High Performance Films: Review of New Materials and Trends

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This paper reviews some modern aspects and trends in the development of high performance polymer materials and processing technologies providing fabrication of advanced film and film structures. Changes in understanding of technical requirements and properties, along with novel approaches in creating high performance films of various thermoplastic materials, are discussed. The most important groups of polymer materials being used in high performance applications are described.

INTRODUCTION

The meaning of the term "High Performance Polymer Materials" has changed during the last several years as a result of significant progress in polymer chemistry and the rapidly growing variety of polymer materials applications. The "classical" definition of high performance polymers and films as High Temperature Materials only has become too "narrow," and the researchers, producers, and users of the materials do not follow it anymore. The main reason is in a large number of new applications requiring high clarity, high or low heat conductivity, special surface properties, high purity, and other special performance properties not necessarily limited to the high temperature requirement. Moreover, in some new applications, properties other than temperature stability may become much more important for providing high performance.

The other "classical" approach in qualifying a polymer as a high performance material was based on business practicality, such as the price of the resin. According to this "logic," all polymers that are more expensive than a certain dollar amount, should, in reality, be considered high performance materials. Some experts even suggested using the price threshold of $10/lb to qualify a material as high performance. Without a doubt, this criterion is no longer realistic and practically has been abandoned. As an example, polyvinylbutyral (PVB) film is relatively inexpensive (much lower than $10/lb for the film; the resin is lower than $5/lb) and does not possess high temperature resistance capability. However, its bondability to glass and extremely high optical quality, i.e. super low haze and high light (luminous) transmittance, have made this thermoplastic material into one of the most successful polymers ever. PVB has dominated the field of high performance applications, such as interlayers for car windshields and architectural safety glazing, for nearly 70 years. In this case, the definition of high performance is based not on thermal but on optical and mechanical properties, along with low cost, enabling this polymer to be used in mass production of safety glass.

The modern industry demands ***advanced materials*** and products (including films and tapes) engineered to have special properties that guarantee performance in certain applications. There is a demand for advanced engineering polymers and plastics with various structures and properties tailored not only to meet high performance criteria, but also to "delight" customers by providing new and unexpected advantages.

An increased demand for flexible packaging and flexible printed circuit boards is driving significant growth in the high performance film markets (1). The unique properties and superior performance of polyesters, nylon, polycarbonates, fluoropolymers, liquid crystal polymers (LCP), and high temperature materials such as polyimides (Kapton by DuPont and Meldin by Saint-Gobain Performance Plastics) and other films will sustain demand from automotive, communications, and packaging industries (2). The world high performance film (HPF) market was estimated to be $7.3 billion in 1996. The revenues are projected to grow to $12.2 billion in 2003, with an average growth rate of 7%–8% during the forecast period (3). However, the higher cost and mature end-user markets for flexible materials could present challenges for vendors over the future period, and requires a creative approach in development of multilayer film structures combining different high-cost and low-cost polymers.

Nevertheless, practically all experts agree with the statement made by B. Mar in the June 2000 issue of *Paper, Film, and Foil Converter*, "It is definitely a bull market for high-performance films" (4).

In this paper, we review some of the modern trends in the development, processing, and applications of high performance thermoplastic materials based on various application requirements demanding high temperature resistance and other performance criteria.

Many polymer materials have abbreviations that are commonly used in the industry. These abbreviations, along with their chemical names, are listed in **Appendix A**.

ADVANCED HIGH PERFORMANCE FLUOROPOLYMER FILMS

New Modified Extrudable Fluoropolymers

The term "extrudable" or "melt-processable" fluoropolymers (FPs) is used to describe fluoropolymers, which can be processed as thermoplastic polymer melts because of relatively low viscosity, enabling the use of production units and lines based on screw extruders and injection molding machines. In contrast, "non-extrudable" (sometimes called "non-meltable") fluoropolymers are processed using the technology that was originally created for shaping metal and ceramic powders. These fluoropolymers (similar to ultrahigh molecular weight polyethylene, UHMWPE) can be molten; however, owing to the extremely high molecular weight (MW), the viscosity of their melts is so high that the use of conventional extrusion or injection molding techniques is impossible. These materials, in the form of fine powder, are precompressed, sintered at high temperatures (gelation point) into billets, and then skived into film and tapes or machined into parts according to the shape required by designers and application engineers.

New fluoropolymers with improved processability and performance, which were developed in the laboratories in late 1980s and early 1990s, are now making a real impact in the industry. These fluoropolymers are easier to process into film and other extruded items; they have better flexibility, surface smoothness, clarity, heat resistance, and purity essential for applications in the semiconductor industry. But scientists and engineers face two major problems when extruding fluoropolymers:

- Extremely high chemical aggressiveness, the property forcing processors to use very expensive equipment made of special steel alloys (Monel, Hastelloy, etc.).
- A very narrow processing "window," i.e., a small margin between the melting and degradation temperatures, which can be merely 10°F–20°F. Very precise temperature control and very skillful operators are mandatory.

In addition, two other difficulties have arisen lately, owing to the intention to increase productivity and to the eagerness to serve fast-growing and profitable high-technology markets, especially the semiconductor industry:

- A very low critical shear rate (typically from 1 s^{-1} to 25 s^{-1}), at which melt fracture starts to cause surface distortion and damages the film and the quality of the other parts. The processors are unable to utilize the possible equipment capacity because of the limited speed at which they can process fluoropolymers without fracturing the surface of the extrudate.
- Constantly increasing purity requirements for the polymer film and other products (tubing and injection molding parts) in terms of metal ion content released by transported liquids used in semiconductor fabrication ("fabs").

Attempts to offer solutions (or at least improvements) to the above problems, along with the intention to minimize "classical" fluoropolymer deficiencies, such as limited bondability to other materials and a high creep (deformation under load, or "cold-flow"), are driving the chemistry development by the resin suppliers.

Typical melt-degradation temperature fields are shown in *Fig. 1* for most important fluoropolymers. The processing window for PCTFE and ECTFE is very narrow, while a wider window between melting and degradation temperatures exists for THV-200 and THV-500 (typical fluoro-tercopolymers produced by Dyneon) than for other melt-processable fluoropolymers (5).

Improvements of fluoropolymers for extrudable high performance film are aimed at the reduction of thermal stress cracking, higher transparency, reduced creep and permeability, improved weldability, higher resistance to certain chemicals, and improved processability.

In terms of processability, the main problems besides the above-mentioned high melting and relatively low degradation temperatures and very low critical shear stress and shear rate (typically one or several s^{-1}) are several problems typical for extrudable fluoropolymer in terms of general rheological phenomena, requiring a lot of experience and engineering skills for proper handling. A very long Newtonian region on the flow curves of fluoropolymers of different nature, in a wide range of MW values (or melt flow rates), leads to a relatively high viscosity of the melt, and shear thinning occurs at high shear stress only when the melt fracture is already heavily pronounced, forcing the slow-down of the extrusion process. *Figure 2* shows the flow curves for FEP of different grades and different MW at the same temperature of 320°C. The prolonged Newtonian regions are exhibited for all samples. The extrusion of film is performed at shear rates corresponding to the end of the Newtonian region or in the very beginning of the area of the viscosity anomaly. Attempts to extrude fluoropolymers at shear stress higher than the melt fracture region (in "Region IV" on flow curves, i.e., beyond the melt fracture shear rate) have had limited success, mainly for tubing.

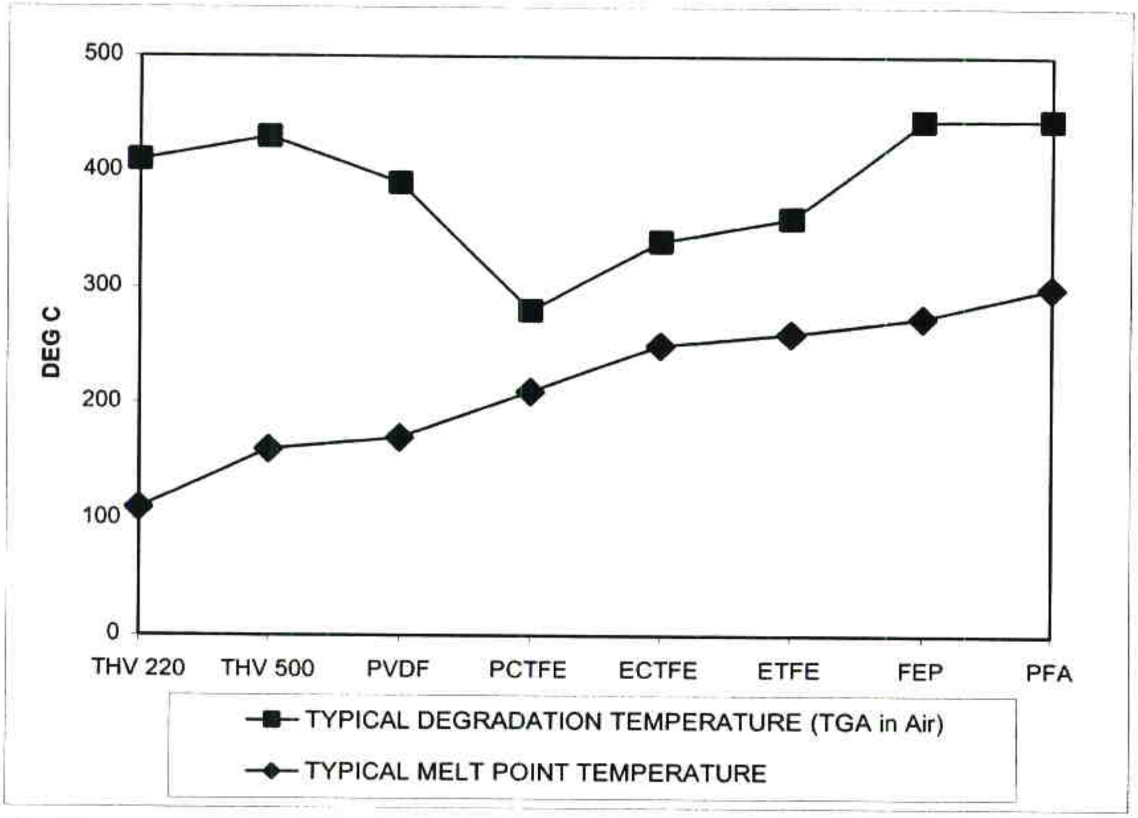


Fig. 1. Typical melting temperatures (lower curve) and degradation temperatures (upper curve) for the most important melt-processable fluoropolymers (5). The field between the two curves represents the processing "window."

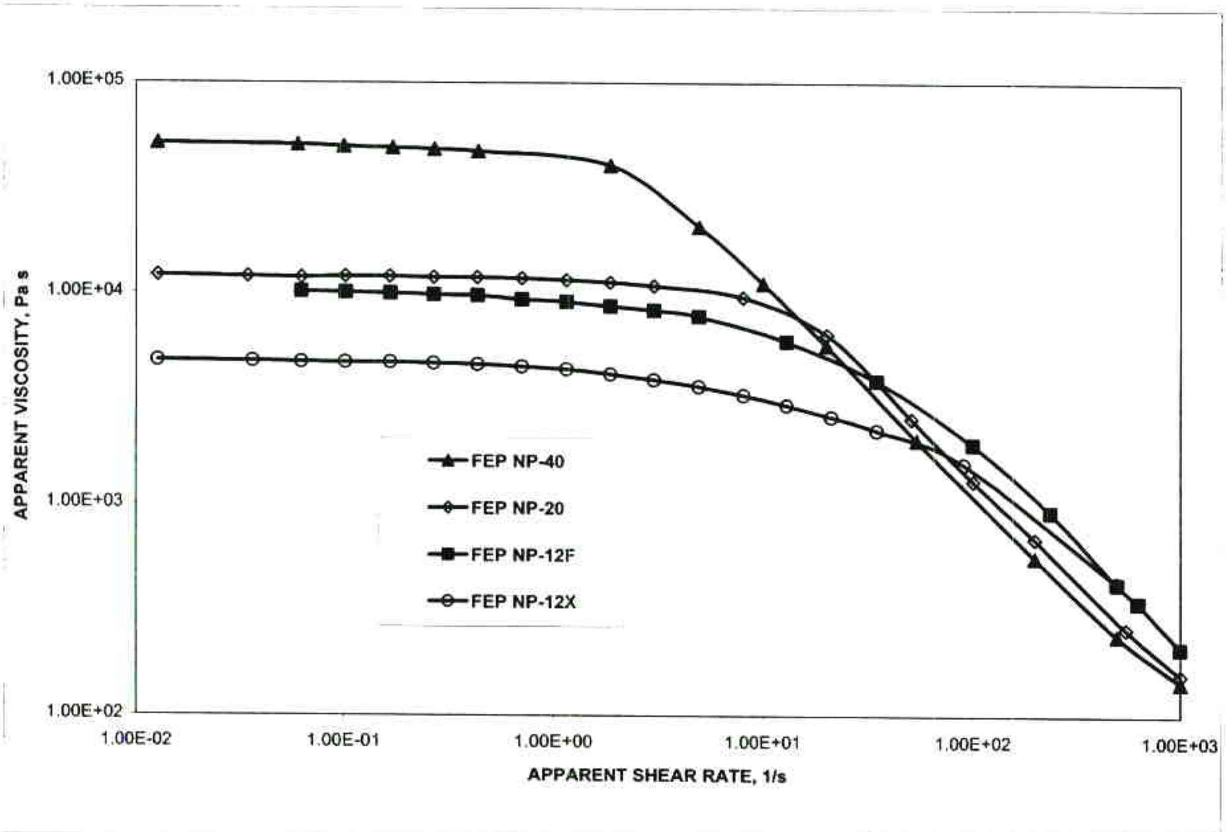


Fig. 2. Melt flow curves for FEP of different grades measured at 320°C.

It is interesting that at high shear rates, the melt viscosities of FEP grades of different MW become very close (practically coinciding), so at the real speed of industrial film extrusion processes, different grades of FEP can be processed at the same (or very close) temperatures in the metering (pumping) section of a single-screw extruder. However, the temperature adjustment should be made for FEP of a very high MW (for grades with melt flow rate (MFR) of 2 g/10 min and lower), a higher temperature is necessary to avoid a significant increase in the extruder's backpressure.

Another bothersome rheological characteristic of typical extrudable fluoropolymer is a very pronounced "stick-slip" phenomenon typical for fluoropolymer melts in general. It leads to the occurrence of another limit to the output and productivity: The increase in the rotation speed of the screw does not translate into the extruder output and can negatively affect quality of the film. Owing to an increase of the residence time for some melt portions, the polymer may be overheated, causing degradation and occurrence of "black specks" of carbonized material in the film.

The modern extrudable film grades of fluoropolymers are produced using different fluoromonomers, as described in many publications (see, for example, (6–8)). They are also summarized in *Table 1*. The chemical structures of the most common comonomers, perfluoropropylvinylether (PPVE), perfluorobutylethylene (PFBE), and perfluorohexylethylene (PFHE), used in quantities less than 5 mol% to modify polymers of tetrafluoroethylene (ETFE), are shown in *Table 1*, along with other alternating ethylene copolymers, such as HFIB, PPVE, and FMB introduced in FEP, PFA, ETFE, ECTFE copolymers and in a relatively new MFA terpolymer. The effect of comonomers on reducing the melting point (T_m) of polymers with an increase of comonomer concentration is shown in *Fig. 3* for three different comonomers. Primary effects of comonomers on the primary monomer is given in *Table 2* for different modifiers. For example, the terpolymer MFA has properties between the "classical" FEP and PFA polymers; it is somewhat closer to the tougher PFA, as one can conclude from the comparative data presented in *Table 3*.

One of the advantages of MFA film and tubing is a much better surface smoothness in comparison to FEP and PFA. This was directly measured in a series of experiments conducted by Saint-Gobain Performance Plastics using a laser profilometer.

New, chemically modified ETFE grades have been introduced during the past several years in an attempt to improve its processability, mixability (compatibilization) with other polymers, and adhesion to different substrates.

New Generation of "Nonmeltable" Fluoropolymers (PTFE)

Major producers of non-melt-extrudable ("non-melt-fabricable") polytetrafluoroethylene (PTFE) are moving forward using the same "chemical" approach. Several versions of modified PTFE-based resins are currently commercially available. All producers claim success in the recent development of a new generation of PTFE, including modified Teflon NXT by DuPont (USA), Hostaflon TFM by Hoechst (Germany), and Polyflon TFE by Daikin (Japan). For example, modern grades of TFM resin are based on PTFE modified with a small amount (approximately 0.1%) of perfluoropropylvinylether (PPVE) during polymerization. This comonomer (as well as hexafluoropropylene, HFP) can increase the amorphous phase without reduction of the MW. Such modification may also be tailored to lead to a significant reduction of the MW (up to 80%) and to branching of the molecules, which, in turn, reduces crystallinity.

New PTFE resins provide wider opportunities for designing and engineering high performance products that deliver new capabilities while retaining the exceptional chemical and thermal resistance, antistick (release) properties, low friction, good wear and abrasion resistance, negligible moisture absorption, weather resistance, toughness, and flexibility of conventional PTFE resins. The main improvements, that the new, advanced resins provide are as follows:

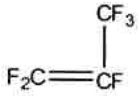
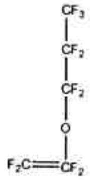
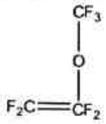
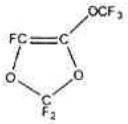
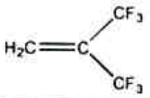
- Improved weldability due to lower melt viscosity
- A much higher creep resistance (lower deformation under load) and higher stiffness
- Reduced chemical permeability
- Better surface smoothness
- Higher clarity of thin film
- Better high voltage insulation (higher dielectric breakdown voltage).

All the improvements are attributed to lower viscosity (however, not low enough to enable direct extrusion) and a higher density ("denser polymer structure").

Film and tapes made from the modified PTFE grades by molding, sintering, and skiving billets have, in comparison to products from regular PTFE, better particle "adhesion" while sintered. Films and tapes of exceptional quality can be made from TFM and other modified PTFE resins filled with various fillers, especially with 25% carbon black.

It is important to emphasize that modified PTFE resins, for example DuPont's Teflon NXT, allow forming of very large billets with virtually no voids or distortion. This helps increase the yield, i.e., to skive the billets efficiently with little scrap loss. In addition, skived film and sheets with a low microvoid content decrease transmigration of aggressive liquids and gases, which translates into reduced chemical permeability. A smooth surface for molded parts and much longer flexlife make these polymers valuable for many different applications. Some typical rapidly growing applications of film, sheets, and molded parts are: piping system components (diaphragms, bellows, gaskets, seals), containers, vessel and pipe linings for pure liquids, chemical bags, laminates for printed circuits, etc. Glass fabric backing can be securely embedded in the film and sheets to help attach linings to

Table 1. TFE & ETFE Based Copolymers and Effects of Copolymerization on PTFE Properties.

Basic Monomer	Comonomer	Resulting Copolymer	Crystalline Modification	Copolymer Properties
TFE (Tetrafluoroethylene) $CF_2 = CF_2$	HFP (Hexafluoropropylene) 5–15 mol.% 	FEP	Intra molecular conformation & packing altered (helix inversion, planar zigzag sequences). CF_3 group enters & distorts crystal lattice. Crystalline melting point (T_m) reduced. Melt processable.	T_m reduced from 327°C to 260°C. MW & melt viscosity reduced. Temperature rating reduced from 260°C to 204°C. Most physical properties retained. Poor creep vs. other melt processable FP.
TFE (Tetrafluoroethylene) $CF_2 = CF_2$	PPVE (Perfluoropropylvinylether) ≥ 1 mol.% 	PFA	Helix inversion & planar zigzag sequences. Perfluoroalkoxy group location: excluded from crystal lattice; enters chain folds or amorphous region. Crystalline melting point (T_m) reduced; more effective than HFP in FEP. Melt processable.	T_m reduced from 327°C to 305°C. MW & melt viscosity reduced. Temperature rating practically equal to PTFE (260°C). Most physical properties similar to PTFE.
TFE (Tetrafluoroethylene) $CF_2 = CF_2$	PMVE (Perfluoromethylvinylether)  PPVE or PFMD (Perfluoromethoxydioxide) 	MFA	Similar to FEP & PFA. (see 1 & 2) Extrudable.	T_m reduced from 327°C to 285°C (between FEP & PFA). MW & melt viscosity reduced. Temperature rating reduced from 260°C to 235°C (between FEP & PFA). Most physical properties between FEP & PFA and similar to PTFE. Higher light transmittance (twice more UV-light transparent vs. PFA). High surface smoothness.
TFE (Tetrafluoroethylene) $CF_2 = CF_2$	PDD (Perfluoro-2,2-dimethyl-1,3-dioxole) > 10 mol%	AF (Amorphous fluoropolymer)	Completely amorphous. Melt processable.	High light transparency. Soluble in fluorocarbons for various coatings.
TFE (Tetrafluoroethylene) $CF_2 = CF_2$	PPVE or PFMD ≤ 1 mol%		Compared to suspension PTFE: 1. Not melt processable 2. Reduced creep 3. Reduced permeability 4. Higher elastic modulus 5. Improved weldability 6. Higher light transparency	Creep reduced from >10% to 6–6.2%. Elastic modulus increased from 80–90 GPSI to 100-110 GPSI. Dielectric strength increased from 85 kV/mm to 95–100 kV/mm.
ETFE (Ethylene-tetrafluoroethylene) $(CH_2CH_2)_n(CF_2CF_2)_m$	PPVE, PFBE (Perfluorobutylether) $CF_3-(CF_2)_3-CF = CH_2$ PFHE (Perfluorohexylether) < 5 mol% $CF_3-(CF_2)_5-CF = CH_2$	Modified ETFE	Less organized crystalline domains. Reduced density of amorphous regions. Thinner lamellae. Enhanced mobility of crystallites.	Improved thermal stress cracking properties.
ECTFE (Ethylene-chlorotrifluoroethylene)	PPVE PFMD HFIB (Hexafluoroisolbutylene) < 5 mol% 	Modified ETFE	Similar to ETFE modification.	Improved thermal stress cracking in the range from 135°C to 175°C.

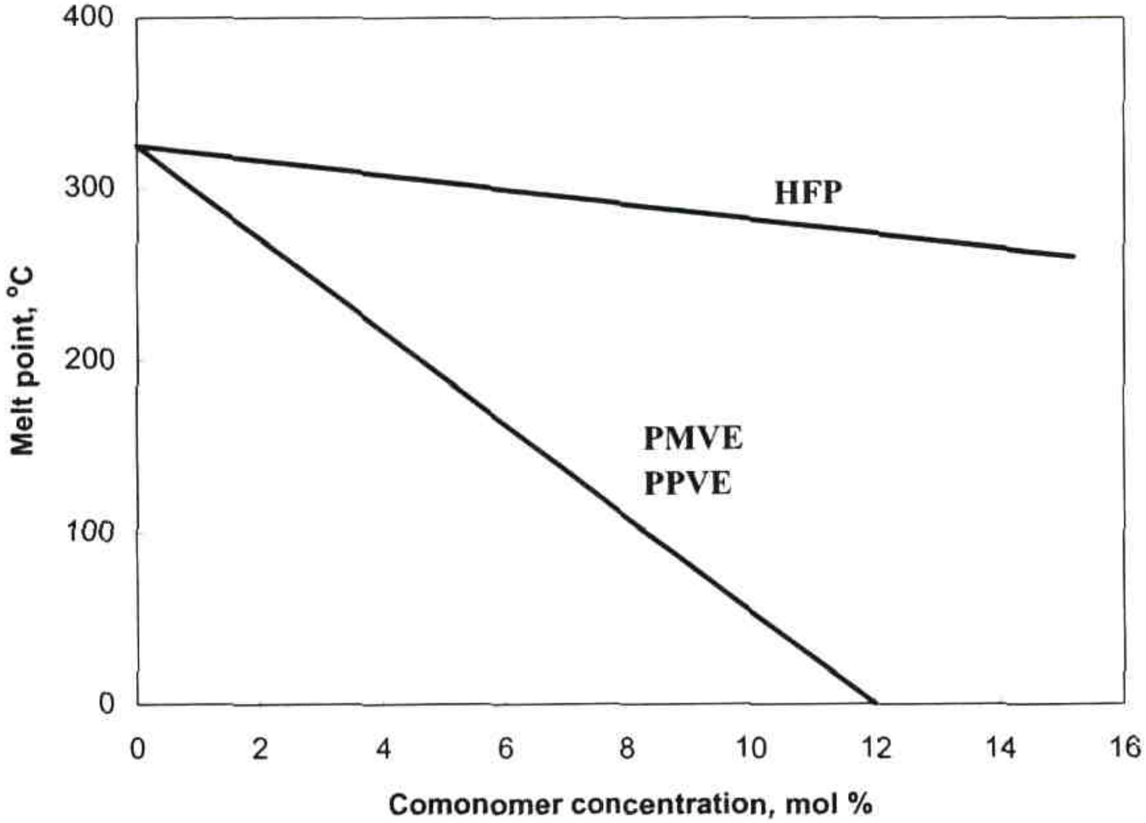


Fig. 3. Effect of three different comonomers concentration on the melting point of fluorocopolymers.

various substrates made of metal, concrete, and other construction materials.

Data on physical and mechanical properties presented in *Table 4*, creep resistance at various temperatures (*Fig. 4*), and results of flex fatigue evaluation using MIT's standard test (*Fig. 5*) illustrate some of the important properties and superiority of modified PTFE compared to conventional PTFE. The data show that new, advanced PTFE-type polymers are exhibiting advantageous mechanical properties, especially at elevated temperatures, and, in many cases, come very close to a tougher PFA.

One very important advantage of the film and molded parts made of the new generation of PTFE resins is high purity. It means not only minimized contamination content, but extraction of a lower amount of metal ions and other impurities to the levels decisive for applications in the semiconductor industry, as shown in *Fig. 6*.

Modification of PTFE for creep reduction can also be achieved by its blending with other, mainly extrudable ("melt-fabricable") fluoropolymers. Mixtures of PTFE with up to 20 wt% of PFA have much less sagging in the sintering cycle and lower cold flow in the final film product.

Table 2. Other Modified Polymers.

Primary Monomer	Modifier	Primary Effect(s)
Vinylidene Fluoride (VDF)	HFP	Flexibility, Impact Strength
	CTFE	Flexibility, Impact Strength
	TrFE	Piezoelectric, Ferroelectric
	TFE	Solubility, Flexibility
	HFA	Optical Clarity
	Ethylene	Base Resistance
Chlorotrifluoroethylene (CTFE)	VDF	Solubility, Processibility

Surface Modification of Fluoropolymer Films for Improved Bondability

Chemical inertness, surface smoothness, resistance to oxidation, all the distinctive advantages of fluoropolymers, become at the same time a real "nightmare" in applications requiring bonding and combinations of fluoropolymers with substrates of a different nature. Most fluoropolymers in the molten state are perfectly adherable to many polymers, metals, and other materials, but do not adhere to substrates of any nature in the solid state, even at elevated temperatures. Strong and economically justified adhesives, which would be applicable and reliable at low and room temperatures, have not yet been identified and introduced on a commercial basis. Modern science and engineering have turned their attention to research and design approaches, which may enable bypassing the direct adhesion problem. The main two developed routes

Table 3. Physical Property Data for MFA 620 Film.

Property	Test Method	MFA 620	PFA	FEP	ECTFE
Tensile Strength at Break*	ASTM D-882				(1 mil film)
MD		5500 psi	5500 psi	3600 psi	10,000 psi
TD		4900 psi	5400 psi	3400 psi	8000 psi
Elongation at Break*	ASTM D-882				(1 mil film)
MD		500%	450%	400%	190%
TD		500%	480%	400%	300%
Specific Gravity	ASTM D-792	2.12–2.17	2.12–2.17	2.13–2.17	1.68
Melting Point	ASTM D-4591	536–554°F	575–590°F	500–536°F	464°F
Thermal Exp. Coefficiency 73 – 300°F	ASTM D-696	$6.6–11.1 \times 10^{-5}$ in/in/F	$4.2–5.4 \times 10^{-5}$ in/in/F	5.2×10^{-5} in/in/F	$4.4–7.5 \times 10^{-5}$ in/in/F
Thermal Conductivity			0.109 BTU/(hr ft F)	0.109 BTU/(hr ft F)	0.092 BTU/(hr ft F)
Specific Heat			0.2799 BTU/lb F	0.2799 BTU/lb F	
Oxygen Index	ASTM D-2863	> 95%	> 95%	> 95%	60%
Flammability	UL94	V-O	V-O	V-O	V-O
Haze*	ASTM D-1003	0.83%	4.54%	0.89%	4.18%
Water Absorption	ASTM D-570	< 0.03%	< 0.03%	< 0.01%	< 0.1%
Volume Resistivity	ASTM D-257	$> 1 \times 10^{17}$ Ω·cm	$> 1 \times 10^{18}$ Ω·cm	$> 1 \times 10^{18}$ Ω·cm	1×10^{15} Ω·cm
Surface Resistivity	ASTM D-257	$> 1 \times 10^{17}$ Ω/sq	$> 1 \times 10^{18}$ Ω/sq	$> 1 \times 10^{18}$ Ω/sq	
Arc Resistance	ASTM D-495	210 sec		> 300 sec	130 sec
Dielectric Strength*	ASTM D-149	3600 V/mil	5000 V/mil	4500 V/mil	6200 V/mil (1 mil film)
Dielectric Constant 23C	ASTM D-150				
at 50 Hz		2.0	2.05	2.052	2.6
at 100 kHz		1.95	2.05	2.052	2.5
Dissipation Factor	ASTM D-150				
at 50 Hz		0.0002	0.0002	0.0002	< 0.0009
at 100 kHz		0.0002	0.0002	0.0002	0.003

*Results obtained on 2-mil-thick samples.

Table 4. Tensile Properties Versus Temperature for Different Grades of PTFE.

Test Temperature Degrees Celsius	TFM N/mm²	TFM (%)	Traditional PTFE N/mm²	Traditional PTFE (%)
−30	54	330	51	140
0	38	460	43	220
23	32	650	30	520
100	20	600	16	570
150	15	500	12	530
200	12	500	9	510
230	9	605	0	N/A

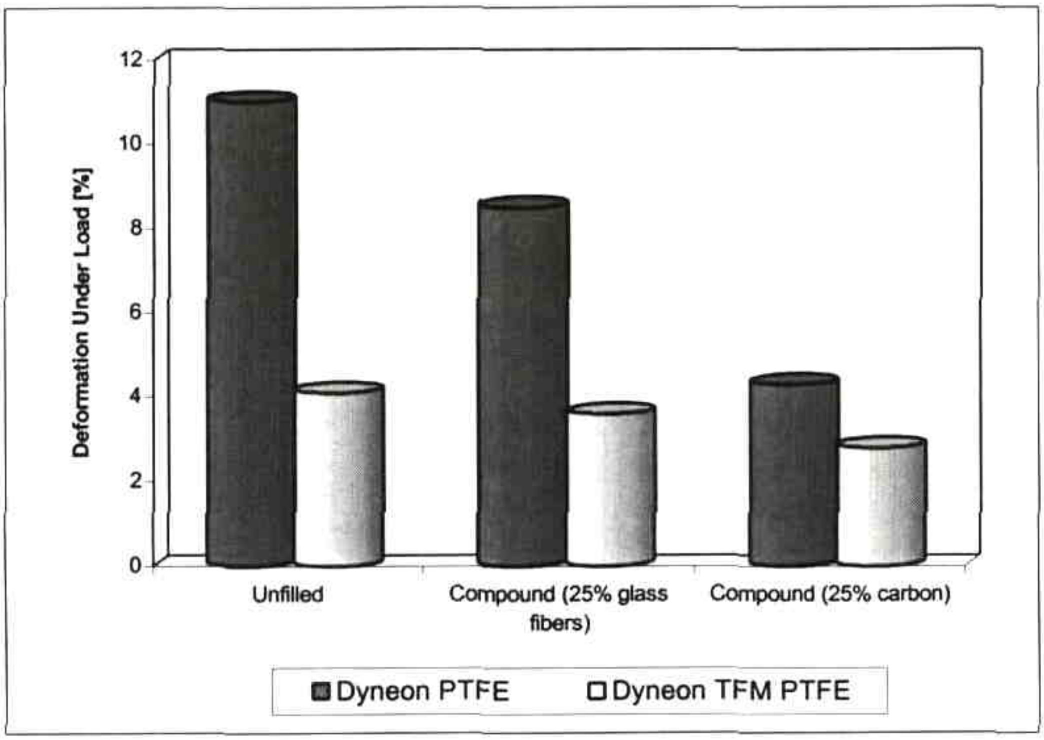
ASTM 1708 die cut from 0.2 mm skived film

are: a) modification of fluoropolymer surfaces to make them adherable to certain substrates, and b) incorporation of a transition layer (tie layer) bondable at the same time to both fluoropolymer and substrate surfaces.

Both basic technologies have been successfully implemented in the industry and are of great interest to scientists and application engineers. These technologies are based on surface treatment for adhesion improvement by changing the surface topography, increasing the surface energy, removal of boundary layers, creating electrical charges and chemically active sites. The modern treatments are helping to realize one or more of the following adhesion mechanisms, respectively: mechanical interlocking, interdiffusion, adsorption, electrostatic attraction, and chemical bonding.

Corona discharge and flame treatment processes as methods of surface modification are currently the dominant techniques used for treating the surfaces of most common thermoplastic films and other substrates, such as foils, paper, etc. This treatment increases the surface energy of substrates, which, in turn, improves wettability, printability, and adhesion (bondability) of the surfaces.

Fluoropolymer surfaces are very inert, and it is quite challenging to treat fluoropolymer films to enhance their surface energy using a dry process. It is



Test Conditions

Loading: 15N/mm^2

Time: 100 Hours

Temp: 23°C

Permanent deformation after 100 hours

under load & 24 hours without load.

Fig. 4. Deformation under load of modified tetrafluoroethylene Hostaflon TFM grades in comparison to regular PTFE at 23°C. Data from Hoechst/Dyneon published product literature.

recognized in scientific and patent literature that modification of fluoropolymer surfaces for improved bondability can be achieved by chemical treatment (etching and/or special grafting reactions), and physical treatment based on the influence of high energy phenomena, such as electrical-electronic (E-beam) and plasma effects. Plasma treatment of polymer materials is well described in books and reviews (9–12). An interesting low-pressure (atmospheric) plasma treatment technology has been recently developed and successfully tested for OPP, PE, PET, and PTFE (13). However, we would like to emphasize that it is difficult (if possible at all) to differentiate chemical and physical treatments due to chemical reactions accompanying any treatment considered to be strictly physical. In fact, only the chemical changes in the material surface are causing changes in reactivity, surface tension, improvement in wettability and adhesion ("cementability"), and capability of bonding to substrates. A number of experimental studies (14–16) have shown that, in fact, the only difference that can be used to identify the fluoropolymer treatment as chemical or physical is the depth of the treatment effectiveness: chemical treatment (for example, chemical etching) provides changes in the surface layer, several micrometers in depth, while known physical treatments such as "C"-treatment and plasma treatment can change the materials in a much more shallow depth measured in nanometers. One of the most effective and popular techniques in industry is the use of thermally activated bonding film to join fluoropolymers and metals and other various substrates to create desired

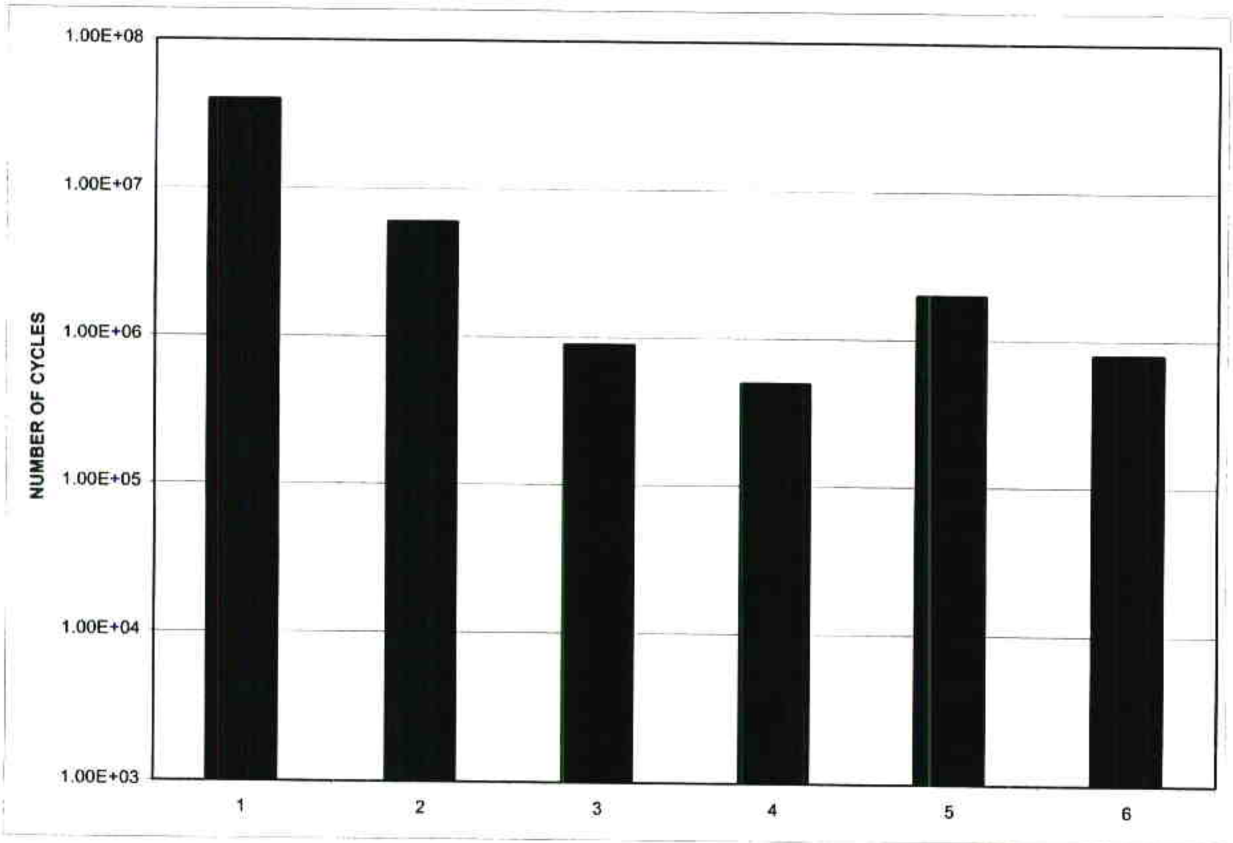


Fig. 5. Flex endurance (number of cycles until the specimen breaks according to ASTM Standard, Test Method D-2178) for film samples 0.5 mm (20 mil) thick (1, 2, 3, & 4) made of unfilled PTFE (1 & 2) and PTFE filled with 10% carbon fibers (3 & 4); and for film samples 0.3 mm (12 mil) thick made of PTFE filled with 10% glass fibers. PTFE of two different grades by Daikin Industries—M-112 (samples 1, 3, & 5) and M-12 (2, 4, & 6).

sandwich-structures (14). However, one has to keep in mind that the tie-layer technology has its limitations. Bonding films for fluoropolymers (for example, PTFE) can be thermoplastics with convenient melting points, such as FEP with T_m 280°C or commercially available chloro-fluoro-copolymer with T_m 200°C, etc. (13–15). The reliability of the bond formed with adhesive film dissimilar to the given fluoropolymer (especially PTFE) is subject to many variables. In all cases, there are two main concerns regarding direct bonding of fluoropolymers with tie layers and substrates. The first is to exclude air during the bond cycle to prevent oxygen degradation of fluoropolymers at exposed edges or oxidation of metal substrates. The second is to handle the differences in thermal expansion of the components (layers), especially in the Z-direction, which is working against the bond and promotes delaminating of the "sandwich."

One of the most successful technologies was developed and widely patented many years ago (17–21). This is based on corona discharge treatment of the film surface. Corona treatment is known as a very efficient method of achieving bondability and improving surface receptivity to various materials for many polymers, and it is widely used for polyolefins and other thermoplastics. For fluoropolymers, the corona treatment of "high enough" energy leads to an increase of wettability and "cementability" as well, but the treatment effect disappears fairly quickly. A film made of a fluoropolymer after corona treatment loses the bonding characteristics in a period from minutes to hours, even if the film has been kept for the entire time in a black bag protected from UV-light, humidity, and elevated temperatures. It was discovered that corona treatment process in an atmosphere of different organic gases provides a much more durable treatment phenomenon: the wettability and cementability of fluoropolymer film treated at high voltage in acetone, methanol, and many other gases last for many months and even years (**"C"-*treatment and "C"-film***, where "C" stands for *Cementable*). The main patents related to corona treatment ("C"-treatment) of various fluoropolymers, suggested organic gases, and applications of treated films are briefly reviewed in *Table 5*. *Figure 7* summarizes some typical data illustrating the efficiency and longevity of special corona treatment of FEP. Experiments confirm that the peel force (i.e. cementability measured according to ASTM's standard procedure for FEP "C"-film treated by corona in two different gases at optimal concentration and discharges) is very stable for many months (data has been presented for a two-year shelf-life period), and,

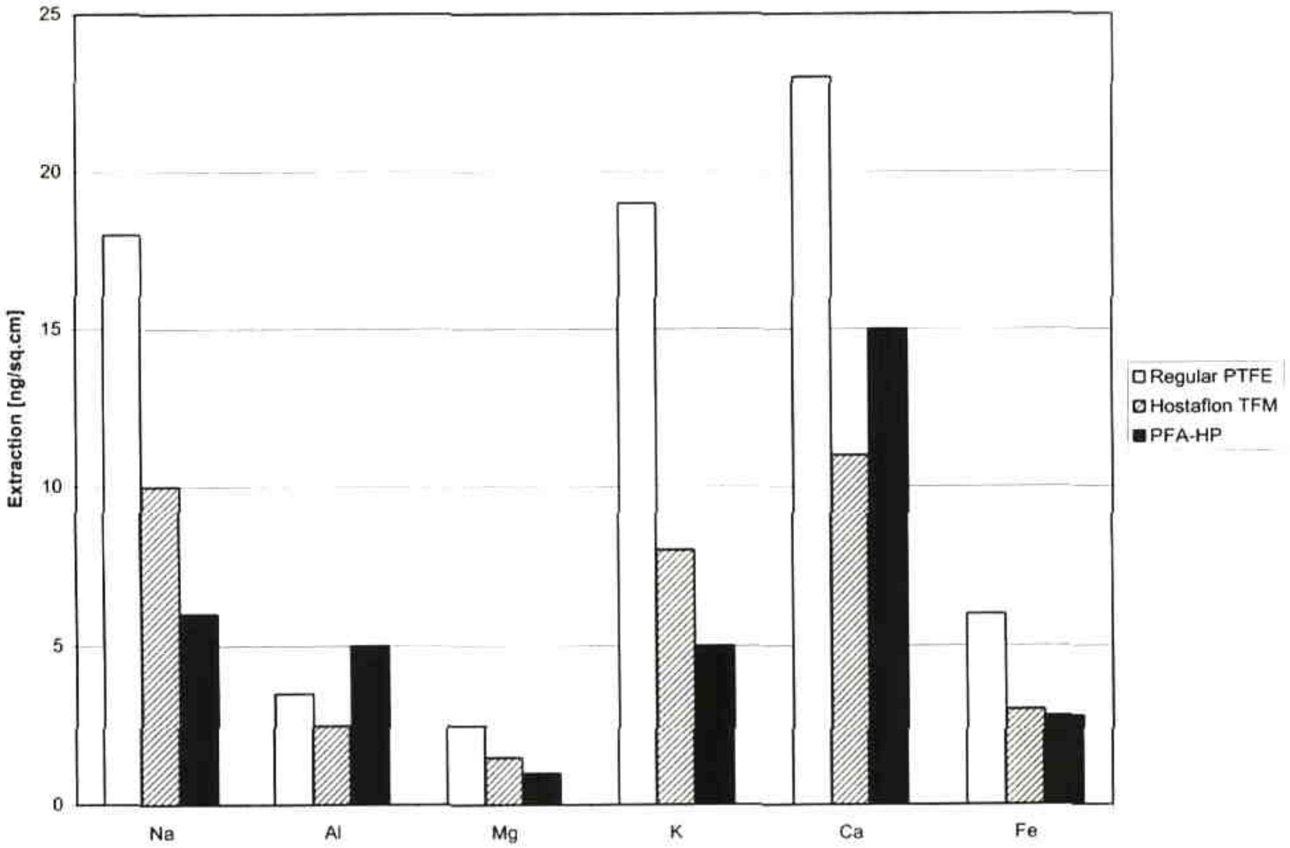


Fig. 6. Hoechst/Dyneon results of various metal ions extraction for Hostaflon in comparison to regular PTFE and high-purity (HP) PFA. Extraction has been performed using 2% HNO_3 for two days at 20°C (68°F).

in all cases, the cementability parameters are much higher than those required by industry standards.

The nature of the surface modification, which takes place during chemical etching by a solution of sodium and naphthalene (Na/Naphth) in tetrahydrofuran (THF), discovered in the 1950s, as well as with other alkali metal mixtures in THF or liquid ammonia, has been under investigation for many years. It is recognized that the surface energy increases after sodium etching based on a similar mechanism for all fluoropolymers, due to defluorination, the main product being unsaturated hydrocarbon and oxygenated species.

To our knowledge, corona discharges of fluoropolymers in an organic gas atmosphere, which eventually leads to a dramatic improvement of surface wettability and bondability, have not been investigated in detail and are much less described for fluoropolymers in scientific literature. However, it is worth mentioning that the surface of a cementable film ("C"-film) is definitely enriched with oxygen and defluorinated to a substantial degree as is typical for chemically etched material. This conclusion can be undoubtedly made from the data in *Table 6*. High energy treatment in the atmosphere of inorganic gases, such as silane SiH_4 introduced by Air Liquide S.A. and Softal Electronic GmbH as the "Aldyne" process (22), showed effectiveness for PP and other polyolefins; however, there is no data on the efficiency of this technology for fluoropolymers.

Chemical methods of modification and surface etching of various fluoropolymers were discussed in a large number of publications. A comprehensive review and investigation into this problem for PTFE, FEP, PFA, and PCTFE, including chemistry, surface topography, depth of etch, and depth profile for functional groups, can be found in many publications from the University of Connecticut and others (23–25). The etching using wet-chemical treatment with solvents and strong acids or bases, or the sodium/liquid ammonia for fluoropolymers is always carried out under pressure and eventually may become increasingly unacceptable because of environmental and safety considerations.

Chemical modification of fluoropolymer film surfaces is becoming more sophisticated because of grafting technology using various monomers and comonomers. The technology mostly used is based on radiation-induced grafting. For example, successfully developed radiation-induced grafting of styrene onto PTFE and properties of the grafted films have been described recently by Nasef and co-authors (26). Films grafted using gamma-radiation from a cobalt source at room temperature are used for ion-exchange

Table 5. Main Patents on Corona Treatment of Fluoropolymers.

Patent #	Gases & Chemicals	Application
3,030,290	Hydrogen or anhydrous ammonia at abs. pressure of 0.2 mm Hg	
3,255,099	Inorganic agent having affinity for electrons (not for FEP)	
3,274,089	N_2 + glycidyl methacrylate (0.5% vol.); or N_2 +: toluene-2, 4-diisocyanate; Vinyl Acetate; 2-vinyl pyrrolidone; acrylonitrile; p-chlorostyrene; hexane; xylene; carbon tetrachloride; styrene sulfonic acid; tetra isopropyl titanate	Liners for pipes & vessels for corrosive chemicals
3,274,089	For PTFE film: N_2 + dimethyl formamide, triethyl phosphite, vinyl ethyl ether, acetone, N-aminopropylmorpholine, acrylic acid	Non-fogging films
3,274,091	For PTFE, PVC, PE, PP, & FEP films: N_2 + acrylic acid or diethyl maleate	Non-fogging films
3,275,540	N_2 + glycidyl methacrylate and/or (diethylene triamine or ammonia or ethylene diamine) or various combinations of Organic/amine: Methylmethacrylate/Triethylene tetramine; Carbon tetrachloride/triethylamine; Methylvinylketone/Tetraethylenepentamine; Tetrahydrofuran/Tertiary butyl amine; Vinyl acetate/Decyl amine; Zylene/Methylisopropylamine; Vinyl butyl ether/Propylene diamine; Acrylonitrile/Ethylene diamine	Liners for pipes & vessels for corrosive chemicals
3,291,712	N_2 + polyamine: diethylene triamine or etylene diamine or triethylene tetramine (0.7% vol.). Also: Cycloheryl amine; Tetraethylene pentamine; Decylamine; Tetriary butyl amine; Methylisopropyl amine; Propylene diamine; Triethylamine	Liners for pipes & vessels for corrosive chemicals
3,296,011	N_2 + (0.5% glyc.methacr. Or acrylonitrile or p-Chlorostyrene or Toluene-2, 4-diisocyanate or Vinyl acetate or Xylene or Hexane or Carbon tetrachloride or Tetraisopropyltitanate	Liners for pipes & vessels for corrosive chemicals
3,397,132	N_2 + (glycidyl methacrylate or acrylonitrile or CCl_3F 3%): for metals and metallized films	Condensers
3,485,734	Air (for polyimide containing fluoropolymer)	Bearings
3,507,763	N_2 + glycidyl methacrylate	
3,676,181	N_2 + acetone (20% vol.); Acrylonitrile, hexane, methyl alcohol, methyl methacrylate, xylene	Printed electrical circuits
4,549,921	N_2 + acetone for lamination using adhesive	Printed circuits, flat electrical cable, corrosion protection, anti-stick surfacing

membranes for various applications. Radiation-grafted acrylic acid onto PFA copolymer films has been also studied (27). Evaluation of rhodium led to a suggestion to use the graft copolymer in the field of rare metal waste treatment. Tough-to-bond polymers like fluoropolymers and UHMW PE are offered with primers. As an example, PTFE and other fluoropolymers, and UHMW PE films treated to be bondable to elastomers have been introduced (27). The films can be supplied with primers that further bond for various septa and pharmaceutical applications. However, these primers are considered to be trade secrets and are not described in the technical literature.

Fluoropolymer Film Surface Modification for Other Effects

There are many fluoropolymer film applications requiring special properties besides improved wettability and bondability. An important example is ***surface topography*** of film. In many applications the gloss of the film has to be reduced and a matte finish or geometrical patterns have to be introduced. Many techniques have been developed to achieve a certain surface structure. The "classical" method of reducing gloss is based on applying (pressing) to the solidifying film web a matte finished roll installed as one of the rolls of the roll-stack of the film take-off unit. The gloss of the final film in this case depends on roughness of the roll finish, temperature of the embossed film surface, speed of the film web, and pressure applied to the roll. Gloss reduction can be achieved by introducing special additives and mineral fillers. A combination of chemicals and physical treatment can be very efficient for melt-extruded fluoropolymer film; one example would be film made of PVDF and its copolymers and blends. In the case of solvent-cast film technology filler(s) with submicronized particle size are introduced into the solvent, and the achievement of a very uniform matted surface does not cause serious difficulties. Additives and fillers can provide a very smooth and satin-finished surface of PVF and other fluoropolymer films. It is important to take into consideration that any additives and fillers should be chosen

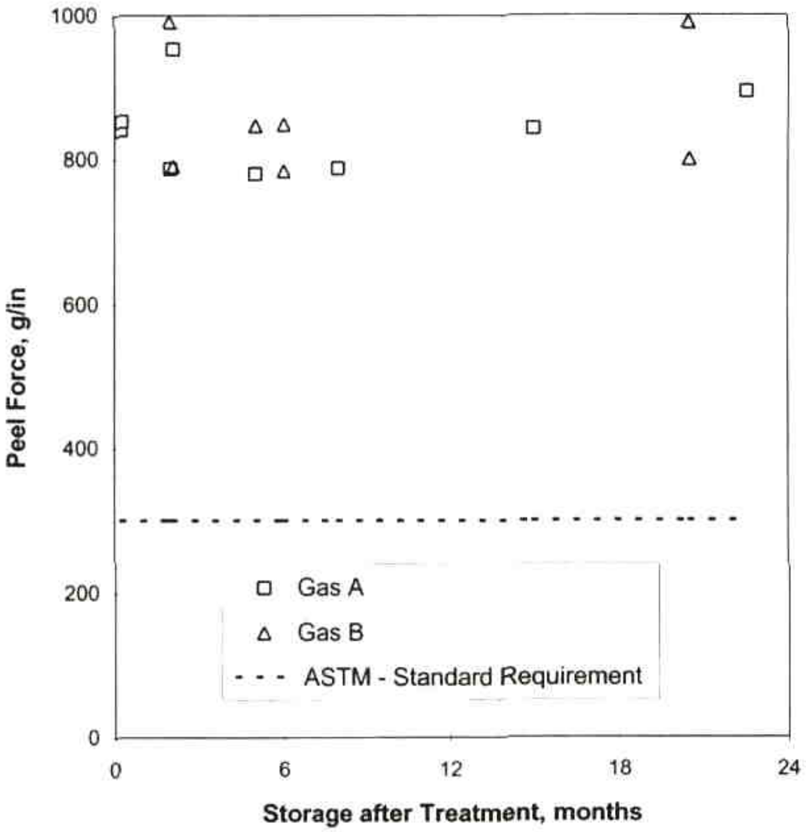


Fig. 7. Cementability (standard peel force) of 25 micron (1 mil) FEP film after corona treatment in two different organic gases versus storage time. Dotted line represents ASTM's standard requirement.

and incorporated into the polymer very carefully because of their ability to influence mechanical, electrical, and other properties of film, and also because they can initiate degradation of the matrix resin. Gloss-reduction additives, which are very well known for low-temperature thermoplastic films and parts made of materials such as PMMA and various acrylic copolymers, have not yet been identified for fluoropolymers. It is very hard to believe that effective chemicals for gloss reduction will be available for fluoropolymers in the near future, owing to very high processing temperatures and chemical aggressiveness of fluoropolymers, which cause decomposition of such additives.

A very interesting technology for forming fluoropolymer films with controlled gloss has been disclosed in a patent (28). A controlled-gloss fluoropolymer film is fabricated by casting a fluoropolymer dispersion onto a substrate, which has been coated with a solution containing a substantially inert particulate material, following by curing, drying, and stripping a fluoropolymer film that has a controlled-gloss or matte finish from the support substrate. The gloss of the matte fluoropolymer film is dependent upon and controlled by the amount of particulate material in the coating solution.

Water-soluble or water-dispersible crosslinkable polymeric surfactants having fluorocarbon and ionic components have been described (29). Such surfactants can be cured into tough, solvent-resistant coatings with low critical surface tension that are useful for protective finishes on fluoropolymer films.

Table 6. Surface Atomic Concentration for FEP Film Samples. (Data Obtained by X-Ray Photoelectron Spectroscopy)

	Chemical Elements, %					
Sample	**C**	**F**	**O**	**N**	**Cl**	**Si**
DuPont "C"-film Non-cementable side	32	68	0.35	—	—	—
Saint-Gobain Performance Plastics Untreated side	30	70	—	—	—	—
DuPont "C"-film Cementable side	62	18	15	3	2	—
Saint-Gobain Performance Plastics Treated side	59	21	12	3.4	—	5

A special and fast-growing area of surface modification is anti-glare (AG) film for liquid crystal displays (LCDs). Usually, AG films are multilayer film structures affixed to the LCDs to reduce the glare from external light. They are produced by laminating a transparent base material film and a hard transparent AG resin layer with an uneven surface (30). Production of fluorine-based AG films is rapidly growing. These films contain a fluorine-based film that acts as an anti-reflection layer. In comparison to glass, which reflects ~10% of external light, the AG film-coated glass reflects less than 1% of incidental light. Applications of AG films include wall-mounted TV sets, digital TV sets utilizing plasma-address liquid crystal (PALC) displays, and others.

Some other special applications of fluoropolymer film with a textured surface, such as adhesive thin film applique for replacement of paint on aircraft, have also been described (31).

Metallization of film (*deposition of very thin metal layers on the surface*) is usually used to improve barrier properties (lower gas and water vapor permeability), reduce water absorption, and improve optical properties such as light reflection along with aesthetics. Metallization of advanced film based on fluoropolymers is a difficult process because of the surface inertness of most of them, especially PTFE. Many studies on metallization of PTFE have been carried out (32–35); however, owing to the surface inertness, adhesion between PTFE and various metals deposited on the polymer surface generally fails to reach the level required by industrial applications. As in the case of fluoropolymer bondability, the surface treatment and modification, e.g. activation of the fluoropolymer film surfaces prior to metallization, have been shown to enhance metal adhesion. The most widely used method of activating the PTFE surface is a treatment with a reducing etchant, such as sodium naphthalenide and potassium sulfoxide (35). Apart from the wet chemical treatment, ion bombardment (e-beam treatment), X-ray irradiation, and cold plasma treatment have also been applied to the surface of PTFE for activation and improvement of metallization quality (review (35–36)). Shi and colleagues reported (37) improvement in adhesion between evaporated CU and ETFE modified with N_2, O_2, H_2, and mixed-gas plasmas. Effectiveness of graft copolymerization with specific functional monomers for metallization improvement has been studied by a group of researchers (38, 39). Good adhesion of fluoropolymers to copper has been achieved by silanization of fluoropolymer film surfaces. The details of the chemistry and technology have been described in several publications (40–42). Studies have been carried out for various fluoropolymers (including PTFE) by silanization of their surfaces through chemisorbtion of some of the aminopropyltrimethoxysilanes in a plasma environment. A comprehensive comparative analysis of different methods of pre-activation of the PTFE surface for electroless deposition of copper, including plasma treatment, graft copolymerization, and silanization has been presented in recent publications (35–41).

In concluding this section, it is worth mentioning that surface fluorination of the performance film surface by cold plasma treatment was developed and successfully implemented in the industry quite a while ago. The main direction was the creation of inexpensive film with enhanced barrier properties, along with various fluorinated barrier coatings. Results of the investigation of barrier properties of fluorinated polyolefins, as well as fluoropolymers such as PVF and PVDF, have been discussed in detail in a number of articles and reviews. For example, the article by Corbin, Cohen, and Baddour (42) discusses elemental and plasma-enhanced reactions, conditions affecting surface fluorination, efficiency of solvent resistance, and solvent permeation in plasma-fluorinated polymers. An efficient modification of fluoropolymer films can be achieved with various coatings. One interesting development in this area has been disclosed in a patent (43). Fluoropolymer films, which combine the attributes of outdoor durability, chemical resistance, and thermoformability with paint-like aesthetics, have a surface coated with a primer of amine-functional polymer and an overcoat of a thermoplastic adhesive of acid-modified polyolefin.

Orientation of Fluoropolymer Films

Orientation (*stretching of the polymer in the visco-elastic state below its melting temperature*) is a recognized method of improvement of mechanical, dielectric, optical, and permeability properties of many thermoplastic films; it was investigated and described in a large number of articles, books, and patents. There is no debate regarding the property improvements and usefulness of orientation for thermoplastic film such as PP, OPP, PET, PS, PE, their blends and alloys in terms of improvement of film clarity, dielectric, barrier, and other properties. These films are widely used, mainly in electrical and electronic industries and packaging. Expansion of fluoropolymer tubing is also recognized as a very efficient method for making shrinkable articles; some examples are tubes and sleeves. Examples include designed housing for roller blinds (44–47), roller covers for electro-photographic copying machines (toner image-transferring devices), and ink-jet printers (48, 49). For instance, expanded FEP tubular films are used as a high-temperature, wear-resistant release roller protector, which is capable of preventing the sticking of ink and other substances in ink-jet printers and other units using solid or foamed rollers. Such fuser back-up rollers can be covered with a multilayer coextruded fluoropolymer film/tube combining an outer layer with high wear resistance, smoothness and anti-static properties, and an interlayer used to provide a bond with a metal shaft and as a "shape holder" during fabrication of the tubular intermediate product.

The situation with flat fluoropolymer films is more complicated. There have been many arguments for pro- and contra- orientation of fluoropolymer films. Supporters for stretching of fluoropolymer films see additional advantages of fluoropolymer orientation in further improvement of properties essential for particular applications. However, design and construction of tenter-frame machines for fluoropolymer orientation needs heavy capital investment for the following reasons. First of all, toughness of fluoropolymers below melting/crystallization temperature requires a very high force for stretching and heavy-duty equipment. Second, the very high orientation temperature and chemical aggressiveness of fluoropolymers at elevated temperatures dictate the use of very expensive steel alloys, sophisticated design, and assembly technology. For example, the very high operation temperature of the gripping units ("clips") of the tenter-frames and complicated design of the mechanism outside the oven of the transverse-orientation machine require unique engineering and high investment. That is why, as of today, the number of industrial scale lines producing oriented fluoropolymer films is very limited. One of the leaders in the field of manufacturing sequentially operating film orientation lines capable of stretching extrudable fluoropolymers such as FEP and ETFE is Brückner Maschinenbau (Siegsdorf, Germany). One of the most interesting developments in the technology of oriented film is simultaneous stretching with the use of linear motors or LISIM technology. It was developed by Brückner in 1994–1998 and is described in many presentations (50–54). This technology was also reviewed by Breil (55). The LISIM technology has been scaled up for the production of BOPP and BOPET for up to 350 meters per minute (approximately 1150 feet per minute). However, the application of this technology for fluoropolymer film has not been described in literature.

The stretchability of fluoropolymers is limited; the commercialized units are capable of extending fluoropolymer films in the range from 30% to 250% only (56). However, there is always a valid question: "Is it worth it?" Are the advantages of oriented fluoropolymers so significant in comparison to the standard extruded fluoropolymer film that the expenses are justified? Answers to these questions are periodically revised, and, in some new applications, orientation of fluoropolymers is considered, nowadays, to have a high potential.

Research and development in orientation of fluoropolymers is moving in two main directions (for example, patents by Levy (57, 58)).

- Equipment: perfection of the existing longitudinal stretching roller units and transverse stretching tenter-frames, suggestion of novel designs of gripping mechanisms in an attempt to make all equipment less costly, more reliable, and requiring lower maintenance expenses.
- Development of special technologies capable of improving the process of stretching of fluoropolymers, providing a higher orientation ratio, and optimizing the ratio of stretching and shrinkage of produced film in longitudinal (machine) and perpendicular (transverse) directions.

Tsai and co-authors have disclosed a method of producing biaxially oriented multilayer fluoropolymer films with high orientation ratio (59, 60). It was proposed to produce films by coextruding or colaminating multilayer films having at least one layer of a fluoropolymer, one layer of a thermoplastic homopolymer or copolymer, and an intermediate adhesive layer. With this structure, the thermoplastic layer allows the fluoropolymer layer to be biaxially stretched many times its original length (from 1.5 up to 10 times). A high orientation ratio for the fluoropolymer film increases the mechanical strength, toughness, and water vapor barrier properties of the film while using a thinner-gauge fluoropolymer film. In addition, coextrusion can be done at higher temperatures in comparison to single-layer film processing (i.e., in the range from 280°C to about 400°C), allowing film to be produced in absence of polymer degradation and melt fracture.

Advanced High-Purity Fluoropolymer Film

The "classical" meaning of and requirements for resin and film purity have changed dramatically because of the rapid increase of usage of polymer materials in the semiconductor industry. "Purity" is no longer only the absence (or at least minimization) of a number of mechanical (mineral) particulates and other contamination of a nonpolymeric nature, which the application can tolerate. The traditional purity requirements are also becoming tougher every year, along with demand for gel-free film, and elimination of enclosures of carbon ("black specs") and brown spots indicating the possible degradation of the polymer material, which may occur during its processing into film or tape and reduce its performance.

The modern film industry serving semiconductor manufacturing is concerned primarily with purity in terms of *metal ion content (MIC)* and the possible "leakage" of metal ions from film, tubing, pumps, valves, and other parts used in the fabrication of semiconductors ("fabs"). This relatively new "MIC-purity" requirement has triggered serious scientific and engineering activities in various directions: changes in polymerization technology including modified catalytic systems, reactors redesign and reengineering, investigation into types of metal ions being released from different polymer materials when they are contacted by water and a number of other chemically active liquids, development of standard procedures of ion content and leakage measurements, etc. The importance of the "advanced polymer purity" is growing consistently, along with the reduction of the acceptable threshold of metal ion content in polymers for semiconductor applications.

Fluoropolymers are considered to be the most pure polymer materials from the point of view of MIC and unwanted chemical products generated during the degradation/destruction of the polymer while exposed to the aggressive chemical liquids used in the industry.

That is why the investigation into purity and its improvements were mainly directed towards fluoropolymers. Practically all major producers of fluoropolymers have developed and launched production of special, high-purity grades of FEP, PFA, MFA, and other fluoropolymers, extruded film, sheets, and other extruded and molded products. Complete fluid-handling systems, including manifold distribution units and pumps, have been developed using fluoropolymers. All parts of these special plastic units are made exclusively of fluoropolymers and assembled in "clean rooms." It is critical for the semiconductor industry to avoid chemical contamination of the highly pure fluids, which are handled by fluoropolymer components.

The fluoropolymer purity is being measured as the quantity in PPM of certain metal ions being released by the material or film specimen during long-term extraction by submerging the specimen in HCl or hot water, or its rinsing with clean and deionized water. The procedures are described in the industry standards, for example Semi Draft Doc. 3038 entitled "Method for Determining Trace Metals in Polymer Materials" (8/6/99). According to this document "... determining the metallic contamination concentration in bulk polymer materials used in either distribution systems for processing fluids or products in direct contact with the wafer is important criterion for deciding the suitability of a material." Data from different tests can be compared to determine the inorganic content in different materials and in the materials produced by different manufacturers. As a rule, the ion chromatography is applied after the specimen has been submerged in hot deionized water at temperature of 80°C for 24 hours or in HCl.

In *Table 7*, results are presented of our "MIC-purity" measurements conducted for FEP and PFA, the most *popular fluoropolymers in semiconductor applications.*

Table 7a. FEP Resin Analysis—Extractable Metal Ions.

		Average Bulk		
Elements	**Grade 1**	**Grade 2**	**Grade 3**	**ppm**
Al	0.0258	0.07	0.086	0.061
Ba	0	0	0	0.000
Ca	0.021	0.018	0.042	0.027
Co	0.0012	0.009	0.012	0.007
Cr	0.0012	0.0012	0.0012	0.001
Cu	0.0036	0.0036	0.0036	0.004
Fe	0.0024	0.0024	0.0024	0.002
K	0.0849	0.0849	0.0849	0.085
Mg	0.001	0.001	0.008	0.003
Mn	0.0006	0	0.001	0.001
Mo	0.0126	0.038	0.035	0.029
Na	0.0099	0.002	0.0099	0.007
Ni	0.0042	0.0042	0.0042	0.004
Sr	0	0.0001	0.001	0.000
Ti	0.0021	0.0021	0.0021	0.002
Zn	0.0003	0.0003	0.0003	0.000
Zr	0.0003	0.0003	0.0003	0.000
Pb	0.0345	0.0345	0.0345	0.035
Sn	0.0057	0.0057	0.0057	0.006

*All numbers are average ppm values measured for pellets ("bulk").

The statistics for nineteen metal ions have been measured for polymer samples from different major vendors. As one can see, the MIC varies for different metal ions in a relatively wide range (keep in mind that some metals are more harmful than others for the semiconductor liquid systems). Another conclusion is high-purity grades of the same fluoropolymer from different vendors may have a significant difference in certain MIC, and the application engineers may have to choose the resin based on the lowest content of the most harmful metal ions for their particular semiconductor fabrication ("fab"). Unfortunately, data described in many technical data sheets and brochures by the vendors are contradictory in terms of qualified comparison of different fluoropolymers. The superiority of MFA and special grades of PFA over other fluoropolymers is recognized; however, the "battle" between these two polymers for the championship in metal ion purity is still ongoing.

HIGH PERFORMANCE (ADVANCED ENGINEERING) FILMS FOR ELECTRICAL AND ELECTRONIC APPLICATIONS

Properties and Applications

This group of films can be characterized in general as film made of polymer materials with high melting temperatures, high toughness, and superb dielectric properties. It is anticipated that these materials are filling the "use temperature space" between polyimides (Kapton-type film) having the highest thermal capabilities and the medium temperature engineering films made of such polymers as polyamides (nylons), polycarbonate, ABS, polypropylene oxide, polymethyl pentene (PMP), and polyesters (PET, PBT, PEN), which are not a subject of this review. This group comprises *a large number of aromatic polycondensation, linear*, semicrystalline thermoplastic polymers such as polyketones, including polyetheretherketone (PEEK), polyetherketoneketone (PEKK), polyaryleneether (PAE) polyaryletherketone (PAEK), polyamidimid (PAI), polyalcanimid (PACI), polyetherimide (PEI), polyethersulfide (PES or PESd), polyphenylene sulfide (PPSd), polysulfone (PPSf), polyethersulfone (PESF or PESf), polyphenylene sulfone (PPS), etc. Thermosetting polyphenyleneether is distinguished by a glass transition temperature (T_g) as high as that of polyimides, a low dielectric constant close to that of fluorine resins, small water absorption, and good adhesion to metals (for example, to copper foil). It appears to be a promising material for printed circuit boards for multichip modules, which are the new generation high-density wiring boards. Probably one of the most known representatives of this group of high performance products is film made of poly (aryl-ether-ether-ketone), more commonly known in the plastics industry as polyetheretherketone (abbreviated as PEEK). This tough, thermally stable aromatic polymer with very attractive properties as an advanced high quality engineering thermoplastic is produced under the trade name

Table 7b. PFA resin Analysis—Extractable Metal Ions.

Elements	Grade 1	Grade 2	Grade 3	Grade 4	Grade 5	Grade 6	Grade 7	Grade 8	Grade 9	Grade 10	Grade 11	Grade 12	ppm
Al	0.017	0.0258	0.023	0.0258	0.355	0.12	0.474	0.432	0.368	2.430	0.570	0.700	1.847
Ba	0.0003	0.01	0.001	0.004	0	0.001	0.005	0.003	0.001	0.001	0.001	0.001	0.009
Ca	0.131	0.009	0.107	0.086	0.148	0.24	0.252	0.065	0.044	0.030	0.250	0.450	0.604
Co	0.0012	0.041	0.0012	0.112	0.0012	0.123	0.027	0.03	0.0012	0.001	0.007	0.007	0.118
Cr	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.002	0.002	0.002	0.006
Cu	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.059	0.0036	0.0036	0.030	0.010	0.010	0.046
Fe	0.0024	0.0024	0.0024	0.053	0.0024	0.21	0.0024	0.0024	0.0024	0.005	0.001	0.001	0.096
K	0.0849	0.0849	0.0849	0.0849	0.0849	0.0849	0.0849	0.0849	0.0849	0.070	0.180	0.170	0.395
Mg	0.003	0.002	0.004	0.008	0.005	0.026	0.007	0.001	0.002	0.020	0.001	0.090	0.056
Mn	0.001	0.009	0.0006	0.0006	0.0006	0.0006	0.001	0.015	0.004	0.020	0.001	0.001	0.018
Mo	0.0126	0.0126	0.063	0.0126	0.0126	0.0126	0.097	0.0126	0.0126	0.008	0.430	0.570	0.419
Na	0.0099	0.026	0.0099	0.0099	0.0099	1.292	0.0099	0.106	0.0099	3.180	0.640	0.610	1.971
Ni	0.0042	0.0042	0.0042	0.0042	0.0042	3.45	0.0042	0.079	0.0042	0.160	0.004	0.004	1.242
Sr	0.002	0.0001	0.001	0.004	0.002	0.01	0.006	0.0001	0.001	0.001	0.001	0.001	0.010
Ti	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.001	0.009	0.009	0.013
Zn	0.0003	0.0003	0.0003	0.004	0.0003	0.018	0.24	0.0003	0.0003	0.002	0.004	0.004	0.091
Zr	0.0003	0.035	0.0003	0.0003	0.0003	0.0003	0.025	0.0003	0.0003	0.005	0.005	0.005	0.026
Pb	0.0345	0.0345	0.0345	0.0345	0.0345	0.0345	0.0345	0.0345	0.0345	0.010	0.040	0.010	0.124
Sn	0.0057	0.0057	0.0057	0.0057	0.0057	0.0057	0.0057	0.0057	0.0057	0.002	0.008	0.008	0.023

*All numbers are average ppm values measured for pellets ("bulk")

"Victrex." PEEK is used in a wide variety of applications (61) demanding high dielectric strength (wire and cable coating and wrapping), high wear and abrasion resistance (motor vehicle bearings), high mechanical strength and elasticity (tennis racquet strings), transportation of hot and aggressive liquids (special tubing and catheters), etc. When reinforced with up to 68% continuous carbon fibers, it is known as APC 2 (Aromatic Polymer Composite 2), a leading thermoplastic composite for aerospace applications.

According to some experts, liquid crystal polymers (LCP) and blends based on them should also be included in the group of advanced high performance materials (62–64).

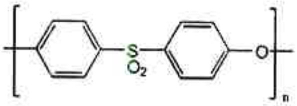
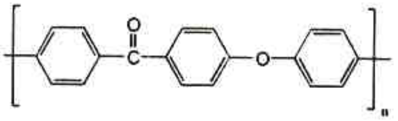
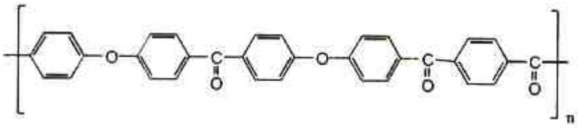
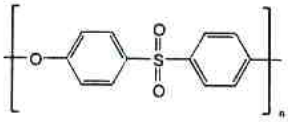
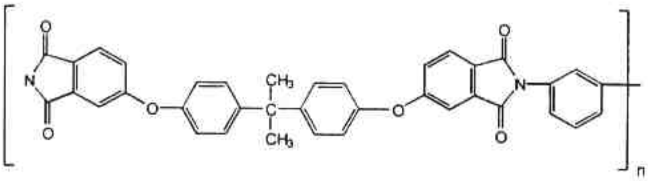
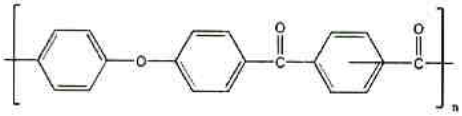
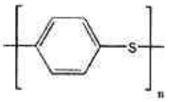
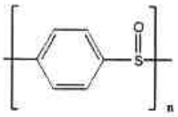
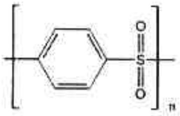
The most industrially important high temperature engineering thermoplastics and their chemical structures are shown in *Table 8*.

All of the above high-temperature polymer materials are produced as neat, filled, reinforced, and modified versions and formulations known in the industry under their trade names. Here are some examples: GE (USA) is producing PEI under the trade name "Ultem"; Ticona (Germany) is offering PPS as "Fortron," and a family of oxygen-modified (oxidized) versions of PPS(d) and PPS(f) under the trade name "Ceramer" and "Ceramer Plus"; high-temperature aromatic polyester based LCPs are known under trade names "Ekonol" from Saint-Gobain Performance Plastics (USA) and "SumicaSuper" from Sumitomo Corporation (Japan); Oxford Performance Materials, Inc. (USA) is producing PEKK under the trade name OXPEKK.

A description of properties for all commercialized polymers can be found in technical data sheets and product literature from major vendors of advanced thermoplastics (62–65). It is worth emphasizing that practically only the neat resin grades of high performance materials are used for fabricating films and tapes, and the reinforced formulations with glass, carbon, and other fibers are mainly applicable in the production of thick sheets, injection and compression molded parts.

The above materials have many characteristics and applications in common. They are providing increased use temperature and toughness in comparison to the general engineering plastics, better rigidity, very high chemical resistance (including at high temperatures), and dielectric strength. Typically, the advanced engineering films for this group of high temperature and high dielectric strength are slit into tapes, which are applied in stretched and/or unstretched versions to wires and cables as a film wrap-jacketing to provide reliable performance of wires/cables at high temperatures. Such cable products are used in aircraft and space carriers. A number of other applications have been developed in an attempt to utilize the advantages of high performance polyketones. For example, PEEK and PAEK films are recommended (66) as an insulation material for two new products in the electrical sector: a metal core circuit and a copper clad laminate for control equipment. These materials were chosen for their chemical resistance, flame and radiation resistance, low smoke emission, and acceptable processability. A wide variety of applications for PEEK film are being described in an increased number of publications, patents, and technical literature. Films that are now finding applications in micro-motor parts for computers, laser printers and other office automation equipment, for optical discs and wear-resistant rings for washers are described in many journals (65–67). A very promising and efficient area is the development and fabrication of micro- and ultrafiltration membranes. A review of PEEK membrane fabrication, their properties and evaluation can be found in several reviews (68). According to one of the modern technologies, high performance asymmetric membranes are obtained by extruding blends of PEEK, polysulfone

Table 8. High-Temperature Polymer Materials.

Chemical Name	Chemical Structure
Polyethersulfone (PES)	
Polyetheretherketone (PEEK)	
Polyaryletherketone (PAEK)	
Polysulfone (PSF)	
Polyetherimide (PEI)	
Polyetherketoneketone (PEKK)	
Polyphenylenesulfide (PPSd)	
Oxidized Polyarylenes/Polyarylene Sulfide/ Polyarylene Sulfone (PAS, Ceramer, PPSO)	 

(PSF), and a small molecule solvent mixture, and then removing the PSF and solvent in a subsequent extraction step. The process for making ultrafiltration membranes differs from that for microfiltration membranes only in the blend component ratios and temperature of the film pick-up rolls.

Properties and applications of some new films and sheets made of PEI and its blends have been described (69, 70). An interesting application is the use of high-temperature, dimensionally stable plastic materials such as PEEK and PEI as substrates for the deposition of amorphous silicon thin-film solar cells (71).

Mechanical, thermal, and dielectric properties of advanced engineering polymers are widely published by producers and researchers. In *Table 9*, we compare different properties for various materials of the discussed group of high performance polymers measured mainly using film specimens. It is important to mention that properties for the majority of the high performance film group depend on the sub-molecular structure and morphology due to substantial crystallization capabilities, if the cooling of the molten film web is slow enough. For example, investigation into properties of PEEK films showing different thermal histories allows for the determination of the main microstructural features governing these properties. Data for tensile mechanical properties can be found (72) over a wide strain rate range, along with a number of references on this particular topic.

In addition to studies of general mechanical and dielectrical properties, researchers are now paying much more attention to such properties of advanced engineering materials as fatigue, aging, wear and tribological properties, structural changes under electrical charges, surface modifications, etc., requiring much more sophisticated devices and procedures. This trend is mainly triggered by the interest in high performance materials not only for above-mentioned and

Table 9. Properties of High-Temperature Engineering Thermoplastics*

			Polymers						
Properties	**Units**	**Test Method/ Standard**	**Polyether-Sulfone (PES)**	**Poly-phenylene Sulfide (PPS)**	**Poly-ether-imide (PEI)**	**Poly-ether-Ketone-Ketone (PEKK)**	**Poly-ether-ether-Ketone (PEEK)**	**Poly-aryl-ether-ketone (PAEK)**	**Poly-phenylene-Sulfone ("Ceramer"/ "Ceramer) Plus") (PPS/PPSO2)**
General Properties									
Specific Gravity	g/cm^3	ASTM D792 (ISO 1183)	1.37	1.350–1.365	1.27–1.29	1.28–1.31	1.30–1.32	1.3	1.31–1.41
Water Absorption 24 hour immersion	%	ASTM D570	–0.006	0.02	0.16–0.25	<0.30	0.1–0.4	0.1–0.8	0.1–0.3
Taber Abrasion (1Kg load CS17 wheel)	mg/1000 revalations	ASTM D1044	6–8	20–45					
Mechanical Properties									
Tensile Strength at 20°C/68°F	MPa	ASTM D638 (DIN 53455- ISO 527)	83–140	33–90	95–115	105–115	90–130	93–118	42–45
Elongation at Break	%	ASTM D638 (DIN 53455- ISO 527)	3–80	3–8	50–150	10–15	20–150	2.8–50	1.2–2.1
Flexural Modulus at 20°C/68°F	GPa	ASTM D790 (ISO 178)	2.6–8.4	3.75–4.2	2.8–2.85	4.5–5.0	3.0	3.65	3.3–3.5
Rockwell Hardness (M scale)	—	ASTM D785	88–98	90–100		99	99–100	86–100	
Izod Impact Strength (6.4 mm specimen)	kJ/m^2	ASTM D256 ISO 170/1A							
Notched			76–120	25–75	1.0	1.3	0.8–1.55	0.8–6.2	
Un-notched			430–540 (some grades no break un-notched)	8.0–45.0	26	no break	no break	no break	
Flexural Strength	MPa	ASTM D790	111–190	125–145	125–130	190–195	170–180	130	89–91
Melting Temperature	°C (°F)	ISO 3146		280–290 (536–554)		354–360 (670–680)	334–340 (633–644)	323–381 –688	
Glass Transition Temperature	°C (°F)			95 (173)	217–225 (393–407)	163 (325)	143–171 (289–340)	170 (338)	> 330
Thermal Properties									
Heat Distortion Temperature at 1.82 MPa	°C (°F)	ASTM D648 (ISO R75)	203–216 (397–421)	110–120 (230–248)	210–227 (400–408)		160–170 (320–340)	162–170 (294–338)	250–295 (482–563)
Vicat Softening Point at Load		ASTM D1525 (ISO R306)							
1 Kg	°C (°F)		222–226 (432–439)		219 (426)			> 240 (> 434)	
5 Kg	°C (°F)								
Coefficient of Linear Thermal Expansion (per °C)	1/°C	ASTM D696	(2.3–5.5) $\times 10^{-5}$	(4.0–5.5) $\times 10^{-5}$		(2.2–3.8) $\times 10^{-5}$	(4.1–4.7) $\times 10^{-5}$	(4.1–4.4) $\times 10^{-5}$	(3.8–4.8) $\times 10^{-5}$
Mold Shrinkage	%	ASTM D955	0.2–0.6	0.3–0.6	0.18–0.35	0.014–0.02	0.1–0.3	0.8–1.45	

(*Table 9 continued on next page*)

Table 9. Continued.

			Polymers						
Properties	Units	Test Method/ Standard	Polyether-Sulfone (PES)	Poly-phenylene Sulfide (PPS)	Poly-ether-imide (PEI)	Poly-ether-Ketone-Ketone (PEKK)	Poly-ether-ether-Ketone (PEEK)	Poly-aryl-ether-ketone (PAEK)	Poly-phenylene-Sulfone ("Ceramer"/ "Ceramer) Plus") (PPS/PPSO2)
Electrical Properties									
Dielectric Strength	kV/mm	ASTM D149 (IEC 243)	15–20	17–18.5	18–26	22–25	14–19	14.2–25	12.4
Volume Resistivity (dry)	Ohm·cm	ASTM D257 (IEC 93)	1.7×10^{15} -1.0×10^{18}	1.0×10^{11}	$(1.1–4) \times 10^{17}$	1.2×10^{16}	1×10^{15} -4.9×10^{16}	$> 10^{16}$	10^{15}
Tracking Resistance (CTI)	Sec	ASTM D495	20–120		101		40		
High Voltage Arc Track Rate	in/min	*UL 746*	0.8–5.5						
Permitivity Relative (Dielectric Constant)	— —	ASTM D150 (IEC 250)							
at 60 Hz			3.51–4.0		3.2		3.2–3.3		
at 10_6 Hz							3.4		
at 10_4 Hz				2.7–3.3	1.7–3.12		3.2–3.3		
at 10_3 Hz			3.5	2.8–3.2		3.3			
Loss Tangent		ASTM D150 (IEC 250)							
at 60 Hz			0.001–0.003		0.0021		0.004		
at 10_4Hz			0.003–0.004			0.04			
Continuous Service Temperature	°C (°F)	Estimated for typical applications		180 (356)	170 (338)	250 (482)	220–250 (398–480)	> 300 (542)	

*Values represent data from different publications.

commonly identified applications, market segments, and niches, but by strong efforts that are being made in an attempt to provide, for these polymers, new opportunities to penetrate the automotive, medical, and consumer products industries. In these segments, food compliance, aging, friction, and structural (bulk and surface) changes may be of great importance. For example, PPS is already offered and successfully used for a wide range of end-uses, including electronic connectors and such automotive parts as torque converters and servo components (65–73). That is why a number of publications have appeared recently on topics like the influence of time and temperature on deformation of PEEK film (74), tribological properties of film during sliding wear of PEEK and its composites (75), effect of physical aging on the properties of film of amorphous PEEK (76), charge dynamics and morphology of PEI films (Ultem 1000 and 5000 grades) (77), electrical breakdown behavior of PEI films (78), surface modification of PAEK film by remote oxygen plasma (79), and effect of physical aging on properties of film (77).

In all cases, the properties of these materials depend on the following major factors: crystallinity, degree of degradation, presence of fillers, and reinforcement. Depending on the processing conditions, the measured crystallinity may be anywhere from 0% to 40% and the crystallization behavior is analogous to that of PET as an example of another rapidly crystallizing thermoplastic film material (64). It has been revealed that the maximum rate of crystallization for PEEK is about 230°C, and the spherulitic growth follows the classical cases known for other semicrystallinic thermoplastic materials. For example, the size of the spherulites increases with crystallization temperature, and the general spherulitic structure is similar to the more widely studied aliphatic crystallizable polymers, such as polyethylene.

Interesting conclusions are made by studying the crystallization process in the presence of fillers (carbon black, graphite) and especially fibers (typically glass and carbon fibers are used). In reinforced compositions, the nucleation of crystals may have several forms, including nucleation within the matrix itself, nucleation from contact points between fibers (or regions where fibers are almost in contact), and nucleation at a free fiber-polymer interface. This makes the crystallization process more complicated than for polymers without reinforcing fibers.

In most applications requiring optimum modulus and solvent resistance, the polymers are being processed in order to develop high crystallinity. These films are usually opaque and matte finished. However, quenching of the molten film web on the casting drum enables the manufacture of very clear film. It is possible to quench samples (practically very thick film and/or sheets up to 40 mil, or 1 mm) such that they are completely amorphous (63). This is realized on a commercial scale in production of amorphous PEEK suitable for thermoforming at a relatively low temperature of about 170°C compared to 350°C required for the thermoforming of crystalline PEEK film.

In conclusion, the key properties of film made from advanced engineering polymers may be summarized as follows:

- *Thermal*: continuous working temperature not lower than 250°C (> 450°F) with ability to retain mechanical properties at over 350°C (> 660°F).
- *Mechanical*: excellent flexural, tensile, impact, and fatigue properties (especially for oriented film).
- *Dielectrical properties*: high dielectric strength remains stable in a wide range of temperatures and frequencies.
- *Chemical resistance*: insoluble in all common solvents, extremely high resistance to water and steam at high temperature and pressure, crystallinity imparts excellent resistance to a wide variety of liquids.
- *Radiation resistance*: exceptionally high for plastics.
- *Flame resistance*: V-O flammability rating (organic additives may have a negative influence, while mineral fillers may enhance flame retardancy). Smoke and toxic gas emission during combustion is extremely low for a thermoplastic material.
- *Wear and abrasion resistance*: very high, excellent tribological properties (low coefficient of friction, high "lubricity") especially for formulations containing graphite and other special fillers and reinforcements.

Processing

The majority of vendors of high performance thermoplastics, such as PEEK, claim that the processing of these polymers is easy (at least "relatively easy") and does not require special equipment or equipment modifications. However, in reality, processing of PEEK, PES, PSF, and other high performance thermoplastics is complicated and requires deep knowledge of chemistry and rheology of these materials, high skills, and experience of processing engineers and extrusion operators. The main difficulties occurring as a result of specific properties of these polymers are as follows:

- Relatively high moisture absorption dictates the need for a *deep drying* of the resin before extrusion or injection molding to a certain level of residual moisture depending on the nature of the polymer and technical requirements to the film, tape, or sheet.
- Processing conditions have to be developed (optimized) and precisely maintained to *avoid any degradation and/or crosslinking* of the polymer, especially in a high-speed process.
- Very efficient *filtration system* is required to produce a gel-free film.
- Almost all polymers of this group have a *limited processing time*: A film with a smooth surface, free of "die lines," can be produced during a limited continuous manufacturing period in the range from several hours to several days, and eventually the extrusion line has to be stopped for complete cleaning; the time limitation is caused mainly by the residue of substances and matter ("buildup") on the lips of the extrusion die.
- Very careful monitored *cooling of the film* web has to be implemented in order to fabricate film with required crystallinity and with desired optical and mechanical properties: Fast quenching produces an almost completely amorphous clear film; on the contrary, slow cooling allows the crystallization of the polymer and produces a semi-opaque or a completely opaque crystalline film; the degree of the required quenching depends on the resin type and grade (MW), thickness of the film, and speed of the extrusion process.
- In many cases, PEEK, PES, PEI, and other film and tapes are being *matte finished* at least from one side for different reasons such as better winding ("non-blocking"), improved surface for adhesive coating, tighter winding-wrapping around a wire or cable, and improved handleability. However, in many cases the matte finish also helps hide the disadvantages of film such as "die lines," visible gels, and contamination.
- *Cleaning of the equipment* is complicated and labor intensive; purging with medium performance materials immediately after extrusion of high performance thermoplastics is usually used to simplify the cleaning procedure to some extent.

It is very important to study the effects of processing on high performance polymers since they are processed at very high temperatures, which in combination with kneading and shearing may strongly influence the structure and properties of the material. Some unexpected phenomena accompanying processing have been revealed for several advanced engineering polymers. For example, a careful study of changes in PES appearance, melt viscosity, MW, and mechanical properties after processing (80) showed that, similar to other advanced polymers, the PES can be greatly influenced by thermal-shear processing cycles, the use of regrind should be strictly controlled, and has been recommended that the number of cycles should be limited to four for injection molded parts and much less for film fabrication. The selection and control of the processing conditions is therefore essential in optimizing the structure and properties of film and other finished parts. Typically, the molecular weight (MW) and melt viscosity of thermoplastics decreases (the melt flow rate increases) after processing, which is usually attributed to thermal, thermal-oxidative, or mechanochemical degradation of the resin. A number of specific chemical reactions may also occur. However, the opposite phenomenon occurs during processing of some advanced thermoplastics. In fact, the thermal stability of the most high-temperature engineering polymers "holds up" well even at high shear deformation. For PES, the degradation temperature is over 500°C (80). It has been shown that the melt viscosity and MW of PES *increases* during kneading and extrusion, which became known as the phenomenon of "*melt thickening*." An increase in MW and melt viscosity of PES is not caused by degradation and crosslinking, since measurements have no distinct proven changes in glass transition point: T_g practically remains constant, irrespective of processing conditions. Results (80) indicate that the reactions, probably grafting reactions, that take place as a consequence of prolonged shear, heating, and thermo-oxidation during processing do not have any notable effect on the structure of PES, but may be responsible for melt thickening.

The problems indicated above may become more complicated when these high-temperature materials are coextruded with other thermoplastic polymers. Nevertheless, these advanced polymers can be successfully coextruded without the use of adhesive or tie layers with nylon-6, PVDF, or phenoxy resins (80). However, it is particularly interesting and important to note that ethylene/methyl acrylate (EMA) copolymers, which are commonly used as tie layers to join two dissimilar polymers, show no adhesion with polyketone polymers.

Blends, Alloys, and Modifications

Processing difficulties are one of the reasons for efforts to develop blends and alloys. Research in the field of blends (alloys) of PEI, PPS, PEEK, and other materials, as well as identification and application of processing additives, is aimed not only toward achieving property improvements, but in many cases, toward their influence on melt rheology and processability. However, the number of efficient melt processing aids for this group of advanced polymer materials is very limited because of very high processing temperatures and tough requirements on the additive's "survival" under the severe combination of high temperature and intensive shear deformation in modern high-speed film-extrusion equipment. That is why most success stories are related to the use of additives (processing aids) based on fluoropolymers and specific (unique) mineral fillers/modifiers. These additives are recommended in technical literature under various trade names. For example, incorporation of Dynamar fluoropolymer additives is described (81) in order to overcome problems with "die lines" (or "weld lines") on the film surface. It is also reported that the free-flowing fluoropolymer additive Dynamar FX 5911X helps shift the start of melt fracture to higher shear rates and to reduce extruder torque. Some other fluoroelastomer processing aids are reviewed (82), but their applications are much more reliable for polymers requiring much lower processing temperatures. Vydax Fluorotelomers are offered (83) as a family of CFC-free dry film lubricants under the trade name Krytox DF and Krytox 2000. This aid, in a form of white waxy fluorotelomer particles, can be added to any formulation as a dry material or in a form of a dispersion either in a solvent (such as isopropyl alcohol) or water. The use of dry-mixed in additive is preferable, owing to elimination of the technological stage of preparation of the dispersion and difficulties in getting rid of the solvent or water base of such concentrates.

The effectiveness of some fine mineral additives as modifiers acting, to some extent, as internal lubricants has been described in recent publications. Among them, the addition of a relatively small quantity of boron nitride seems to be very useful, not only for fighting "melt fracture" (eliminating "sharkskin" on the film surface), but also for "unloading" extruders, as well by reducing the apparent viscosity, backpressure, and torque required for high-speed processing (84).

The most investigated and developed in the industry are binary blends of PEEK and polyethylene naphthalate (PEN), PEEK and polyetherimide (PEI), PAEK and PEI, polysulfone (PSF) and polycarbonate (PC), and PEI and PC. Investigations into their morphology and properties have been described in a number of publications and patents. Kohlman and Petrie have described the mixability and mechanical properties of PPSf-PC and PEI-PC, including low-speed and high-speed impact resistance versus the content of components (85). The influence of blend composition on the deformation behavior of the cast amorphous PEN/PEI blends was investigated (86) above their respective glass transition temperatures (T_g). PEN inherently shows a sharp necking phenomenon when it is subjected to stretching at temperatures as high as 20°C above its T_g. This is attributed to highly localized rapid alignment of naphthalene planes parallel to the surface of the films. The addition of PEI is observed (87) to reduce this necking behavior, and the necking completely disappears when the content of PEI in the blends exceeds 10%. The increase of the PEI hinders the rapid alignment of naphthalene planes, increases the friction between polymer chains in the blend, and prevents the formation of localized necks.

The deformation behavior of amorphous thin films of PEEK/PEI blends was investigated over a wide temperature range by use of optical and TEM microscopes (88). It was shown that in pure PEI and in blends with up to 60 wt% PEEK content, a transition from shear deformation to disentanglement crazing occurred as the temperature was raised. This transition has not been revealed for PEEK, which deformed by shear over the whole temperature range. Similar behavior was found for PEI/PEEK with 80 wt% of PEEK. The thin film deformation was found to be consistent with their bulk deformation. A high-temperature ductile-brittle transition was observed in tensile tests at low PEEK content.

The thermal, mechanical and optical properties of stretched cast film samples made from blends of PEI/PET as a function of composition and draw ratio were investigated (70, 71). Very interesting ternary blends of PEEK/PEI/PEN were investigated (88, 89) in order to eliminate the neck formation in the rubbery state, while maintaining the strain-induced crystallizability, and also to increase the T_g. The increase of PEI concentration elevated the T_g along with the reduction of the ability to crystallize. It was revealed that to compensate for the latter, the concentration of PEEK should be increased to recover the strain hardening and to boost the T_g of the final films. PEN crystallization was hindered in blends with 40% PEI. Although PEEK can be crystallized at concentrations as low as 10%, PEN remains amorphous. The annealing of film leads to an interesting phenomenon: Both PEEK and PEN separate from PEI and crystallize into their own phases (domains).

A large number of high performance blends and polymer modifications, especially with different fillers, have been developed recently for special applications as *"thermal interface management" materials (TIM)*. This direction in high performance materials, films, and tapes development is related to heat removal from microprocessors. Heat sink for semiconductor chips and other heat-removal applications are among the last areas where thermoplastics–inherent thermal insulators have yet to replace metals and solve problems of heat buildup in electronics, appliances, lighting, automotive, and industrial products. It is anticipated that bondable, flexible and lightweight films/tapes made of thermoplastic materials filled and modified by ceramic grains, high conductive fillers such as metal powder, carbon black, graphite, nanoparticulates, carbon fibers, nanofibers, nanotubes, "Buckytubes," and whiskers have an excellent chance to create interface products capable of beating the previous generation of TIM based on grease and other "less user-friendly" materials.

Thermally conductive compounds are usually created based on crystalline advanced engineering polymer resins because of their high heat resistance, high thermal stability, and very low melt viscosity, which does not limit the filler load and does not create processability problems. It should be pointed out that films and tapes made of filled high performance resins have higher stiffness and tensile strength, but lower elongation at break and impact resistance than unfilled or reinforced compositions.

The most thermally conductive additives are specialty graphite fibers (conductivity values up of 500–1000 W/mK) in comparison to structural grade carbon fibers based on PAN having values less than 10 W/mK and electrically insulative ceramic fillers with 60–80 W/mK for boron nitride and 300 W/mK for aluminum nitride powders. High fiber loading (up to 70 wt%) can provide high-quality TIM materials based on LCP and PPS because of their low viscosity and excellent interface compatibility with graphite fibers.

Theoretical investigation and modeling of heat transfusivity of polymers and composites with different types of fillers and modifiers have been conducted and described many times in academic and technical literature devoted to "thermal packing" and "thermal management" analysis, modeling, and applications (89–96). Some interesting history and trends have been described in recently published reviews (93, 94). Thermal conductivity of heterophase polymer compositions has been carefully analyzed and reviewed in a cycle of original publications and reviews by Wong and Bollampally (97), and Bigg (98) for filled formulations, and by Godovski (99) and Kassiba and co-authors (100) for nanocomposites. Several comprehensive technical reviews of TIM principles, materials, and test methods have been recently published as well (100, 101). According to some experts (99), "... this ability to control heat build-up, yet also provide lightweight, flexible, and low-cost applications will make these plastics one of the most important technological developments for decades to come..."

Polymer range for TIM materials expands consistently, and in addition to LCP, PPSd, PEEK, PPSf, and PEI, high performance films and tapes for TIM applications are being created using medium-temperature resins such as ABS, PBT, PA, PC, as well as lower-temperature commodity thermoplastics like PP, PS, and PMP. Even thermoplastic elastomers are getting thermal-conductivity treatment (102), offering various grades with conductivity in the wide range from 18 W/mK to 60 W/mK.

The following three general classes of fillers can be used to increase the thermal conductivity of thermoplastic films and tapes (95, 99–102):

- *Carbon Fillers:* carbon black powder, graphite powder, carbon fibers, graphite fibers, carbon and graphite nanofibers, nanotubes and nanowhiskers.
- *Metallic Fillers:* copper powder, steel and aluminum powders, and aluminum flake.
- *Ceramic Fillers:* boron nitride, aluminum nitride, and aluminum oxide.

Each filler type has advantages and disadvantages; for example, the carbon and metallic fillers are electrically conductive, as well as thermally conductive. The ceramic fillers will provide materials that are electrical insulators. The fiber or flake fillers have generally more efficient ingredients, in terms of loading needed to achieve conductivity; however, because of their high aspect ratio, film extruded at high speed (high shear rates) may have orientation dependence. The metallic fillers have high specific gravity, which leads to a weight disadvantage in some applications.

Powdered fillers may require higher loading, but will not show an influence of particulate orientation.

With regard to the thermoplastic polymer matrixes, TIM are usually formulated based on crystalline and amorphous engineering resins because of their high heat resistance, lower melt viscosity, and high bondability to metal interfaces.

One of the most interesting developments would be a thermally conductive film placed between the coils of a radiant floor-heating system. Such a film could allow water to be run at lower temperatures.

The heat-transfer requirements of ever-smaller and "power-hungry" electronics have opened the door for this new generation of cooling materials. Unfilled thermoplastics have thermal conductivity around 0.2 W/mK, and most thermally conductive compounds have 10–50 times higher conductivity (in the range from 1 W/mK to 20 W/mK) (97, 100). Polymer-based products with 10–100 W/mK conductivity have been offered recently, i.e. 100–500 times higher than that for neat (basic) polymers. For comparison, some die-cast metal alloys (magnesium or aluminum) are in the 50–100 W/mK range. It is emphasized (97, 102) that the metal's high thermal conductivity cannot be effectively utilized if it conducts heat faster than the air-flow convection can remove heat from the surface. There are cases when the application (design) is convection-limited and (not conduction-limited) thermally conductive plastics can provide heat transfer with efficiency equivalent to those of aluminum and copper designs. In addition, the lower coefficient of thermal expansion (CTE) of plastics can be a plus capable of reducing the stresses occurring as a result of differential expansion, since the plastics more closely match the CTE of silicon or ceramics that they contact (99, 102). Specially formulated grease and silicone rubber has dominated the previous generation of TIM materials. The most advanced grease materials have been disclosed by Shin-Etsu Chemical Company in a series of patents published during 1999–2001. Their formulations have been based on silicone grease comprising high conductive fillers, preferably aluminum nitride (AlN) because of its higher conductivity than other fillers such as ZnO, BN, and SiC (103–108). A liquid silicone is being used to provide a better wetting effect on the substrates and increase the contact conductivity. In addition to creating a "moisture barrier" around the AlN to preserve the conductivity, the coating may also help keep the particulates dispersed in the liquid silicone through a kind of associative linkage mechanism. This high dispersion would help increase conductivity and its consistency over the entire article, forming a film media, rather than being concentrated in one spot.

In spite of successful implementation of silicone grease and rubber for forming TIM films, most experts now agree (102, 109) that various new TIM materials including highly filled advanced polymer tapes and phase change materials (cooling the microprocessor's units by absorbing heat during their melting) will soon take over for thermal grease type materials. Scientists and engineers have to solve several difficult technical problems to provide successful implementation of the next generation of TIM. Besides increased thermal conductivity, rheological aspects of processing of highly filled materials into film and tapes, and adhesion of these interface materials to metal parts of chips and sinks, a serious concern may be the thermal-expansion behavior of thermoplastic composites (101, 102). This problem has been examined for a variety of thermoplastic composites based on PEEK and other materials by Barnes (110). It was shown that when each of the composites is raised above the T_g of the polymer matrix, considerable permanent distortion occurs, though the effect is not evident below T_g. This was attributed to relaxation of process-induced residual stresses. A number of models are used to calculate the thermal-expansion behavior of the fiber transverse to their long axis. Unfortunately, in many cases, the results are inconsistent and in poor agreement with directly measured properties, and further perfection of the models is required.

LCP for High Performance Films

Liquid crystal polymers (LCP) are distinguished by high heat resistance, good mechanical properties, and moldability. Hoechst Celanese ("Vectra"), Amoco Polymers ("Xydar"), and DuPont ("Zenite") produce various liquid crystal polymers (LCPs) in increasing quantities. It is important to emphasize that a range of special grades of LCPs have been developed recently for use in mono- and multi-layer high performance film structures, as well as for blending with other thermoplastic polymers. These films were meant, at the beginning, for advanced barrier packaging applications. LCPs are often co-processed with conventional resins such as polyolefins, polyesters, and polyamides in multilayer films (111). Some experts believe that co-extrusion equipment capable of fabrication of multilayer film comprising polyvinylalcohol (PVOH) barrier grades can be suitable to switch to LCPs without any additional major outlay.

The main problem in processing of neat LCPs into film, limiting their consumption, has always been the strong orientation of the polymer in the longitudinal (extrusion or "machine") direction and the resulting anisotropy of properties in "machine" and transverse directions. The extremely rigid polymer molecules remain aligned in the melt and in the solid state. The orientation of LCPs in the melt "freezes" into the solid state because of the very long relaxation times. The strong orientation of LCPs does not create too many difficulties in injection molding processes, including injection molding and modern coinjection molding of filled and reinforced compositions. The amount of fillers and fibers may be quite high because of the very low viscosity of the neat LCP matrixes and a very sharp decline of the apparent viscosity with increase of temperature. These materials include grades that can be processed at temperatures as low as 220°C and as high as 400°C (111). Applications and properties of LCPs are reviewed in *Table 10.*

A number of interesting blends comprising LCPs have been developed and implemented in the last few years. Morphology of blends with LCPs influences the properties, along with additives and compatibilizers. On the other hand, the rheology of such blends, specifically the viscosity ratio of components, has a strong effect on morphology (112). Blends of LCPs with polyolefins, polyesters, polycarbonate, and other thermoplastics are used in increasing quantities. It is worth mentioning the following effects of LCPs on blend properties and their processing:

- At low levels, LCPs can be used as *processing aids* and reduce the viscosity of the main polymer "partner"; small quantities of LCPs may also improve the surface of parts, sheets, and film.
- LCPs can *increase the modulus and stiffness* of the matrix component and practically provide reinforcement for thin wall parts, sheets, and film; blends in this case may be considered "in-situ" composites; a good example is long duration improvement of weather balloons made of PE achieved by NASA together with Penn State University by incorporating 10% of LCP fibers into PE film (113, 114).
- Blends with LCPs as matrixes exhibit *excellent barrier and enhanced thermal and physical properties* versus non-LCP blends.
- LCPs and blends based on them display *improved adhesion* in various laminates.
- The interfacial tension between LCP and the thermoplastic component in the blend can be substantial; for example, it was shown by Kenig (115) that the tension on the interface LCP/PC is between 4 and 6 dyne/cm. This may negatively influence the compatibility and adhesion between components.

Various methods of reducing the undesirable flow-induced orientation and anisotropy of mechanical properties have been suggested for many applications. We cannot discuss them all in detail, because many companies are considering this information to be their

Table 10. Applications & Properties of LCPs.

Typical Applications	Key Properties
Electrical/Electronic	
Sockets	Excellent processability
Bobbins, Switches	Ability to fill thin wall parts
Connectors - Electrical, Fiberoptic	Excellent dimensional stability
Fiberoptic Cables	Ability to withstand IR & vapor phase soldering temperatures
Chip Carriers	Very high relative thermal indexes
Printed Circuit Boards	Excellent flame resistance
Surface Mount Technology Parts	UL ratings—50% regrind approval
Health Care	
Sterilization Trays	Very high strength & stiffness
Dental Tools	Excellent flowability
Surgical Instruments	Smooth surfaces
	Excellent creep resistance
	Excellent radiation, chemical & steam resistance: USP Class VI
Industrial/Consumer	
Printers, Copiers, Fax Machines	High strength to weight ratio
Business Machine Housings	Excellent flammability ratings
	Low smoke generation
	Conductive grades with electrostatic dissipation & shielding characteristics
Telecom	
Shields/Frames	Excellent flowability, processability
Chip Card Reader	Excellent temperature, dimensional stability
Antenna Parts	Excellent mechanical strength & stiffness
	Platability
Cryogenics	
Food Packaging Vessels	Very high strength & stiffness
Waste Containers	Excellent low-temperature properties
	Excellent radiation, chemical & steam resistance
Packaging & Film	
Food & Liquid Packaging	Excellent barrier properties
Coatings	Excellent stiffness & strength
Fuel Tanks	Excellent dimensional stability
Printed Circuit Boards	
Fibers & Yarns	
Cables, Ropes, Fishing Poles	Very high stiffness & strength
Sailcloth	Low moisture absorption
Cut-Resistant Gloves	Good flex strength

"know-how." The most published and widely advertised method is the use of an extrusion die with a rotating mandrel or with counter-rotating die matrix and mandrel. For example, Superex Polymer, Inc., suggested a counter-rotating die for blow molding of multilayer tubing, beer bottles, and blown extruded film made of a combination of LCP with PET (116). R. Lusignea and his colleagues have described Superex technology in many technical publications and reviews for regular LCP films (117) and oriented films and structures (118). In spite of the fact that the theory and technology of extrusion through dies with rotating mandrels were developed quite a while ago (119–121) and the influence of helicoidal flow on the reorientation of the melt was proven theoretically and experimentally, the use of dies with high-speed rotating parts for LCP is still limited. A process for producing thin LCP films with improved tear resistance, balance of physical properties, and wrinkle-free surface has been disclosed (122). The use of an annular coextrusion die was suggested for lining the LCP with one or more surface layers of a nonadherent polymer before the LCP becomes shear-oriented. The multilayer tube (sleeve) formed by the coextrusion is sealed, stretched, and cooled by passing it over a sizing mandrel. The tube is slit open into a flat configured film.

A lot of attention has been paid to the development of isotropic LCP films for various applications, first of all for printed circuit boards. Potential applications targeted for the new films are copper-clad laminates, both single and double-sided (123). Thermal expansion equivalent to silicon, low dielectric constant, and extremely high hygroscopic capabilities make these films particularly suitable for packaging of integrated circuits. Surface topography and chemistry may be important in the above applications, and some inventions have disclosed processes for roughening LCP film surface (124) and for improving its bondability by modifying the polymer (125). The advanced blown and cast films containing blends of LCPs and PO and reinforcing fibers have been successfully fabricated for various applications requiring toughness and modulus enhancement of approximately 400% over the neat PO matrix (126).

ADVANCED LOW-TEMPERATURE POLYMER FILMS

As stated in the **Introduction** to this review, it is our belief that low-temperature thermoplastic materials are being increasingly considered as a valuable source for fabricating high performance products, and first of all film for advanced applications required by modern technologies. This approach has been strengthened during the last few years by the following very efficient "breakthrough" technologies:

- New polymerization chemistry and technology, first of all *metallocene catalyzed polymerization* of polyethylene (m-PE), polypropylene (m-PP), polystyrene (m-PS), and cyclic polyolefins like ethylene norbornene copolymers (m-ENC).
- Various *catalytic modifications* of low-temperature thermoplastics.
- Further progress in development of *blends and alloys.*
- A widespread increase in efficiency of *coextrusion* of various thermoplastics including the design of *multi-manifold coextrusion dies* enabling the combination of polymers with significant differences in apparent melt viscosity and other rheological properties.
- Development of *polyamides with higher melting and use temperatures* or "high-temperature nylons" (HTN); the demand for HTN and semi-aromatic and aromatic family polyamides (aramid) has been growing recently in automotive and electrical/electronic applications because of their high flame resistance, arc and tracking resistance, and formability into thin-wall parts.
- Development and implementation of *nanocomposites* based on various thermoplastics such as PA (nylons), PP, PBT, PE, and progress in melt compounding of nanomaterials.

The main directions in development and application areas of low-temperature advanced film may be summarized as follows:

- High performance specialty mono and multilayer *packaging* (LLDPE, PA, PMP, PP with superb impact resistance, clarity, barrier, and heat-seal properties).
- *Release* film for low and medium temperature applications (high temperature PA, PMP, m-PE, etc.).
- Film with enhanced *optical* properties for solar panels, safety glazing, and special optical effects such as light-emitting materials.

For example, metallocene catalyzed low and super-low density PE recently enabled the introduction of various families of "enhanced" resins for blown film with very *high impact resistance*, outstanding hot-tack and heat-seal properties (127, 128), a line of thin (0.5–2.0 mil) high performance polyolefinic *shrink films* (129), and a novel "self-contracting," high elasticity seal and wrapping film (130).

The new chemistry and achievements in "in-line" quality control (131) have led to a strong improvement in optical properties of various polymers and opened *the door for the creation of families of film and sheets* with superb *optical properties* including films with extremely low haze (< 0.4% at thickness of 15 mil and higher), which was achievable in the past by using PVB only. These mono and multilayer films based on ionomers (132), ethylenemethacrylates (133), PU, PC (134), and m-PO (135–137) may successfully compete in the future with PVB as a lower cost, plasticizer-free interlayer for optical laminates, protective, and safety glazing products. Multilayer sandwiches with EVA as "skin" layers coextruded to the core of the main m-PO resin (136) have successfully solved the adhesion problem in terms of lamination of m-PO to glass.

According to some experts (138), new advanced films, for example made of PMP, may successfully compete with high-end release liners of fluoropolymers (FEP and ETFE) in applications in which FP liners are "over-engineered" or as an alternative film when the users are facing FEP shortage. It was proven that one of the disadvantages of PMP film, its low elongation at break and the release properties of PMP, can be significantly improved by blending PMP grades having a low content of atactic fraction (< 2%) and a high MW (200,000–700,000), with PP of medium MW in the range from 150,000 to 350,000 (139). Elongation at break of such blends increases to 200%–350%, and for some optimized formulations up to 500%, in comparison to 20%–100% typically observed for neat PMP. At the same time, the release parameter (force required to peel the film specimen of a standard acrylic-based pressure sensitive adhesive coated substrate) decreases to the load less than 0.6 lb/inch in comparison to 2.0 lb/inch typical for a neat PMP film.

Unexpected capabilities of another polyolefin, namely metallocene catalyzed LLDPE (m-LLDPE), to perform as a release film (liner) was discovered and studied (140). It is known that m-PE is tacky because of ultra-low density. Processing of m-PO causes problems with winding in rolls owing to "self-blocking" of film layers. It is anticipated that m-PE may hardly be considered a good choice of material for application as a release liner. However, surprisingly, m-LLDPE with certain density, MW, and MWD shows pretty good release properties when applied to acrylic-based pressure-sensitive adhesives. A "window" in densities from about 0.865 g/ccm to 0.900 g/ccm has been determined for m-LLDPE with a narrow MWD (with index of polydispersity, PI less than 5.0), which produces a film providing release force values in an adhesive peel test lower than 39 g/cm (see *Fig. 8*). The film shows optimal release properties when the resin density is lower than 0.88 g/ccm and the PI is close to or less than 2.0. The film is useful in manufacturing rolls and sheets of PSA tape especially when a silicone-free release film is desired.

There is no doubt that creation of new materials with improved properties and lower costs will continue, and new low-temperature advanced film products will be offered to various end-users. For example, it has recently been reported in the U.S. and the U.K. (141) that the newly developed family of iron-based

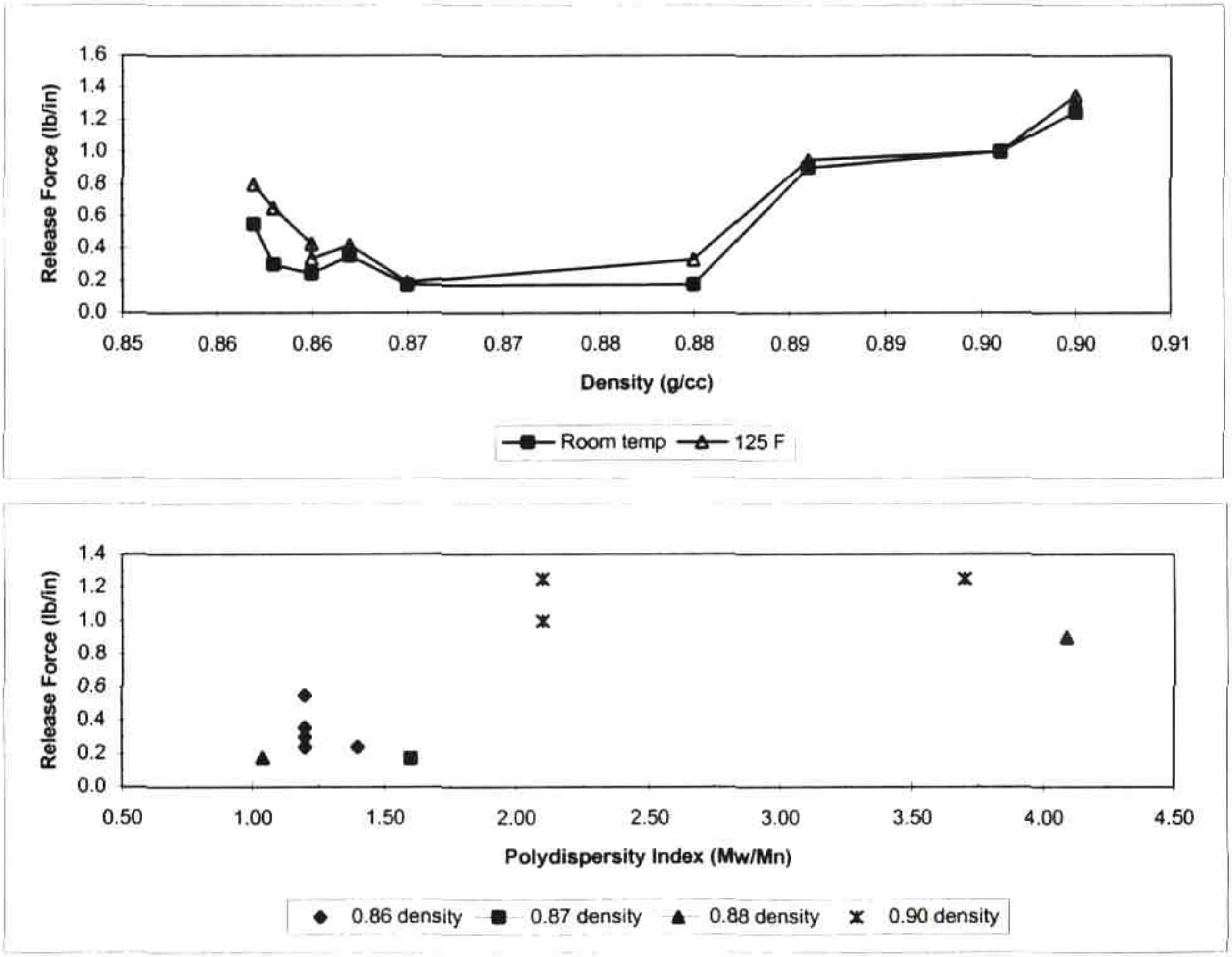


Fig. 8. Force to release (peel-off) metallocene LLDPE of the acrylic pressure-sensitive adhesive versus density of the PE.

catalysts is able to rival the effectiveness of both conventional organometallic and metallocene catalysts in the polymerization of olefins. The new catalyst family shares many of the advantages of metallocene catalysts in terms of activity and control of polymer molecular structure and properties. In addition, it offers the potential for producing a much broader range of polymeric materials at low cost.

Another new trend in advanced film and sheet development is the growing use of *lightweight nanocomposite materials* with just 2%–8% loading of fillers. For example, the organo-clay hybrid incorporated into nylon through a compounding process improves the oxygen transmission rate in film by four times compared to unfilled nylon 6 (142). The material also has properties equivalent to usual mineral-filled compounds with a much higher loading (20%–30%). The orientation of the organo-clay platelets prevents degradation of viscosity and allows lower viscosity at high shear rates. The stiffness of the compound at 5% weight loading is comparable to a conventional 20% mineral-filled nylon with minimum rise in specific gravity.

Advanced conductive and super-paramagnetic films may be possible to produce using a process that embeds magnemite nanoclusters into polyaniline and other electrical conductive polymers (143). These films are expected to have applications in a range of technologies including interference shielding and optical systems.

It is anticipated that nanofillers will help in developing films and coatings with "super-barrier" capabilities, improved flammability, rigidity, and toughness. Nanocomposite films are being developed as monolayer items with various mineral nanofillers based on thermoplastic resins (144–147) and polyimides (148), as well as components in multilayer coatings and structures (149). It is worth mentioning that the significant progress in design and fabrication of multimanifold dies enables the coextrusion of polymers of a different nature with dissimilarity in apparent viscosity of two or more orders of magnitude. The triple-manifold extrusion system may also contribute to a high-quality appearance of film made of filled and unfilled components (150). However, scientists and engineers should keep in mind that, for some combinations of thermoplastic materials, best results could be achieved with coextrusion feedblocks rather than multi-manifold dies. The reason is related to the fact that different melt layers in a multi-manifold die may not be in contact long enough, just in the die land area to achieve a reliable mutual diffusion before being cooled to the solid state.

In most cases, the trend is to combine the two modern technologies: blending and coextrusion, i.e., to utilize the best combination of thermoplastic materials within each layer, and to utilize the best possible combination of different layers in the "sandwiched" film. For example, in addition to blends based on PMP (139), further development is moving in the direction of creating multilayer structures based on PMP and other thermoplastics in an attempt to make them more competitive with fluoropolymers in release film applications. One interesting recent invention (151) provides a multilayered polymethylpentene-containing release film for various applications with improved release properties when exposed to high temperatures in processes using epoxy resins. These films are non-oriented and comprise a polyamide layer, a PMP layer, and an adhesive layer between. It has been suggested to extrude the polyamide layer with a ternary blend of nylon 6, nylon 6,6 copolymer, and nylon 6,12 copolymer, and to combine this layer with a film made of a blend of PMP and PMP-based copolymer. It seems that combinations of sophisticated blending and coextrusion techniques are able to produce film variations practically without limits in developing advanced film structures.

Combinations of alloys and multilayered structures of engineering plastics are being thoroughly developed utilizing precise chemical structure and morphology control based on advanced compatibilizers and reactive processing technologies (152). Experts anticipate that these trends in developing engineering plastics and polyolefins, alloys, and blends coextruded in various combinations will be the focus for efforts of researchers and engineers for a long period of time. An important example below shows the summarized information collected by Okada (153) on polymer alloys and blends produced or being actively developed (*Table 11*), along with notable new compatibilizers, polymer blends, and alloy products (*Table 12*) recently commercialized in Japan.

BIOMIMETIC STRUCTURES—POTENTIAL FOR CREATION OF ADVANCED FILM

Biomimetic is the abstraction of a good design from nature and shows a very high potential for the creation of new advanced composite materials and film with intriguing properties. Biological materials are virtually all nanocomposites and have hierarchical structures, organized interactively at the molecular, nanoscopic, microscopic, and macroscopic levels (153). This integrated approach seems to be the key strategy by which nature balances strength and stiffness without sacrificing toughness of the materials. According to many experts, the mimicking of natural nanocomposite structures may open the way to the creation of materials for the future, including not only bones and shell-type materials, but film structures as well. Experiments are at an early stage, but already there are indications helpful to the design of synthetic nanoscale hybrid materials. There are some general "ideas of nature" that from our point of view may be very useful in the development of advanced film structures.

Experimental investigation by reflection spectroscopy, elipsometry, and transmission electron microscopy of optical properties of colored wing scales of butterflies and moths produced very interesting results (154, 155): the outer surfaces of these scales incorporate a regular layered structure of alternating dense

Table 11. Polymer Alloys & Blends Made by Japanese Companies.

	Minor Component**									
Main Component	**PPE**	**PC**	**PA**	**PBT PET**	**PPS**	**ABS PS**	**PO**	**PVC**	**LCP**	**SPS**	**Elastomer**
Polyphenylene Ether (PPE)			◆	◆	◆	●	◆*			•	◆
Polycarbonate (PC)			◆	●		●*	•		◆*		◆
Polyamide (PA)	●			◆	◆	◆	◆*				◆
Polyester (PBT, PET)		◆		◆		◆	◆*		•		◆
Polyoxymethylene (POM)				◆			◆				◆*
Polyphenylene Sulfide (PPS)	◆*		◆*				•		•		◆
ABS & Polystyrene (PS)		◆*	◆*	◆*			◆	●		◆*	●
Polyolefin (PO)			◆*	•		•	●*				●*
Polyvinyl Chloride (PVC)											●
Liquid Crystal Polymer (LCP)		•		•					•		
Thermosetting Plastics											●

● = Consumption over 5000 tons per year
◆ = Consumption less than 5000 tons per year
• = Under intense research & development
* = Includes copolymer & modified polymer

Table 12. Polymer Alloys & Blends Recently Commercialized or Developed in Japan.

Polymer	Company	Product
Compatibilizer, Modifiers		
TPE graft copolymers	NOF	Nofally
Block copolymers:		
for surface modification	NOF	Modiper F, FS
for decreasing curing shrinkage	NOF	Modiper SV, MS
SEBS for PP/PS blends	JSR	Dynaron new grades*
Terminal functional PP & PP macromonomers	Tonen Chemical	(under development)
Modifiers for recycled PET	Toyobo/Toyoda Gosei	Ecoviropet
Modifiers for recycled ABS	Nippon A&L	Repelle System
Comb-shaped functional copolymers	Mitsubishi Chemical	(under development)
Commodity Plastics Blends		
PS/syndiotactic PS blends	Idemitsu Petrochemical	Zarec E, D
Reversibly crosslinkable polyolefin blends	Mitsubishi Chemical	TRC Polymer*
Engineering Plastics Alloys		
ABS/PA6 alloy new grade for Honda's Insight	Nippon A&L	Techniace
PPE/PA/elastomer alloy with nano-network structure	Mitsubishi Chemical	(under development)
Super Engineered Plastics Alloys		
PEEK/PEI blend film	Mitsubishi Plastics	Ibuki
Polymer/Silica Hybrids (Sol-Gel Method)		
Epoxy resin/silica	Arakawa Chemical	Compoceran E*
Polyurethane/silica	Arakawa Chemical	Compoceran U*
Polyamideimide/silica	Arakawa Chemical/Furukawa Electric	(under development)
Thermoplastic Elastomers		
In-reactor TPO	Idemitsu Petrochemical	(under development)

*Commercialization in near future

and less-dense material, which reflects light by the "classical" *interference* process. In other words, without doubt, the coloration of the surface of biological materials is due to the structural architecture and is in no way related to pigmentation. Nature has found a way of fabricating sophisticated photonic bandgap structures that are more advanced than those fabricated in leading laboratories. Maybe the key to the creation of new film and coatings with intriguing optical properties such as brilliant colors, strong UV-reflection capabilities, and metallic appearance is in the microscopic geometry of surfaces as is typically observed in thin-film biological reflectors. This could enable fabrication of advanced optical film at "room temperature without nasty solvents" (156).

Investigation of mechanical properties and fracture mechanisms of shell, nacre, and other biomaterials in correlation to structural hierarchy showed the significant advantages of organo-mineral cross-lamellar microstructures in flexural strength and preventing crack propagation (157, 158). Nanocomposite assemblies achieved in efficient processing of layered organic-inorganic composites should be considered as a very difficult, but very desirable, way to fabricate films and coatings in the future. One proposed technology to mimic nature includes (159) organic polymerization (induced by light or heat), combined with continued inorganic polymerization, lock-in the nanocomposite architecture and covalently bonds the organic-inorganic interface. Another lesson from biology, which also proves the importance of hierarchical structures and highly specific interactions between the levels, has been derived from the investigation of tendon, intestine, vertebral disc, and other collagen composite systems (160). Functional macromolecular assemblies are considered to be important for the creation of multilayer and oriented composite systems (161), film and fibers (162).

CONCLUSION

It is understood that it would be very difficult (if possible at all) to cover in one paper, even one with many pages, all advanced high performance films and innovations influencing their development and applications. Any review is a "snapshot" of a "moving target," in this case on a changing picture of a very dynamic industry characterized by high-speed growth in terms of volume, as well as scientific and technical sophistication. Nevertheless, our opinion is that some trends in science and industry of high performance films will be retained and even strengthened as high-priority research and development directions. *The most important trends, to our understanding, are described below:*

- There is no doubt that further progress and development of high-tech applications in the electrical, electronic, and semiconductor industries, as well as in aircraft and space engineering, will fuel continuous efforts in the creation of ***high and ultra-high thermal resistant polymer films*** in the U.S., Europe, Japan, and other countries around the world. For example, a group of melt-processable rigid-rod polymers with polyphenylene backbone and relatively simple side groups, developed quite a while ago (163), may be implemented on an industrial scale in the next few years for various applications. In addition to aromatic high temperature materials, fluoropolymer films will continue to be in growing demand. This trend, which started in the early to mid-1990s (164, 165), is still true today especially for the new generation of fluoropolymers. One interesting direction is further progress in tailoring the crystallinity of fluoropolymers. Materials like "amorphous fluoropolymers" (such as the Teflon AF family by DuPont) will be used for various coatings, providing a combination of excellent weatherability and easier processability in comparison to regular fluoropolymers. Amorphous fluoropolymers have shown limited solubility (3%–15%) in selected perfluorinated solvents, allowing solution-cast ultrathin coatings in the submicron thickness range. At the same time, these fluoropolymers are capable of retaining chemical resistance to all other solvents and process chemicals, along with outstanding optical clarity and transmission. Another example may be related to new developments of fluoroalkyl surfactant polymers providing clear, durable crosslinked film with an adhesive on one side and antistick properties on the other side (166).
- Another strong trend is based on further development and diversification of ***combinations of ultra-high temperature polymers and fluoropolymers.*** Multilayer structures made of polyimide (Kapton) and Teflon PTFE were presented early in the 1970s (167). This material was developed as a high-end insulation system with particular emphasis on the reduction of weight and space, and was spurred by the demanding requirements of space exploration efforts. More recently, this class of materials is being used in increasing quantities in military and commercial aircraft industries. A thin PI-FP film (tape) can be wrapped around a conductor and heat-sealed. The two leading technological trends are development and implementation of various combinations of thin PI overcoated with dispersions of mixtures of PTFE with FEP, PVF and other TFE copolymers (168, 169), or overcoated using separated dispersion layers of PTFE and FEP and other fluoropolymers (170–172). The addition of FEP promotes the bonding of PTFE to PI during the sintering of the multilayer tapes at high temperatures (around 700°F) when the FEP is being molten and *adheres to PI from one side and PTFE from the other one.* There is no doubt that these high performance films will gain many other applications.
- Future films include ***ultra-thin, highly oriented, and porous film*** (173) made of modified and new fluoropolymers, copolymers, blends and alloys, and chemically combined fluoro and alkane polymers (perfluoroalkanes). Besides release film applications, researchers are focusing a lot of attention on the development of porous film and microporous electrolyte membranes for effective fuel cells (174).
- New ***high and ultra-high purity materials and film*** for semiconductor applications will constantly lower the level of acceptable metal ion linkage. New materials, their purification in polymerization and compounding, modified and perfected purity testing methods will be developed, along with "metal ion-clean" film-processing equipment.
- Films made of a group of ***mineral-organic materials*** comprising polymer-ceramic combinations, polymer nanocomposites, and "mineral polymers" (for example, polysilazenes) (175, 176) will be developed for more diversified applications, and will help solve many technical and medical problems.

These directions in advanced material development were firmly supported by the experts during the First World Congress "Nanocomposites–2001," which took place in Chicago (177).

- More ***advanced low-temperature films*** for a wide variety of applications with specific requirements will keep emerging. There is a very high probability that the demand for film made of novel resins produced using ***metallocene catalysts*** will grow not for packaging only, but also for applications requiring high optical clarity, extremely high elasticity, special surface properties, performance capabilities at extremely low temperatures, etc. Among them, super-low density PE, syndiotactic polystyrene (s-PS), cyclic m-ENBC, and various multilayer film structures. However, ***metal catalysts*** are "fighting back," and iron-based catalysts will soon be able to provide film materials, which may excite the industry.
- A large number of applications will need thermoplastic film filled with ***nanoparticulates, nanofibers, nanotubes, "Buckytubes," nanowhiskers, and combinations*** of particulated fillers and reinforcements, allowing the creation of materials with "many faces" typical for different composites. It is anticipated that nanocomposites will allow the development of films with improved properties, as well as new properties because of the fine particle disperse effect along with the interfacial phase increase phenomenon (178).
- Film with ***special optical, light, laser, and solar properties*** are being developed on an accelerated path. Ten years ago, no one imagined that polymers would be used with a light-emitting layer in light-emitting diodes. Now they form the basis of a new display technology that may develop to rival LCP (71, 179). Plastics are definitely expanding their opportunities in solar energy production, and this trend will grow thanks to low specific gravity, high clarity, dimensional stability, and dielectric properties of the modern polymers, especially metallocene PE and cyclic PO (180).
- ***Multilayer film structures*** will dominate many applications requiring combinations of materials with various high performance parameters; another trend would be the use of ***coextrusion and "co-lamination"*** for cost reduction of expensive high performance resin grades.
- ***Super-thin film*** (6–20 mcm and lower) made from polyimides, polyketones, polyesters, and other advanced engineering materials are increasingly attracting attention as cold and heat resistant coatings for various applications.
- ***Film made of mineral-organic hybrids with hierarchical structures mimicking "Mother Nature"*** will be developed, providing superb mechanical and optical properties along with high flex endurance and high resistance to fatigue for many applications in various industries.

APPENDIX A

ABS: Acrylonitro butyldienestyrene terpolymer
BOPET: Biaxially oriented polyethylene terephthalate
BOPP: Biaxially oriented polypropylene
ECTFE: Polyethylene chlorotrifluoroethylene copolymer
ETFE: Polyethylene tetrafluoroethylene copolymer
EMA: Ethylene methylacrylate copolymer
EVA: Ethylene vinylacetate copolymer
EPDM: Ethylene propylene diene monomer
FEP: Fluorinated ethylene/propylene copolymer
FP: Fluoropolymer
HFP: Hexafluoropropylene
HIPS: High impact polystyrene
LCP: Liquid Crystal Polymer
LDPE: Low density polyethylene
LLDPE: Linear low density polyethylene
m-LLDPE: Metallocene catalyzed linear low density polyethylene
MFA: Polytetrafluoroethylene-Polymethylvinylether
OPP: Oriented polypropylene
PA: Polyamide
PAE: Polyaryleneether
PAEK: Polyaryletherketone
PACI: Polyalcanimid
PAI: Polyamidimid
PAN: Polyacrylonitrile
PBT: Poly (butyl) terephthalate
PC: Polycarbonate
PCTFE: Polychlorotrifluoroethylene (mono chloro)
PE: Polyethylene
PEEK: Polyetheretherketone
PEI: Polyetherimide (Ultem)
PEKK: Polyetherketoneketone
PES (PESd): Polyethersulfide
PESF (PESf): Polyethersulfone
PFA: Perfluoronated alkoxy resin
PFBE: Perfluorobutyl ethylene
PFHE: Perfluorohexyl ethylene
PET: Polyethylene terephthalate
PEN: Polyethylene naphthalate
PI: Polyimide
PMMA: Polymethyl methacrylate
PMP: Polymethyl pentene
PO: Polyolefin
PP: Polypropylene
PPE: Polyphenylene ether
PPO: Polypropylene oxide
PPSf: Polyphenylene sulfone
PPSd: Polyphenylene sulfide
PPS: Polysulfone
PPVE: Perfluoropropyl vinyl ether
PS: Polystyrene
PTFE: Polytetrafluoroethylene
PVB: Polyvinyl butyral
PVC: Polyvinyl chloride
PVDC: Polyvinylidene chloride
PVDF: Polyvinylidene fluoride

PVF: Polyvinyl fluoride
PVOH: Polyvinyl alcohol
THF: Tetrahydrofuran
TPU: Thermoplastic urethane
UHMWPE: Ultrahigh molecular weight polyethylene

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REFERENCES

1. *US High Performance Film Markets*, Frost & Sullivan, Sullivan House, London (2000).
2. *The World Market for High Performance Films*, Frost & Sullivan, Sullivan House, London (1998).
3. *The World Market for High Performance Films*, Frost & Sullivan, Sullivan House, London (1997).
4. B. Mar, *Paper, Film & Foil Converter*, **74(6)**, 78 (2000).
5. J. DeGaspari, *Plastics Technology*, **42(5)**, 15 (1996).
6. *Modern Plastics International*, **27(12)**, 114 (1996).
7. *Plastics News*, **9**, 34 (1997).
8. *Rubber World*, **215(6)**, March, 62 (1997).
9. M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley, New York (1994).
10. N. Inayaki, *Plasma Surface Modification and Plasma Polymerization*, Technomic, Lancaster, Pa. (1996).
11. O. A. Popov, *High Density Plasma Sources*, Noyes, N.J. (1995).
12. M. Sugawara, *Plasma Etching*, Oxford Science, U.K. (1998).
13. Yializis and D. A. Markgraf, *Atmospheric Plasma—The New Functional Treatment for Films*, 2000 Tappi Polymers, Laminations & Coatings Conference, p. 1343 (2000).
14. E. M. Liston, L. Martinu, and M. R. Wertheimer, *J. Adhesion Science & Technology*, **7(10)**, 1091 (1993).
15. G. R. Traut, *Applied Microwave*, Summer, 86 (1990).
16. Q. C. Sun, D. D. Zhang, and L. C. Wadsworth, *Tappi Journal*, **81(8)**, 177 (1998).
17. D. L. Ryan, DuPont, *US Patent #3030290* (1962).
18. L. E. Wolinski, DuPont, *US Patent #3255099* (1966).
19. R. T. McBride, DuPont, *US Patent #3275540* (1966).
20. A. J. Kowalewski, DuPont, *US Patent #3676181* (1972).
21. R. T. McBride and L. E. Wolinski, DuPont, *US Patent #3296011* (1967).
22. P. Cocolios, F. Coeuret, E. Prinz, and F. Foester, *1998 Tappi Polymers, Laminations & Coatings Conference*, p. 31 (1998).
23. J. T. Marchesi, *Adhesion to Fluoropolymers*, PhD thesis, University of Connecticut (1993).
24. R. M. Podhajny, *Converting Magazine*, **13(12)**, 36 (1994).
25. J. A. Rusnock, *11th Annual Microwave Integrated Circuit Workshop "MIC-92,"* San Diego, Calif. (April 1992).
26. M. M. Nasef, H. Saidi, A. M. Dessouki, and E. M. El-Nesr, *Polymer International*, **49(4)**, 399 (2000).
27. *J. Materials Engineering & Performance*, **5(4)**, 418 (1996).
28. R. E. Uschold and T. R. Armusewicz, DuPont, *US Patent #5972472* (1999).
29. D. L. Schmidt, C. E. Coburn, and J. McCrackin, *US Patent #5006624* (1991).
30. S. Nakamura, ed., *Japanese R&D Trend Analysis, Advanced Materials*, p. 70, Kansai Research Institute Report, Kyoto, Japan (July 2000).
31. *Advanced Materials & Processes*, **153(1)**, 18 (1998).
32. C. A. Chang, Y. K. Kim, and A. G. Scrott, *J. Vac. Sci. Technology*, **A8**, 330A (1990).
33. M. K. Shi, B. Lamentagne, and A. Selmani, *J. Vac. Sci. Technology*, **A12**, 29 (1994).
34. E. Sacher, *Progr. Surface Science*, **47**, 273 (1994).
35. S. Wu, E. T. Kang, K. G. Neoh, and K. L. Tan, *Langmuir*, **16**, 5192 (2000).
36. E. M. Liston, L. Martinn, and M. R. Wetheiner, *J. Adhes. Sci. Technology*, **7**, 1091 (1993).
37. M. K. Shi, *et al.*, *Polymer Surface Modifications: Relevance to Adhesion, Metal Ed.*, p. 73, VSP, Zeist (1995).
38. T. G. Vargo, *et al.*, *M. Science*, **262**, 1711 (1993).
39. D. J. Hook, T. G. Vargo, and J. A. Gardella, *Langmuir*, **7**, 142 (1991).
40. R. C. Benning and T. J. MacCarthy, *Macromolecules*, **23**, 2648 (1990).
41. M. Huang and R. R. Burch, *J. Applied Polymer Science*, **55**, 549 (1995).
42. G. A. Corbin, R. E. Cohen, and R. F. Baddour, *Polymer*, **23**, 1546 (1982).
43. J. Schmidt and L. Snow, *WO Patent #00/22032* (2000).
44. G. Herms, *US Patent #3658111* (1970).
45. H. Kameda and S. Inayaki, *US Patent #3978268* (1976).
46. R. Tschudin-Mahrer, *US Patent #4837064* (1989).
47. H. Nou and M. Wanou, *US Patent #5331383* (1994).
48. R. Tschudin-Mahrer, *EP Patent #87118678, US Patent #139465(871230)* (1997).
9. M. D. Bessette and R. B. Jerard, *US Patent #4412962* (1983).
50. P. Kurth, *BOPP Markets and Growth-Development in Technology, PP'94 Applications, Markets and Business Development in Zürich, Switzerland*, (Oct. 4–5, 1994).
51. J. Breil, *LISIM® Linear Motor Simultaneous Stretching Technology, CMM International Conference, Chicago* (April 16, 1997).
52. J. Breil, G. Oedl, and B. Sieber, *Synchronous Linear Drives for Many Secondaries with Open Loop Control, 2nd International Symposium LDIA '98, Tokyo* (April 6–8, 1998).
53. J. Nentwig, *Entwicklungen bei der Simultanreckung vol Folien, Papier + Kunststoff-Verarbeiter 12-98*, S. 22–28.
54. J. Breil, *S-BOPP: Film Enhancement by LISIM® Technology, SP'98 14th Annual World Congress in Düsseldorf, Germany* (October 19–21, 1998).
55. Brückner Maschinenbau and J. Breil, *Specialty Plastics Films 1999, Global Films Resins, Markets, Applications 15th Annual World Congress, Zürich, Switzerland* (December 13–15, 1999).
56. C. F. Bosse and R. R. Kowligi, *US Patent #5512229* (1996).
57. S. B. Levy, *US Patent #4510300 & 4510301* (1985).
58. D. Shannon and S. B. Levy, *et al.*, *US Patent #6099791* (2000).
59. M. L. Tsai, Y. P. Khanna, and J. E. Mackey, *US Patent #5874035* (1999).
60. M. L. Tsai, Y. P. Khanna, J. E. Mackey, R. L. Schneider, and A. Degrassi, *US Patent #5945221* (1999).
61. D. J. Kemmish, *RAPRA Review Reports*, R. Meredith, ed., Vol. 16, Polyetheretherketone, Pergamon Press, Oxford, New York (1990).
62. Review, *Modern Plastics*, **70**, 78 (1993).
63. W. Chinsizikul, T. C. Hsu, and I. R. Harrison, *Polymeric Materials Science & Engineering*, Conference Proceedings, **75**, p. 18 (1996).
64. J. A. Grande, *Modern Plastics*, **57(11)**, 84 (1998).
65. V. Hillyard, *Machine Design*, **12(10)**, 66 (1993).
66. *Plastics & Rubber Weekly*, **1683(4)**, 25 (1997).
67. Y. Wong, *Asian Plastics News*, November, 21 (1999).
68. M.F. Sonnenschein, *J. Applied Polymer Science*, **74(5)**, 1146 (1999).
69. *Sampe Journal*, **33(5)**, 10 (1997).

70. J. Choi and M. Cakmak, *ANTEC 99*, Conference Proceedings, p. 1656 (1999).
71. V. Wigotsky, *Plastics Engineering*, January 2001, p. 24.
72. N. D. Alberola, P. Mele, and C. Bas, *J. Applied Polymer Science*, **64(6)**, 1053 (1997).
73. Review: Engineering Resins, *Modern Plastics*, **70**, 76 (1993).
74. R. Russo, C. D'Aniello, G. Romano, and V. Vittoria, *European Polymer J.*, **36(8)**, 1571 (2000).
75. X. Feng and R. Zhang, *J. Materials Research*, **13(6)**, 645 (1999).
76. R. Russo, V. Capodanno, E. Petrillo, G. Romano, and V. Vittoria, *J. Applied Polymer Science*, **65(13)**, 2635 (1996).
77. E. Krause, G. M. Yang, and G. M. Sessler, *Polymer International*, **46(1)**, 59 (1998).
78. N. Zebouchi, V. Troung, and R. Essolbi, *Polymer International*, **46(1)**, 54 (1998).
79. N. Inagaki, S. Tasaka, T. Horiuchi, and R. Suyama, *J. Applied Polymer Science*, **68(2)**, 271 (1998).
80. Q. Kun and R. Huang, *Polym.-Plast. Technol. Eng.*, **33(2)**, 121 (1994).
81. P. S. Byrd and D. G. Waters, *US Patent #5300338* (1994).
82. "Dynamar," *Plastics News International*, November, 6 (2000).
83. L. M. Sherman, *Plastics Technology*, **46(7)**, 47 (2000).
84. DuPont Press Release, *"A smooth run: proven high-performance dry film lubricant from DuPont now CFC-free: Krytox DF"* (1996).
85. ANTEC 2001 Review, *Plastics Engineering*, July 2001, p. 93.
86. W. G. Kohlman and S. P. Petrie, *Advances in Polymer Technology*, **14(2)**, 111 (1995).
87. M. Cakmak and J. C. Kim, *J. Applied Polymer Science*, **65(11)**, 2059 (1997).
88. R. Gensler, C. J. Plummer, H. H. Kausch, and H. Muenstedf, *J. Materials Science*, **32(11)**, 3037 (1997).
89. S. Bicakci and M. Cakmak, *Polymer*, **39(22)**, 5405 (1998).
90. D. S. McLachlan, M. Blaszkiewicz, and R. E. Newnham, *J. American Ceramics Society*, **73(8)**, 2187 (1990).
91. G. R. Ruschau, S. Yoshikawa, and R. E. Newnham, *J. Applied Physics*, **72(3)**, 953 (1992).
92. O. W. Kaeding, H. Skurk, A. A. Maznev, and E. Mattias, *Appl. Physics*, **A61**, 253 (1995).
93. R. A. Vaia, J. W. Lee, C. S. Wang, B. Click, and G. Price, *Chem. Mater.*, **10**, 2030 (1998).
94. A. Bar-Cohen, *Electronics Cooling*, **6(1)**, 32 (2000).
95. S. Addison, *Electronics Cooling*, **6(1)**, 56 (2000).
96. J. M. Finan, *Plastics Engineering*, May 2000, p. 51.
97. C. P. Wong and R. S. Bollampally, *J. Applied Polymer Science*, **74(4)**, 3396 (1999).
98. D. M. Bigg, *Adv. Polymer Science*, **119**, 1 (1995).
99. Y. K. Godovski, *Adv. Polymer Science*, **119**, 79 (1995).
100. A. Kassiba, M. Tabellout, S. Charpentier, N. Herlin, and J. R. Emery, *Solid State Communications*, **115**, 389 (2000).
101. C-P. Chiu, R. Viswanath, and G. L. Solbrekken, *Semicon International*, **3**, 16 (1999).
102. L. M. Sherman, *Plastics Technology*, **47(6)**, 52 (2001).
103. T. Takahashi, M. Minemura, and T. Ohkawara, *US Patent #5981641* (1999).
104. K. Yamada, T. Takahashi, and K. Isobe, *US Patent #6114429* (2000).
105. K. Yamada, T. Takahashi, and K. Isobe, *US Patent #6136758* (2000).
106. T. Shimizu, M. Watanabe, and T. Iida, *US Patent #6159910* (2000).
107. A. Nakano and T. Hashimoto, *US Patent #6169142* (2001).
108. K. Yamada, K. Isobe, and T. Takahashi, *US Patent #6174841* (2001).
109. C. Latham, *Electronics Cooling*, **6(1)**, 6 (2000).
110. J. A. Barnes, *J. Material Science*, **28(18)**, 4974 (1993).
111. *Plastics & Rubber Weekly*, November 10, 4 (2000).
112. L. C. Sawyer, H. C. Linstid, and M. Römer, *Plastics Engineering*, December 1998, p. 37.
113. *European Plastics News*, **23(7)**, 17 (1996).
114. W. Chinsirikul, T. C. Hsu, and I. R. Harrison, Conference Proceedings: *Polymeric Materials Science & Engineering*, **75**, 18 (1996).
115. S. Kenig, *SPE ANTEC 94* Conference Proceedings, p. 1590 (1994).
116. *Plastics World*, **54 (8)**, 16 (1996).
117. R. W. Lusignea, *Polym. Eng. Sci.*, **39**, 2326 (1999).
118. R. W. Lusignea and J. Perdikoulias, *TAPPI Conference Proceedings, Polymers, Laminations & Coatings*, v1, p. 271 (1997).
119. A. N. Procunin, M. L. Friedman, and G. V. Vinogradov, *Mechanika Polymerov*, **3**, 497 (1971).
120. M. L. Friedman, *Technology of Processing of Crystalline Polyolefins*, Chimia, Moscow (1977).
121. M. L. Friedman, S. L. Peshkovsky, and G. V. Vinogradov, *Polym. Eng. Sci.*, **21**, 755 (1981).
122. R. D. Jester and J. A. Penoyer, *US Patent #5789042* (1998).
123. *Japan Chemical Week*, **38 (1930)**, 3 (1997).
124. M. Onodera, *et al.*, *US Patent #5843562* (1998).
125. C. Edwin, R. D. Jester, and J. A. Penoyer, *US Patent #5885668* (1999).
126. W. Chinsirikul, T. C. Hsu, and I. R. Harrison, *Polym. Eng. Sci.*, **36(12)**, 2708 (1996).
127. L. M. Sherman, *Plastics Technology*, **46(9)**, 37 (2000).
128. *News Materials Japan*, 33 (5/1/2001).
129. *Modern Plastics International*, **31(12)**, 73 (2001).
130. M. L. Friedman, *US Patent #6100341* (2000).
131. J. Spirgatis and J. Wortberg, *Kunststoffe*, **91(5)**, 35 (2001).
132. S. J. Bennison, *et al.*, *Patent # WO 99/58334* (1999).
133. M. L. Friedman and L. F. Laucirica, *Patent # WO 95/26377* (1995).
134. R. Miel, *Plastics News*, **5(14)**, 19 (2001).
135. M. L. Friedman and L. F. Laucirica, *US Patent #5792560* (1998).
136. M. L. Friedman, L. F. Laucirica, and G. T. Visscher, *US Patent #5908704* (1999).
137. M. L. Friedman and G. T. Visscher, *US Patent #6159608* (2000).
138. *High-Performance Composites*, March/April, 12 (1998).
139. M. L. Friedman, *US Patent #5534593* (1996).
140. M. Adamko, M. L. Friedman, and D. Waldenberger, *US Patent #5948517* (1999).
141. G. Marsh, *Materials Today*, **1(4)** (2001).
142. *Asian Plastics News*, **10(17)**, 35 (2000).
143. *Chemtech*, **29(11)**, 7 (1999).
144. *Modern Plastics International*, **29(2)**, 29 (1999).
145. G. Carotennto and L. Nicolais, *Adv. Composite Letters*, **5(3)**, 87 (1996).
146. A. Goel, D. J. Bray, S. C. Martin, and K. A. Blakly, *US Patent #5638251* (1997).
147. K. Fukimoto, M. Yoshikawa, and K. Yasue, *Kobulshi Ronbunshu*, **57(7)**, 233 (2000).
148. Y. Tong, Y. Li, F. Xie, and M. Dong, *Polymer International*, **49(11)**, 1543 (2000).
149. P. Etienne, J. Phalippou, and R. Sempere, *J. Material Science*, **33(15)**, 8, 3999 (1998).
150. T. Callahan and S. G. Iuliano, *EDI Advances, EDI Brochure—"News & Concepts," "Multi-Manifold Coextrusion: Key to Uniformity and Quality in BOPP and BOPET Films"* (Spring 2001).
151. J. D. Moulton, E. L. Healy, and T. Nakahara, *US Patent #6270909* (2001).

152. H. Okada, "*Polymer Alloys & Blends in: Recent Trends in Japanese Industry & Markets*," p. 17, Kansai Research Institute (KRI), Kyoto, Japan (June 2001).
153. R. Allington, D. Porter, and G. Stringer, *J. Defense Science*, **6(1)**, 40 (2001).
154. H. Chizadella, *Applied Optics*, **30(17)**, 3492 (1991).
155. D. J. Brink and M. Lee, *Applied Optics*, **37(19)**, 4212 (1998).
156. O. Graydon, *OLE*, (June, 31 1998).
157. L. T. Kuhn-Spearing, H. Kessler, E. Chateau, and R. Ballarini, *J. Material Science*, **31**, 6583 (1996).
158. J. S. Jennings and N. H. MacMillan, *J. Material Science*, **21**, 1517 (1986).
159. A. Sellinger, P. M. Weiss, A. Nguyen, *et al.*, *Nature*, **394(16)**, 256 (1998).
160. E. Baer, J. J. Cassidy, and A. Hiltner, *33rd IUPAC Intern. Symposium of Macromolecules, Macro-90*, Montreal (July 8–13, 1990).
161. M. Xu and R. V. Lewis, *Proc. Natl. Acad. Sci. USA*, **87**, p. 1720 (1990).
162. *Advances in Material Research in Japan, Phase V*, Kansai Research Institute (KRI), Japan (1998).
163. Maxdem, Inc., Technical Bulletin, *Chemical & Engineering News*, **27**, February, 15 (1993).
164. J. C. Wittman and P. Smith, *Nature*, **352(8)**, 414 (1991).
165. R. Daganig, *Science & Technology*, **10**, 26 (1995).
166. D. Schmidt, J. McCrakin, and C. E. Coburn, *US Patent #4929666* (1990) and *US Patent #5006624* (1991).
167. R. E. Smith, *Proceedings of the 19th International Wire & Cable Symposium*, p. 209, Atlantic City, N.J., (December 1-3, 1970).
168. J. A. Effenberger, K. G. Koerber, and E. C. Lupton, *WO Patent #90009853* (1991).
169. R. A. Sahatjian and M. G. Steckel, *EP Patent #00202996* (1993).
170. P. R. LaCourt, *EP Patent #811483* (1997).
171. P. R. LaCourt, *Japanese Patent #10100340* (1998).
172. P. R. LaCourt, *US Patent #5731088* (1998).
173. D. Shannon, C. Kuo, R. Peterson, and C. McCollam, *US Patent #5552100* (1996).
174. K. M. Nouel and P. S. Fedkiw, *Elechtrochimica/Acta*, **43(16)**, 2381 (1998).
175. A. Lukacs and R. Matsumoto, Kion Corporation, *US Patent #5389588* (1995).
176. R. Hinton, A. Lukacs, J. Jensen, and K. Becker, Kion Corporation, *US Patent #5884688* (1999) & *US Patent #6165551* (2000).
177. *Nanocomposites 2001, First World Congress Proceedings*, Chicago (June 25–27, 2001).
178. *Plastics*, **46(9)**, 20 (1995).
179. *Polymer Science & Technology: News*, **1**, 27 (2000).
180. N. Tessler, G. J. Denton, and R. H. Friend, *Nature*, **382(2)**, 695 (1996).