyesters" , Research Disclosure 29.487 (1988).
2. US Patent 4,963,644 to The Goodyear Tire & Rubber Company, 10/16/90.
3. US Patent 5,750,644 to Shell Oil Company, 5/12/98.
4. US Patent 5,744,578 to Shell Oil Company, 4/28/98.

## Health and Safety Information

The product described herein may require precautions in handling and use because of toxicity, flammability, or other considerations. The available product health safety information for NDC and NDA is contained in the Material Safety Data Sheet (MSDS) that may be obtained from your BP sales representative or by written request to the office address listed below. Before using any material a customer is advised to consult the MSDS for the product under consideration for use.

For additional information, on samples, pricing and availability, please contact:

### **BP**

Sales Administration and Customer Service  
150 West Warrenville Road, 605-CS 3  
Naperville, Illinois 60563-8460  
Toll-free: 877/701-2726  
Fax: 630/961-7700

### **BP**

Building A, Chertsey Road  
Sunbury-on-Thames  
Middlesex TW16 7LL  
United Kingdom  
Telephone: 44 (0) 1932 767627  
Fax: 44 (0) 1932 767914

### **BP**

Petro House 3rd Floor  
4-5-21 Kojimachi  
Chiyoda-ku, Tokyo, Japan 102-0083  
Telephone: 81 (0) 3 3238 7319  
Fax: 81 (0) 3 3238 7343

### **BP**

22nd Floor, Devon House  
Taikoo Place  
979 King's Road  
Quarry Bay  
Hong Kong, China  
Telephone: 852 2586 8899  
Fax: 852 2827 1609

### **BP**

Paseo de los Tamarindos 400  
Torre A Piso 17  
05120 Mexico, D.F.  
Telephone: 52 508 12100  
Fax: 52 508 12124

---

Technical information contained herein is furnished without charge or obligation, and is given and accepted at recipient's sole risk. Because conditions of use may vary and are beyond our control, BP makes no representation about, and is not responsible or liable for the accuracy or reliability of data, nor for toxicological effects or Industrial Hygiene requirements associated with particular uses of any product described herein. Nothing contained in this document shall be considered a recommendation for any use that may infringe patent rights, or an endorsement of any particular material, equipment, service, or other item not supplied by BP. "The Properties" and "Applications" listed in this document are not specifications. They are provided as information only and in no way modify, amend, enlarge, or create any specification or warranty, and ALL WARRANTIES, EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION THE WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, ARE EXCLUDED.

The letters bp and the Helios logo are trademarks of BP p.l.c.  
N-17, June, 2001

© 2001 BP p.l.c.