CARILON® Polymer Blend Strategies, Past, Present and Future

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Summary

The following study involves an analysis of the current blend market and attempts to apply past blend strategies to a blend strategy for CARILON polymer while considering CARILON polymer strengths and weaknesses. Included in this report is a summary table of the results of this study, reports on current blend technologies, CARILON blend ideas with experimental approaches and potential end use markets, and references

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Introduction

The purpose of this study was to evaluate current commercial and non commercial blend strategies and attempt to apply the knowledge gained to an end-use oriented CARILON polymer blend strategy. The idea was to take advantage of CARILON polymer strong points and to assist CARILON polymer where it is weak by blending with other polymers.

Initially the team divided up the "polymer world" into fourteen classifications, e.g., polyolefins, polyamides etc., and assigned each polymer group to a team member for analysis; see the Meeting 1 minutes in the Appendix. The initial analysis was to report on property sets of the base polymers, current blends and reasoning behind the blend strategy, end-uses, compatibilization technology and reactive chemistry, patent ideas for CARILON polymer, and key references. Much of this information is not listed in this report but is available upon request in the form of meeting minutes and interim reports. In addition, a list of CARILON blends that had been studied to date was compiled; refer to the Appendix under the subtitle, CARILON Polymer Literature Survey.

Finally, for the 5th and last meeting, the team reported on potentially viable blend strategies between CARILON and other polymers. These reports are listed in the Appendix under the subtitle of Future Blend Studies with CARILON Polymer. Table 1 is a summary of those reports. Included in Table 1 for each blend are the advantages to CARILON and the advantages to the other component. Also listed, are the compatibilization technology, potential end-uses, competitive resins and a relative ranking for that each blend. The ranking criteria involved evaluating the blends' usefulness to CARILON polymer, likelihood of success, economics, and need in the targeted end-use. The ranking was from 0 to 10 with 10 being the highest rating. Rankings below 4 were not included, which is why all of the polymer classifications are not represented in the summary table.

The economic viability of a blend is a difficult subject to address. In this study there was not a lot of effort to evaluate potential blends from a financial point of view. However, ranking criteria was based loosely on whether a component contributed properties but resulted in cost dilution (highest ranking), e.g., CARILON/polyolefins, a components cost was diluted by CARILON, e.g., Polysulfone/CARILON, the components had equal cost to CARILON (based on $1.60/lb) but improvements in properties, etc. The cost of blending (reactive or otherwise), compatibilizers etc., was not considered.

Finally, Table 1 can be distilled into several polymer groups that should be evaluated for future studies. The list in order of importance (based loosely on ranking criteria) is as follows:

1. Polyolefins - Improve the compatibility with CARILON polymer. Reduce WVTR of CARILON. Reduce oxygen barrier of Polyolefins. Modify mechanical properties.

2. Polyamides - Evaluate as compatibilizers for CARILON polymers and other polymers. Reduce moisture absorbance of Nylons. Modify CARILON and Nylon mechanical properties.

3. Amorphous Polymers - Replace Nylon in Noryl GTX (PPE/Nylon 66/rubber modifier), improve dimensional stability of CARILON, modify mechanical properties of polycarbonates and polysulfones.

4. Impact Modifications - Improve notched Izod at room temperature and low temperatures for CARILON polymer.

References for this study were many but several stand out as exceptional references. These are:

"Specialty Polymeric Blends and Alloys," Skeist Incorporated, Whippany, New Jersey (1991).

Much of the volume, price, and polymer blend property information in this report was taken from the Skeist report. In addition, there was a substantial amount of compatibilization technology reported in the Skeist study.

"Japanese R&D Trend Analysis; Polymer Alloys and Blends," KRI International, Incorporated, Minato-ku, Tokyo (1991)

This study provided useful information on where blend technology may be a few years down the road. Also, it was a great source of ideas for potentially useful CARILON blends.

Table 1. A Summary of the Blend Study

Blend (CARILON WITH:)	Advantages to CARILON	Advantages to Other Component	Compatibilization Technology	Potential End-Use/Competition	Ranking/Comments
NYLON x and NYLON xy	inc.[1] stiffness (Nylon xy), inc. Izod, compatible	dimensional stability, inc. Izod, O_2 barrier, compatible	Nylon end-group driven (NH_2), no compatibilizers, refer to Machado, MRS June 1989, MRS Dec. 1988	fuel tanks, fuel lines/ polyethylene, Selar, Nylon 66, Steel	8/CARILON,Nylon blend as compatibilizers for other systems
NYLON 6 (Bicomponent Fibers)	compatible, softness, processability, cost dilution, UV stability,	lower moisture absorbency, stiffness, good wear properties	none needed	tufted carpet/PP, Nylon 6	4/ may be naturally crimping fiber due to crystallization rates
POLYOLEFINS (Selar Structures, low compatibility)	water barrier, processability, UV stability, cost dilution	stiffness, O_2 barrier, value added	Nylon xy and carboxylated or maleated polyolefins, Novalac/modified POs	film, fuel tank, fuel lines, rigid packaging/PE, Selar, PET, Nylon 66, steel,	8/ semi-compatibilized system,
POLYOLEFINS (Compatible Systems)	water barrier, processability, UV stability, inc. Izod, softness	stiffness for PP impact copolymers, O_2 barrier, creep resistance	Nylon xy and carboxylated or maleated polyolefins, Novalac/modified POs, copolymers of PE and n-vinyl formamide low molecular weight diamines	automotive, outdoor, packaging, broad usage/Nylon (toughened), high stiffness PP copolymers	9/ polyolefins: PP, HDPE, PB, TPO EPDM (toughener), multilayer containers and film could be target for these products
POLYOLEFINS (Bicomponent Fibers)	UV stability, processability, cost dilution, stain resistance, softness	creep resistance, wear resistance, dyeable fibers	Nylon xy and carboxylated or maleated polyolefins, Novalac/modified POs, possibly none needed	tufted carpet fiber, clothing/Nylon 6, PP	4/ polyolefins as an external coating would be more useful in this application
POLYCARBONATES (with an impact modifier)	improve low temp Izod, dimensional stability, retain modulus, low water absorbance, inc thermal endurance	dec.[2] thickness sensitivity, improve chemical resistance	polyurethanes, Dexcarb (a PC/Nylon blend),glutarimide	automotive, electrical, broad usage/Noryl GTX, Xenoy	8/impact modifiers can be polybutadiene or other elastomers, refer to US pat.4880908
POLYCARBONATE AND ABS	improved impact and toughness, wider molding window, cost dilution, dimensional stability	chemical resistance, improve tensile strength	polyurethanes, Dexcarb (a PC/Nylon blend),glutarimide	exterior car body panels, business equipment, housings/Noryl GTX, Xenoy, PPE/HIPS	8/investigate high AN content ABS for better compatibility

1. Increase
2. Decrease

Table 1. (continued)

Blend (CARILON WITH:)	Advantages to CARILON	Advantages to Other Component	Compatibilization Technology	Potential End-Use/Competition	Ranking/Comments
POLYURETHANES	inc. abrasion resistance inc. impact strength; Izod or Gardner, retain chemical resistance, flexibility	inc. tensile strength and flexural modulus	compatibility is dependent on hard segment and soft segment length and composition, refer to TPR199-90, Machado	Automotive, sporting goods, and footwear/TPU, Nylon (toughened), POM & TPU	7/increases in Izod strength with rubber rich polyether based soft segment, inc. in Gardner with rubber poor soft segment, see US patent 4851482
POLYURETHANES AND ABS OR POLYCARBONATE	inc. impact strength, dimensional stability, cost dilution (ABS), chemical resistance, flexibility	-	compatibility is dependent on hard segment and soft segment length and composition	Automotive, medical/ABS & TPU, PC & TPU	7/PC and ABS can control the size of the dispersed urethane phase.
POLYSULFONE	inc. dimensional stability	cost dilution, solvent resistance, strength retention	may not be needed	electrical and aerospace/ polysulfone & PET	4/refer to US patent 4839435 and 4904744
POLYPHENYLENE ETHER	inc. dimensional stability, inc. heat distortion temperature, low water absorbence over Nylon	low water absorbence over Nylon, processability, inc. chemical/solvent resistance	polystyrene - graft - SAN copolymers with high AN content, Kraton FG 1901x, diamines or Nylon 66, maleic anhydride modified PPE, PS copolymers	Automotive body panels and exterior hardware, tool housings/ Noryl GTX, Dimension and Ultranyl	8
POLYVINYLIDENE FLUORIDE	no loss of mechanical properties, inc. chemical and weather resistance, improved continuous use temperature	cost dilution, inc. wear resistance, improved mechanical properties, improved electrical properties	good compatibility, refer to Machado, MRS June 1991	fuel line, fuel related applications, valves, gaskets/Nylon 66, PVDF	6
POLYTETRA-FLUOROETHYLENE AND POLYVINYLIDENE FLUORIDE	improve wear resistance and lubricity, small reduction in mechanical properties, inc. chemical resistance, improved processability	-	PVDF could improve compatibility of PTFE with CARILON	gears, moving parts/ lubricated grades of POM, Nylon, PC, and PBT	5
POLYETHYLENE-TEREPHTHALATE	improve water barrier, cost dilution	improve oxygen barrier, dimensional stability, improve mold ability	may not be needed	stretch blow molded containers, film/PET, Nylon, PP, PE	5 / refer to US patent 4857605

Table 1 (continued)

Blend (CARILON WITH:)	**Advantages to CARILON**	**Advantages to Other Component**	**Compatibilization Technology**	**Potential End-Use/Competition**	**Ranking/Comments**
IMPACT MODIFIERS (BLENDEX, PARALOID, ACRYLOID, HYTREL, PEBAX, etc.)	impact modification, increases in Izod or Gardner or both	-	refer to TPR 199-90	Automotive, appliances, broad applications	7/BLENDEX 338 offered the best balance of properties
POLYOXYMETHYLENE (POLYACETAL)	Lower COF, low water absorption, depending on the compatibilizer, higher modulus and tensile strength	inc. chemical resistance, improved wear resistance, improved impact properties	Poly(vinyl phenol), polyurethane, new technology may be needed, see Machado MRS June 1990	appliance housings, gears, bearings, machinery parts	4/ no cost dilution for either component, high temperatures required to process CARILON would degrade polyacetal, refer to US patent 4880863

APPENDIX

MEETING ONE MINUTES

Minutes to the first Blend Team meeting.

BLEND TEAM MEETING MINUTES

Meeting #1
May 13, 1992

Participants: John Flood (JEF)
John Kastelic (JRK)
Don Weinkauf (DHW)

Absent: Michelle Londa (ML)

Agenda:

1. Establish Charter
2. List current blends strategies
3. Individual assignments
4. Establish timeline
5. List resources

1. Establish Charter

JEF opened the meeting with the proposed charter.

"We will evaluate current and past blends studies with CARILON® polymer for insight into potential end-use applications. In addition, we will review the open blend literature in order to aid in the creation of a blend strategy and program starting in 1992."

The charter was approved by a vote of 3-0 without modification.

2. List Current Blend Strategies

It was agreed that the blend strategy for CARILON polymer will be strongly influenced by polymer needs and strengths. Our first assignments would then be to assemble a list of "Needs and Strengths" for CARILON polymer. It was agreed that Paul Byrd and Dick Danforth might be excellent resources for such a list, since they have had the most contact with customers. Needs and strengths necessary for other markets can be assembled from a review of the literature.

Action Items: (All) Assemble needs and strengths list for CARILON polymer.

(JRK) Get Paul Byrd's list of Strengths/Needs and also a copy of the 35 questions that customers have asked about CARILON polymer.

3. Individual Assignments

The group discussed for a few moments how the Blends Review would be approached. While the charter is "end use" focused, it was agreed that the best way to research the area would be to examine the blends derived from individual polymers. A list of polymers was assembled with the assistance of the textbook by Utracki.

CARILON polymer (ML and JEF)
PVC (DHW)
ABS, Butadiene copolymers (JRK)
PPO (PPE) (DHW)
Polycarbonate (ML)
Polysulfone, Polyarylate, PPS (ML)
PVDF, Teflon (JRK and DHW)

Polyolefins (DHW and JEF)
PS (JRK)
Polyamides (JEF)
Polyesters (JRK)
POM (JEF)
TPU (ML)
PMMA, Acrylates (DHW)
Phenolics - ML

The initials next to each polymer family denote the individual assignments of the blends team.

The information to be assembled for each of the above families should include:

1. Property Sets
2. Current Blends with reasoning behind blend strategy
3. End Uses
4. Compatibilization Technology and Reactive Chemistry
5. Patent Ideas with CARILON polymer
6. Key References

The format of the presentations should follow the above list.

4. Timeline

May 27, 1992	Format Meeting to discuss early results and problems.
June 19, 1992	Information Meeting to present compiled information. Presentations with view graphs.
July 8, 1992	Blend Strategy meeting. (D.R. Paul in attendance)
Mid July, 1992	Interim Report to D.S. Brath
Sept, 1992	Final Report to D.S. Brath

5. Resources

Dreams
Lab Notebooks
CARILON polymer Field Presentation (Byrd, Danforth)
WRC Library
Research Notes
Paul Byrd
Dick Danforth
Nick Michaels
Don Brath
Bill Gergen
Dale Handlin
Joe Machado
KSLA
Don Paul

In addition, JEF noted that he will assemble a temporary blends library in his office with key references on blends and blends strategies.

Minutes submitted by D. H. Weinkauf

DHW/ddb

CARILON POLYMER LITERATURE SURVEY

The following list includes most of the blend work done to date with CARILON polymer. The database is evergreen and will continue to be updated as we make corrections, locate work done previously that was not listed and do new work.

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
APATITE / CARILON EP	LR20279	121-122	George/ Coker	
ABS (UL CONTINUOUS TEST)	MRS AUG 1988		George /Coker	
ABS / EP CARILON	LR20279	68	George	
ABS / NUCREL / EP CARILON	LR20279	68	George	
ABS / POLYETHYLENE / EP CARILON	LR20279	68	George	
AC OXIDIZED HDPE/ CARILON EP	LR20279	152	George/ Coker	
ACRYLIC SHELL CORE MODIFIER / CARILON	USPAT.5132360		MACHADO AND GERGEN	
ACRYLOID KM680 / EP CARILON	WRC 199-90		Machado and Gingrich	(Acryloid is an MBS modifier from G. E.)
AEPD	LR20240		WATERS (PROCESSING AID STUDY)	2-Amino-2-Ethyl-1,3-Propanediol
ALKALENE CARBONATE /CARILON (PLASTICIZER)	US PAT. 4775708		SMUTNY	
ALKALINE EARTH METAL CARBONATE / CARILON	US PAT.4761449		LUTZ	
ALKALINE EARTH METAL HYDROXIDE / CARILON (FLAME RETARDANT)	USPAT. 4885328		DANFORTH AND SMITH	
Alkaterge-E	LR20240		WATERS (PROCESSING AID STUDY)	2-Heptadecenyl-4-Ethyl-2-Oxazoline-4-Methanol
Alkaterge-T	LR20240		WATERS (PROCESSING AID STUDY)	2-Heptadecenyl-4,4(5H)-Oxazoledimethanol
ALUMINUM PHENOXIDE / CARILON (STABILIZED)	USPAT.4950703		SMUTNY	
Aluminum Stearate	LR20240		WATERS (PROCESSING AID STUDY)	Aluminum distearate
ALUMINUM STEARATE / CARILON	USPAT. 495555		SMUTNY AND LUTZ	
Amgard EDAP (1)	LR20240		WATERS (PROCESSING AID STUDY)	Ethylenediamine Phosphate
Amgard TBEP	LR20240		WATERS (PROCESSING AID STUDY)	Tri (Butoxyethyl) Phosphate
AMINE (AROMATIC) / CARILON (STABILIZER)	US PAT. 4795774		KLUTTZ	
AMINES (POLAR LUBRICATING COMPOUNDS) / CARILON	USPAT.5115009		SMUTNY ET. AL.	
ANALOG CALORIMETRY TO SCREEN CARILON	WRC310-89		FRENCH	
ANILINE SUBSTITUTED TRIAZINES /CARILON	USPAT.5019614		KLEI	
Antiblaze	LR20240		WATERS (PROCESSING AID STUDY)	Dimethyl methylphosphonate
APATITE / ALUMINA HYDROGEL / CARILON	USPAT.5122565		GEORGE	
APATITE / CARILON EP	MRS SEPT. 1990		GEORGE, COKER,	
APATITE / CUPRIC CHROMITE / CARILON	USPAT.5077333		GEORGE	
APATITE / EP CARILON	LR20279	107	George	
APATITE / GLASS FIBERS / CARILON	USPAT.5122564		GEORGE	
APATITE / MERCAPTOBENZIMIDAZOLE / CARILON	USPAT.5115003		GEORGE	
APATITE / ZINC ALUMINATE / CARILON	USPAT.5066701		GEORGE AND SLAUGH	
APATITE FILLER / CARILON	USPAT. 5021496		MACHADO AND GEORGE	
APATITE/ CARILON EP			GEORGE, COKE, VINSON	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
APATITE/ CARILON EP (STABILIZATION)	MARCH 1990?		GEORGE, COKER, CHUAH, STEWART	
BARIUM OR TITANIUM ACETYLACETONATE /	USPAT. 4954552		SMUTNY	
Barium Stearate	LR20240		WATERS (PROCESSING AID STUDY)	Barium Stearate
BASIC ADDITIVE / CARILON (FORCES CROSSLINKS)	USPAT.5079340		AUERBACH AND HANLEY	
Bee's Wax (1)	LR20240		WATERS (PROCESSING AID STUDY)	
BENZOQUINONE (ALKYLATED) / CARILON	USPAT. 4988754		KLUTTZ	
BEXLOY	WRC1859		GEORGE, COKER, BYRD, DANFORTH, MACHADO	(AMORPHOUS NYLON)
BEXLOY (GENERAL PROPERTIES)	MRS DEC 1987	56	GEORGE, DANFORTH, COKER (AMORPHOUS NYLON)	
BIAXIALLY ORIENTED CARILON FILM	USPAT.5073327		KLINGENSMITH AND CAMPBELL	
BLENDEX /WALLASTONITE/GLASS/FOR FUEL	LR20279	188	George Coker	
BLENDEX 310 / EP CARILON	WRC 199-90		Machado and Gingrich	(Blendex is an ABS modifier)
BLENDEX 336 / EP CARILON	WRC 199-90, MRS MAY 1990		Machado and Gingrich	
BLENDEX 338 / CARILON	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
BLENDEX 338 / EP CARILON	WRC 199-90		Machado and Gingrich	
Brij 30	LR20240		WATERS (PROCESSING AID STUDY)	Polyoxyethylene 4 lauryl ether
BUTADIENE - ACRYLONITRILE COPOLYMER / CARILON EP	MRS AUG. 1990		Machado/ Lee	
Butanediol (BID)	LR20240		WATERS (PROCESSING AID STUDY)	1,4 Butanediol
CALCIUM CARBONATE / CARILON EP	MRS MAY 1989.	138	GEORGE, COKER	
CALCIUM HYDROXYAPATITES (SEE APATITE)				
CALCIUM PHOSPHATES (SEE APATITE)				
Calcium Stearate EA Food Grade	LR20240		WATERS (PROCESSING AID STUDY)	
CAPRON(KEN-REACT COUPLING AGENT) CARILON EP	LR20279	140	George/Coker	
CARBON DIOXIDE / CARILON	USPAT. 5006638		KLUTTZ	
CARBON FIBERS/ CARILON EP	LR20279	173	George/ Coker	
CARBOXYLATED , HYDROGENATED BLOCK COPOLYMER / CARILON	US PAT. 5064901		MACHADO	
CARILON E / CARILON EP	MRS JAN 1991	70	GEORGE, COKER	
CARILON EAS NUCLEATING AGENT IN CARILON EP	LR20279	176	George / Coker	
CARILON EP BLENDS (SCREENING STUDY)	WRC155-88		LUTZ (EVERYTHING KNOWN TO MANKIND WAS BLENDED WITH CARILON)	
CARILON EP (AUTOMOTIVE BODY PANELS)	WRC1859		GEORGE, COKER, BYRD, DANFORTH, MACHADO	
CARILON EP (FORD FENDER TEST)	MRS DEC 1987	56	GEORGE, DANFORTH, COKER	
CARILON EP (PAINTABILITY / MODULUS Vs TEMP.)	MRS MAY 1988	107	GEORGE, WILLIAMS, COKER	
CARILON EP (PAINTABILITY)	MRS MAY 1990	118	ADAMSKI, YEATES, GEORGE	
CARILON EP (UL CONTINUOUS TEST)	MRS AUG. 1988		George /Coker	
CARILON THERMOPLASTIC FIBERS	USPAT. 5045258		VAN BREEN, VAN DEURSEN, AND WETSER	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
Carnauba Wax (1)	LR20240		WATERS (PROCESSING AID STUDY)	Refined Carnauba Wax
CELLULOSE / CARILON	USPAT. 4983649		SMUTNY	
Ceresin Wax (1)	LR20240		WATERS (PROCESSING AID STUDY)	Refined Mineral Hydrocarbon Wax
Cerium Stearate	LR20240		WATERS (PROCESSING AID STUDY)	Cerium Stearate
CLAY / CARILON EP	MRS MAY 1989.	138	GEORGE, COKER	
COPOLYESTER / CARILON	US PAT.4818798		GERGEN	
CPH-31-H	LR20240		WATERS (PROCESSING AID STUDY)	
Crodamide 203 DS2031	LR20240		WATERS (PROCESSING AID STUDY)	Oleyl Palmitamide
Crodamide 212 Beads	LR20240		WATERS (PROCESSING AID STUDY)	N-Octadecanyl-Cis-13-Docosenoamide
CUPRIC CHROMATE / CARILON EP (STABILIZATION)	MARCH 1990?		GEORGE, COKER, CHUAH, STEWART	
DIAMINE (AROMATIC) / CARBON BLACK / CARILON	USPAT. 4954548		KINGENSMITH	
DIHYDROCARBYLDITHIOCARBAMATE SALT / CARILON	USPAT. 4994511		KLUTTZ	
DOP	LR20240		WATERS (PROCESSING AID STUDY)	Dioctyl Phthalate; bis(2-Ethylhexyl) Phthalate
Duron 180	LR20240		WATERS (PROCESSING AID STUDY)	
E CARILON	LR20279	89, 90 91, 92, 93, 94, 96, 97, 98, 111	George	
E CARILON / EP CARILON	LR20279	53,55,54,55,56,57,59,63,71,72,73,76,77,83,86	George	
EHTYLENE - ACRYLIC ACIDS (SEE PRIMACOR, NUCREL, SURLYN)				
ELVAX/ CARILON EP	LR20279	161	George/ Coker	
EP CARILON	LR20279	92, 93, 94, 95, 96, 97, 98, 111, 114	George	
Epolene C-16	LR20240		WATERS (PROCESSING AID STUDY)	Modified (maleated?) Polyethylene
Epolene E-43P Wax	LR20240		WATERS (PROCESSING AID STUDY)	Maleated Polypropylene
ESB Wax	LR20240		WATERS (PROCESSING AID STUDY)	N,N'-Ethylene Bisstearamide
ESTANE 58133 / EP CARILON	WRC 199-90, MRS MAY 1990		Machado and Gingrich	(Estane is a polyurethane-b-ester from Goodrich)
ESTANE 58881 / EP CARILON	WRC 199-90		Machado and Gingrich	
ESTERS (POLAR LUBRICATING COMPOUNDS) / CARILON	USPAT.5115009		SMUTNY ET. AL.	
ETHYLENE - ACID COPOLYMER / OXY-BRIDGED ZINC-ALUMINUM / CARILON	US PAT. 4999399		SMUTNY	
ETHYLENE - ACRYLIC ACID COPOLYMER / CARILON	WRC8-89		GEORGE, COKER (SURLYN, NUCREL, PRIMACOR)	
ETHYLENE - ACRYLIC ACID COPOLYMER / KRATON 1901X / CARILON EP	WRC8-89		GEORGE, COKER (SURLYN, NUCREL, PRIMACOR)	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
ETHYLENE ACID COPOLYMER / ZINC ALUMINATE / CARILON	USPAT. 5028652		SMUTNY AND SLAUGH	
ETHYLENE-CARBOXYLIC ACIDS (ALSO SEE PRIMACOR, NUCREL, SURLYN)	MRS JUNE 1989	120	GEORGE, COKER, BYRD, AND TITUS (FLAME SPRAYING)	
ETHYLENE-PROPYLENE COPOLYMER / CARILON	LR20882	16	FLOOD AND CLASBY	MW EFFECT
EVA/ CARILON EP	LR20279	159	George/ Coker	
EVAL F / EP CARILON	WRC 199-90		Machado and Gingrich	(EVA copolymer from Evalca)
EXXOLOR RUBBER/ CARILON EP	LR20279	143	George / Coker	
FLAME SPRAYING CARILON	US PAT.4861675		GEORGE	
Flexol Plasticizer LOE	LR20240		WATERS (PROCESSING AID STUDY)	
Flexricin P-8	LR20240		WATERS (PROCESSING AID STUDY)	Glyceryl tri(acetyl risoleate
FLUORINATED CARILON	USPAT. 4879358		KASTELIC	
Fryol 6	LR20240		WATERS (PROCESSING AID STUDY)	Dimethyl N,N-Bis (2-Hydroxyethyl) Aminomethyl Phosphonate
Fyrol 76	LR20240		WATERS (PROCESSING AID STUDY)	Polyunsaturated Vinyl Phosphate Ester
GLASS / APATITE / CARILON EP	MRS APRIL 1991	85	George /Coker	
GLASS / CARILON (GLASS SCREENING)	WRC252-89		GEORGE, COKER	(GLASS - 492AA, 408AA, 497DB, 415CA, 457)
GLASS / CARILON EP	MRS JUNE 1987	30	GEORGE, COKER	
GLASS / CARILON EP	WRC12-88		GEORGE, COKER	
GLASS / CARILON EP (AUTOMOTIVE BODY PANELS)	WRC1859		GEORGE, COKER, BYRD, DANFORTH, MACHADO	
GLASS / CARILON EP (LONG FIBER)	AMGR.86.352		GILLEMANS	
GLASS / EP CARILON (FORD FENDER TEST)	MRS DEC 1987	56	GEORGE, DANFORTH, COKER	
GLASS / NYLON / CARILON EP	WRC252-89		GEORGE, COKER	
GLASS / PRIMACOR / NYLON / CARILON EP	WRC252-89		GEORGE, COKER	
GLASS FIBER (AMINOSILANE SIZING AND POLYURETHANE OR EPOXY FILM FORMER) / CARILON	USPAT. 5034431		HANLEY	
GLASS FIBER /CARILON (SHEET)	US PAT.4861428		VAN BREEN AND GILLEMANS	
GLASS FIFERS (ISOCYANATE SIZING) / CARILON	USPAT.5114992		HANLEY	
GLASS FILLED EP CARILON	MRS JAN 1991		Machado and Gingrich	
GLASS FILLED EP CARILON	LR20279	85, 100, 107	George	
GLASS FILLED NYLON 6 AND 66 IN CARILON EP	LR20279	129-130	George/ Coker	
GLASS, NYLON66 / CARILON EP (LONG GLASS NYLON)	MRS MAY 1991	93	GEORGE, COKER	
HEXENE-PROPYLENE COPOLYMER / CARILON	LR20882	18	FLOOD AND CLASBY	MW EFFECT
Hostalub WE 4 Powder	LR20240		WATERS (PROCESSING AID STUDY)	Montan Wax Acid, Ester Mixture
HYDROBENZOTRIAZOLES / CARILON	USPAT.5019614		KLEI	
HYDROXYAPATITE (SEE APATITE)				

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
HYDROXYBNEOPHENONES / CARILON	USPAT.5019614		KLEI	
HYTREL / CARILON EP (INJECTION MOLDING PARAMETERS)	MRS JAN 1990	206	MACHADO, GEORGE, COKER, GINGRICH	
HYTREL / EP CARILON	WRC 199-90, MRS MAY 1990		Machado and Gingrich	(Hytrel 4056 is a pol;yester-b-ether from DuPont)
Kan-React LICA 38	LR20240		WATERS (PROCESSING AID STUDY)	Titanium IV Neoalkanolato, Tris (diisooctyl) Pryophosphato-o
Kantstik 139	LR20240		WATERS (PROCESSING AID STUDY)	Mixed Fluorocarbon, Polyolefins, Phosphate esters
Kantstik FX-9	LR20240		WATERS (PROCESSING AID STUDY)	Complex Organic Polymer and Esters
Kenplast ESI	LR20240		WATERS (PROCESSING AID STUDY)	Biscumylphenyl Isophthalate
KG1901X /GLASS OR MICA FILLED SYSTEMS	LR20279	129-130	George/ Coker	
KRATON / CARILON	US PAT. 4866128		GERGEN AND LUTZ	
KRATON 1901 X / NUCREL / CARILON EP	MRS APRIL 1991	89	George	
KRATON 1901X / ACID FUNC. PP / CARILON EP	MRS FEB 1991	105	Gerlowski / George / Kinneberg	
KRATON 1901X / CARILON	US PAT. 4868242		GEORGE AND GERGEN	
KRATON 1901X / CARILON	USPAT. 4904728		GEORGE	
KRATON 1901X / CARILON E	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
KRATON 1901X / CARILON EP	WRC8-89		GEORGE, COKER	
KRATON 1901X / CARION EP	MRS OCT 1988	159	GEORGE, COKER	
KRATON 1901X / NUCREL 535 / CARILON EP	MRS JAN 1991	62	GEORGE, KINNEBERG, COKER, PECK	
KRATON 1901X/ NUCREL/ CARILON EP	LR20279	118-119	George / Coker	
KRATON D / SURLYN / EP CARILON	LR20279	65,82,109	George	
KRATON D / NUCREL / EP CARILON	LR20279	65,82	George	(Nucrel is an ethylene-methacrylic acid copolymer)
KRATON G1901X / NUCREL / CARILON EP (FENDER)	MRS JUNE 1988	40	GEORGE, COKER	
Kronitex 100	LR20240		WATERS (PROCESSING AID STUDY)	Mixed Isopropylphenyl Phenyl Phosphate
LAMINAR STRUCTURE FOR WVTR	USPAT.5077385		GERLOWSKI AND KASTELIC	
LIQUID CRYSTAL POLYMER / CARILON EP	LR20279, MRS JAN 1989	141	George/ Coker,	
LIQUID CRYSTAL POLYMER / E CARILON	LR20279	55	George	
LIQUID CRYSTAL POLYMER / KRATON 190H / NUCREL / EP CARILON	LR20279	52,53, 54, 55, 56,57,87	George	
Lithium Stearate #306	LR20240		WATERS (PROCESSING AID STUDY)	Lithium Salt of Commercial Stearic Acid
Loxiol G33	LR20240		WATERS (PROCESSING AID STUDY)	Ester of Fatty Acids and Fatty Alcohols
Loxiol HOB7131	LR20240		WATERS (PROCESSING AID STUDY)	Glycerol Monostearate
Loxiol VGS1877	LR20240		WATERS (PROCESSING AID STUDY)	Calcium Soap
Luwax EVA 2	LR20240		WATERS (PROCESSING AID STUDY)	Ethylene-Vinyl Acetate Copolymer

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
MAGNESIUM OXIDE / ALUMINA / CARILON	USPAT.5126496		SLAUGH	
Magnesium Stearate D	LR20240		WATERS (PROCESSING AID STUDY)	Mangnesium Salt of Commercial Stearic AcidMagnesium Salt of Commercial Stearic Acid
MALEIC ACID / EP CARILON	LR20279	65	George	
MERCAPTONBENZIIMIDAZOLE / CARILON EP (STABILIZATION)	MARCH 1990?		GEORGE, COKER, CHUAH, STEWART	
MICA / APATITE / CARILON EP	MRS APRIL 1991	85	George /Coker	
MICA / CARILON EP	MRS NOV 1988, MRS JAN 1990	71, 197	George /Coker, MACHADO, GEORGE, GINGRICH COKER	
MICA / CARILON EP	MRS MAY 1989.	138	GEORGE, COKER	
MICA / CARILON EP	LR20279	107	George	
MICA / FIBERGLASS / NUCREL / CARILON EP (FENDER)	MRS JUNE 1988	40	GEORGE, COKER	
MICA / GLASS / CARILON	USPAT. 4880865		GEORGE	
MICA / GLASS / CARILON EP	MRS JAN 1991	100	GEORGE, COKER	
MINERAL (ALSO SEE MICA, WOLLASTONITE, TALC)				
MINERAL FILLED CARILON	US PAT4851470		GEORGE	
Mixed Normal Alkyl Phthalate	LR20240		WATERS (PROCESSING AID STUDY)	1,2-Benzenedicarboxylic acid
Mold Wiz AZN	LR20240		WATERS (PROCESSING AID STUDY)	Complex Mixture of Organic Phosphate esters in Combination with Otherwise Modified Fatty Acids in Aerosol Propellant.
Mold Wiz INT-EQ6	LR20240		WATERS (PROCESSING AID STUDY)	Condensation Product of Synthetic Resins, Glycerides & Organic Acid Derivatives with Copolymers of Organic Phosphate Esters in an Intimate Combination with Otherwise Modified Fatty Acids
Molybdenum Disulfide	LR20240		WATERS (PROCESSING AID STUDY)	Molybdenum Disulfide
Monoplex S75	LR20240		WATERS (PROCESSING AID STUDY)	Epoxidised Soybean Oil
NORYL GTS	WRX1859		GEORGE, COKER, BYRD, DANFORTH, MACHADO (PPO/NYLON)	
NORYL GTX (GENERAL PROPERTIES)	MRS DEC 1987	56	GEORGE, DANFORTH, COKER (NYLON, PPO BLEND)	
NORYL GTX (PAINTABILITY / MODULUS Vs TEMP.)	MRS MAY 1988	107	GEORGE, WILLIAMS, COKER	
NOVALAC RESINS / CARILON EP REACTOR POWDER	LR20279	166	George/ Coker	
NOVOLAC / CARILON EP	MRS JUNE 1991, MRS MAY 1991		Machado / Gingrich / French / Westbrook / Kinneberg,	Novolac = alkyl substituted phenol formaldehyde polymers
NUCREL / CARILON	USPAT. 4874819		GEORGE, LUTZ, SMUTNY	(Nucrel = ethylene acrylic acid copolymer)

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
NUCREL / CARILON (FLAME SPRAY COATING)	USPAT.4985278		GEORGE	
NUCREL / CARILON EP	MRS APRIL 1991	89	George	
NUCREL / GLASS FIBERS / CARILON	USPAT. 4874801		GEORGE, DANFORTH, BYRD	(Nucrel = ethylene acrylic acid copolymer)
NUCREL / TEREPTHALIC ACID / EP CARILON	LR20279	65,82	George	
NUCREL 535 / NYLON 66 / CARILON EP	MRS MAR. 1989		Machado/Gingrich/Gergen	
NYLON (AMORPHOUS) -SEE BEXLOY				
NYLON (AMORPHOUS) / CARILON	USPAT.4960838		GERGEN AND HART	
NYLON (AMORPHOUS) / CARILON	USPAT.5084518		GEORGE AND KORCZ	(NUCREL MAY BE A COMPONENT OF THIS PATENT)
NYLON (SUPERTOUGH) / CARILON	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
NYLON / ABS ALLOY (SEE TRIAX)				
NYLON / CARILON	US PAT.4839437		GERGEN AND LUTZ	
NYLON / CHOPPED GLASS/ CARILON EP	LR20279	190	George/ Coker	
NYLON / KRATON / OLEFIN-CARBOXYLIC ACID COPOLYMER / CARILON	USPAT. 5039743		MACHADO	
NYLON / NUCREL / GLASS FIBER / CARILON	USPAT.5068289		GEORGE AND GERGEN	
NYLON / OLEFIN-CARBOXYLIC ACID COPOLYMER / CARILON	USPAT. 5043389		GERGEN, MACHADO, WATERS, GINGRICH	
NYLON / POLYPROPYLENE / EP CARILON	LR20279	53,59,63,73,74,75,83	George	
NYLON / POLYPROPYLENE/E CARILON	LR20279	63	George	
NYLON 6 / CARILON	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
NYLON 66 (ZYTEL 103 HS-L) / KRATON G1901X / CARILON EP	MRS MAY 1990		Machaco / Gingruch / Campbell	
NYLON 66 / BLENDEX 338 / CARILON E	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
NYLON 66 / CARILON	LR20882	35	FLOOD, LONDA, GINGRICH AND COKER	
NYLON 66 / KRATON FG1901X / CARILON EP	MRS JUN 1990		Machado/Gingrich	
NYLON 66 SUPER TOUGH (UL CONTINUOUS TEST)	MRS AUG 1988		George /Coker	
NYLON 66/CARILON EP	MRS DEC. 1988, MRS JUN. 1989,		Machado/Gingrich	
OK 139	LR20240		WATERS (PROCESSING AID STUDY)	Microcrystalline Wax
OLEFIN - CARBOXYLIC ACID COPOLYMER (SEE NUCREL, PRIMACOR, SURLYN)				
OLEFIN-CARBOXYLIC ACID COPOLYMER /METAL SALT / CARILON	USPAT.5071916		GERGEN AND LUTZ	
ORGANO HALIDES / CARILON (FLAME RETARDANTS)	USPAT.4885318		DANFORTH AND SMITH	DECO BROMO
OXIDIZED HDPE/CARILON EP	LR2O279	105-106	George/Coker	
PAINT SYSTEMS (AUTOMOTIVE)	MRS MAY 1989	143	GEORGE, COKER	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
PARALOID XL-3691 / EP CARILON	WRC 199-90		Machado and Gingrich	(Paraloid is an MBS modifier from Rohm and Haas)
Paraplex G25	LR20240		WATERS (PROCESSING AID STUDY)	Polyester Sebacate
Paraplex G30	LR20240		WATERS (PROCESSING AID STUDY)	Mixed Dibasic Acid Polyester
Paraplex G40	LR20240		WATERS (PROCESSING AID STUDY)	Polyester Adipate
Paraplex G56	LR20240		WATERS (PROCESSING AID STUDY)	Polyester Adipate
PBT / SAN/ PRIMECOR / EP CARILON	LR20279	68, 69	George	
PEBAX / 2533 / TALC / CARILON EP	MRS JAN 1990		Machado / Gingrich / George	
PEBAX / NUCREL TO DEC. WVTR	LR20279	131, 141	George/ Coker	
PEBAX / NUCREL / CARILON EP	MRS APRIL 1991	89	George	
PEBAX / TALC / CARILON EP (INJECTIN MOLDING PARAMETERS)	MRS JAN 1990	206	MACHADO, GEORGE, COKER, GINGRICH	
PEBAX 2533 / EP CARILON	WRC 199-90, MRS MAY 1990, MRS JAN 1990		Machado and Gingrich	(Pebax is a polyamide-b-ether from Atochem)
PEBAX 4033 / EP CARILON	WRC 199-90		Machado and Gingrich	
PEBAX/ NUCREL/ CARILON EP	LR20279	118-119	George/ Coker	
PEBAX/ NUCREL/CARILON EP	LR20279	141	George/ Coker	
PEBAX/ PP5520/ CARILON EP	LR20279	118-119	George/Coker	
PHENOL FORMALDEHYDE POLYMER (SEE NOVOLAC)				
PHENOLIC BLENDS/CARILON EP DEC. WVTR	LR20279	148-149	George/ Coker	
PHENOLICS / CARILON	USPAT.5082885		KLUTTZ AND SYRIER	
Phosflex 71-B (1)	LR20240		WATERS (PROCESSING AID STUDY)	Butylated Triphenyl Phosphate Ester
PHOSPHONATE ESTER / TEFLON / CARILON	USPAT. 5030674		NOTORGIACOMO	
Plasthall ESO	LR20240		WATERS (PROCESSING AID STUDY)	Epoxidized Soybean Oil
Plasthall P550	LR20240		WATERS (PROCESSING AID STUDY)	Polyester Gluterol
Plasthall TOTM	LR20240		WATERS (PROCESSING AID STUDY)	1,2,4-Benzenetricarboxylic acid. Tris (2-ethylhexyl) ester
Plastisan B	LR20240		WATERS (PROCESSING AID STUDY)	
Pliabrac 519 (1)	LR20240		WATERS (PROCESSING AID STUDY)	Triaryl Phosphate Esters
POLY (TETRAFLUOROETHYLENE) SEE TEFLON				
POLY(2-OXAZOLINE) / CARILON	US PAT.4826926		LUTZ	
POLY(ALPHA-OLEFIN) / CARILON	US PAT.4816514		LUTZ	
POLY(VINYLPYRIDINE) / CARILON	US PAT.4824910		LUTZ	
POLYACETAL / CARILON EP	US PAT.4816530		LUTZ	
POLYACETAL (UL CONTINUOUS TEST)	MRS AUG. 1988		George /Coker	
POLYACETAL / CARILON	USPAT. 4880863		LUTZ AND SMUTNY	
POLYACETAL / POLYVINYL PHENOL	MRS JUN. 1990		Machado/ Gingrich	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
POLYACRYLIC ACID / NYLON 66 / CARILON EP	MRS MAR. 1989		Machado/Gingrich/Gergen	
POLYAMIDE (SEE NYLON)				
POLYAMIDE-ETHER (SEE PEBAX)				
POLYBOND / PP5520/ CARILON EP	LR20279	141	George/ Coker	
POLYBUTYLENE / CARILON	LR20882	23	FLOOD AND CLASBY	MW EFFECT
POLYBUTYLENE (ALSO SEE POLY(ALPHA-OLEFIN))				
POLYBUTYLENE / EP CARILON	LR20279	26, 27,28,29,30,32,33,34,35,36,37,38,43,48,50,61	George	
POLYCARBONATE / CARILON	USPAT.4880908		LUTZ AND GERGEN	
Polycizer DOTP	LR20240		WATERS (PROCESSING AID STUDY)	Bis (2-ethylhexyl) terephthalate
POLYDIOXOLANES / CARILON	US PAT.4826932		WONG	
POLYESTER (ALSO SEE COPOLYESTER)				
POLYESTER / CARILON	US PAT.4857605		LUTZ	
POLYETHER / CARILON EP	MRS MAY 1991		French / Machado	
POLYETHER ESTERAMIDE / CARILON	USPAT. 4874825		GERGEN	
POLYETHER ESTERAMIDE POLYMERS / FILLER / CARILON	USPAT.5102942		MACHADO AND GEORGE	
POLYETHYLENE	LR20279	65,68,81,82,105,106,108,109	George	
POLYETHYLENE (ALSO SEE POLY(ALPHA-OLEFIN))				
POLYETHYLENE / KRATON D / EP CARILON	LR20279	68	George	
POLYETHYLENE GLYCOL / NYLON 66 / EP CARILON	LR20279	70	George	
POLYETHYLENE OXIDE / NYLON 66 / EP CARILON	LR20279	70	George	
POLYMETHACRYLONITRILE HOMOPOLOLYMER / CARILON EP	MRS JAN 1990		Machado / French / Grebowicz	
POLYOXYMETHYLENE (SEE POLYACETAL)				
POLYPHENYLENE OXIDE (PS MODIFIED) / CARILON	USPAT.5084515		GERGEN	
POLYPHENYLENESULFIDE / EP CARILON	LR20279	65,82	George	
POLYPHOSPHONATE / EP CARILON	LR20279	68	George	
POLYPROPYLENE (5348) / ACID FUNC. PP / CARILON	MRS FEB 1991	105	Gerlowski / George / Kinneberg	
POLYPROPYLENE (5520) / KRATON 1901X / CARILON	MRS APRIL 1991	89	George	
POLYPROPYLENE (5520) / PEBAX / CARILON EP	MRS APRIL 1991	89	George	
POLYPROPYLENE (ALSO SEE POLY(ALPHA-OLEFIN))				
POLYPROPYLENE / CARILON	LR20882	17	FLOOD AND CLASBY	MW EFFECT
POLYPROPYLENE / CARILON EP	MRS OCT 1990	180	GEORGE, COKER, BYRD	
POLYPROPYLENE / EP CARILON	LR20279	29,31,42,49,50,51,59,60,62,101,102,103,116	George	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
POLYSTYRENE (MALEATED) /CARILON	US PAT.4814378		LUTZ	
POLYSULFONE (OLIGOMER) / CARILON	USPAT. 4904716		GERGEN AND LUTZ	
POLYSULFONE / CARILON	USPAT. 4904744		GERGEN AND LUTZ	
POLYSULFONE / CARILON	US PAT.4839435		GERGEN	
POLYURETHANE / CARILON	USPAT.4851482		DANFORTH, HANDLIN, GERGEN, AND LUTZ	
POLYURETHANE / CARILON (WIRE COATING)	USPAT.4935304		DANFORTH	
POLYURETHANE / EP CARILON	LR20279	58	George	
POLYVINYL PHENOL / CARILON	US PAT.4812522		HANDLIN	
POLYVINYL ALCOHOL / CARILON	US PAT. 4866122		GERLOWSKI, KASTELIC, AND LUTZ	
POLYVINYLIDENE CHLORIDE / CARILON (LAYERED STRUCTURE)	USPAT.4996086		GERLOWSKI, KASTELIC, AND KORCZ	
POLYVINYLIDENE FLUORIDE / CARILON EP	MRS JUNE 1991		Machado / Kinneberg, Gingrich	
POLYVINYLIDINE FLUORIDE / CARILON	US PAT.4818786		GERGEN, LUTZ	
PP5520 / KG1901X/ KG1651/CARILON EP	LR20279	121-122	George/ Coker	
PP5520/ KRATON 1901X/ CARILON EP	LR20279	118-119	George/Coker	
PRIMACOR 1430 / CARILON EP	MRS OCT. 1987	202	GEORGE, COKER	
PRIMACOR / CARILON EP	WRC12-88		GEORGE, COKER	
PTFE (SEE TEFLON)				
PVC / EP CARILON	LR20279	69	George	
PVP / EP CARILON	WRC 199-90		Machado and Gingrich	(PVP-50k is a poly(vinyl phenol) Mw = 50000 from Hoechst Celanese)
PYRAZOLINONE (SUSTITUTED) / CARILON	USPAT.5079285		KLUTTZ	
Rosswax 165	LR20240		WATERS (PROCESSING AID STUDY)	Clay Treated Paraffin Wax
SMA / EP CARILON	LR20279	68	George	
SMA / KRATON G / EP CARILON	LR20279	69	George	
STREARIC ACID/ NYLON 66 / CARILON EP	MRS MAR. 1989		Machado/Gingrich/Gergen	
STYRENE-ACRYLIC ACID COPOLYMER / NYLON 66 / CARILON EP	MRS MAR. 1989		Machado/Gingrich/Gergen	
STYRENE-ACRYLONITRILE COPOLYMER (SAN58) / CARILON EP	MRS JAN 1990		Machado / French / Grebowicz	
SULFONE (ORGANIC) / CARILON (PLASTICIZER)	US PAT. 4795773		SMUTNY	
SULFONE (ORGANIC) / CARILON (PLASTICIZER)	US PAT 4859729		SMUTNY	
SURLYN / EP CARILON	LR20279	108	George	
SURLYN / METAL SALT / CARILON	USPAT. 5049630		SMUTNY	
SURLYN 9520 / NYLON 66 / CARILON EP	MRS MAR. 1989		Machado/Gingrich/Gergen	
SYRENE-ACRYLONITRILE COPOLYMER / CARILON EP	MRS FEB 1991	105	Gerlowski / George / Kinneberg	
TALC / CARILON EP	MRS MAY 1989.	138	GEORGE, COKER	

CARILON POLYMER BLENDS

BLEND	REFERENCE	PAGE NUMBER	AUTHOR	COMMENTS
TALC / CARILON EP (INJECTION MOLDING CONDITIONS)	MRS JAN 1990	162	GEORGE, MACHADO	
TEFLON / CARILON	US PAT. 4870133		LUTZ AND GERGEN	
TEFLON / CARILON EP	MRS FEB 1991	105	Gerlowski / George / Kinneberg	
TEXTIN POLYURETHANE/ LCP/CARILON EP	LR20279	141	George/ Coker	
TI BUTOXIDE CATALYSTS CARILON EP	MRS NOV. 1991		George, Chuck, and Coker	
TI BUTOXIDE CATALYSTS CARILON EP	LR20279	174	George / Coker	
TRIAX 1180 / EP CARILON	WRC 199-90		Machado and Gingrich	
Tributyl Phosphate(1)	LR20240		WATERS (PROCESSING AID STUDY)	Tributy Phosphate
TRIPHENYL PHOSPHITES / CARILON EP(STABILITY)	LR20279	198	George/ Coker	
URETHANE RUBBER IN GLASS AND MICA FILLED	LR2022279	129-130	George/ Coker	
VECTRA (SEE LIQUID CRYSTAL POLYMER)				
Victastab HMP	LR20240		WATERS (PROCESSING AID STUDY)	Di-Polyoxyethylene Hydroxymethyl Phosphonate
VISTALON RUBBER/ CARILON EP	LR20279	143	George/ Coker	
VISTALON RUBBER/PP/CARILON EP	LR20279	129-130	George/ Coker	
VISTALON RUBBERS/ NUCREL/ CARILON EP	LR20279	152	George/ Coker	
WATER / CARILON	USPAT. 4876307		ALLEN	
WATER / CARILON	US PAT. 4761753		ALLEN	
WAX C / APATITE/CARILON EP	LR20279	172	George /Coker	
Wax E Powder	LR20240		WATERS (PROCESSING AID STUDY)	Montan Wax Acid, Ester Mixture
Wax OP Powder	LR20240		WATERS (PROCESSING AID STUDY)	Montan Ester Wax Mixture
Wax PE 190	LR20240		WATERS (PROCESSING AID STUDY)	Polyethylene wax
Wax PED 191	LR20240		WATERS (PROCESSING AID STUDY)	Polyethylene Wax, Oxidized
Whitcon TL-5	LR20240		WATERS (PROCESSING AID STUDY)	PTFE Resin
WOLLASTONITE / APATITE / CARILON EP	MRS APRIL 1991	85	George /Coker	
WOLLASTONITE / CARILON EP	MRS MAY 1989.	138	GEORGE, COKER	
ZEOLITE / CARILON	USPAT.5115002		VAN HELDEN, GILSON, AND SYRIER	
ZINC BORATE / CARILON (FLAME RETARDANT)	USPAT. 4921897		DANFORTH AND SMITH	
ZINC OXIDE / ZINC SULFATE / TRIALKYLPHOSPHATE / CARILON	US PAT. 4960807		SMUTNY	

FUTURE BLEND STUDIES WITH CARILON POLYMER

The following section is an undiluted version of Table 1. It includes a brief analysis of other polymer systems and potential blends with CARILON polymer.

CARILON Blend Strategies
J. E. Flood

A. Polyolefins

In general, polyolefins offer good water vapor transmission rates and good processability. Polyolefins have good chemical resistance and are good dielectric materials. Polyolefin stabilization technology is mature. Antioxidants, processing stabilizers, heat aging stabilizers and UV stabilizers are available. Polyethylene's possess good melt strength. Modulus and tensile strength are low compared to CARILON and the printability is poor on untreated polyolefin surfaces. Polyolefins are poor oxygen barriers. Impact copolymers are available with good low temperature impact strength. Polyolefins are cheap. Finally, polyolefins are incompatible with CARILON [1].

Blends with Polyolefins

1. SELAR® RB type structures (CARILON blends with HDPE) - SELAR when blended with HDPE or MDPE in the 3 - 15 wt% SELAR range decreases the oxygen permeability of the polyethylene by a factor of 3 to 4 and greatly reduces the permeability of chlorinated solvents through polyolefins [2]. Due to limited compatibility with the polyethylene and specific processing conditions platelets form that essentially block oxygen or other chemicals from migrating through the polymer [3].

Primary Purpose: To improve oxygen barrier properties of polyolefins and the water barrier of CARILON. A secondary purpose is to improve barrier properties of polyolefins to hydrocarbons and chlorinated solvents.

Applications: Packaging for solvents and pesticides, gas tanks, oxygen and water barrier films and containers.

Competition: Nylon 66 or Nylon 6 and maleated PE (SELAR RB).

Current Volume/Price of SELAR RB: unknown, but volume is expected to increase at a high rate [4].

Approach: Use Nylon and a maleated or carboxylated polyolefin as compatibilizers for a CARILON/HDPE blend. Nylon when blended with a maleated or carboxylated polyolefin (PE) is compatible with polyethylene [2]. Nylon is compatible with CARILON [5]. All of the above reactions are probably dependent on what end-groups are available. In the case of Nylon 6 the end-groups are COOH and NH2 for Nylon 66 both of the end-groups can be NH2 [5].

CARILON with the appropriate compatibilizers would be sold as a master batch to be added to polyethylene (blow molded products) or polypropylene (film). CARILON has certain advantages over nylon in that it is less water absorbent, it is a better oxygen barrier and could have a lower price. However, this system would be a three component system (four components when blended with a polyolefin) as compared to SELAR RB which is a two component system (three components when blended with a polyolefin).

Strategies for producing the masterbatch blends should take into account which components are blended first and their respective concentrations. Toughened nylon 6 or nylon 66 could be used as compatibilizers between HDPE and CARILON. Different tougheners such as carboxylated polyolefins or maleated polyolefins should be considered. In addition, modified polyolefins (maleated or carboxylated) should be blended separately with Nylon 6 or Nylon 66 to produce compatibilizers; refer to the Appendix for information on Nylon reactions with maleated and carboxylated polyolefins.

Dry blends of the CARILON/Nylon/modified polyolefin masterbatch with the polyolefin should be evaluated at different concentrations and extrusion conditions. A sheet extrusion process followed by biaxial stretching of the sheet on the T. M. Long biaxial film stretcher may produce the desired "platelet" morphology. Also, a dry blend of the above masterbatch with HDPE could be tried in a stretch blow molding process.

The other alternative to the dry blends would be to produce a value added HDPE or PP in which the pelletized CARILON/compatibilizer masterbatch is added to the polyolefin which is in turn pelletized and is sold as a stand-alone resin. This method may not produce the desired platelet structures in the final product due to the extra heat and shear histories involved.

2. Totally compatible blends of polyolefins with CARILON - Unlike the previous blend idea, which involved limited compatibility for barrier properties, this idea involves total compatibility where CARILON and a polyolefin are both major components and their respective mechanical, chemical, and thermal properties can be taken advantage of for an improved product. Like the previous idea, similar compatibilizers can be used but in larger quantities. Also, new compatibilizer technology may be needed for this applications [6].

Primary Purpose: To produce value added polyolefins with improved modulus, oxygen barrier, tensile strength, and possibly impact strength. If CARILON could be made an integral part of the polypropylene homopolymer matrix in an impact copolymer it could greatly improve the impact/stiffness balance of a polypropylene impact copolymer. Secondary Purpose - Improve barrier properties of CARILON (water barrier) and polyolefins (oxygen barrier).

Applications: Automotive batteries, toys, luggage, packaging, fuel tanks and lines, cast and oriented polypropylene or polyethylene film, polyester film.

Competition: current high stiffness polypropylene impact copolymers, PE fuel tanks, SELAR based fuel tanks, SELAR rigid packaging for chlorinated solvents and pesticides, metallized PP film. The economics of blending CARILON with polypropylene to increase stiffness may be marginal but are better than other engineering thermoplastics when one considers future CARILON fixed and variable costs.

Current Volume and Price - Polypropylene Impact Copolymers (800 MM lb @ 55 cents/lb)

Approach: Do the easy thing first. Attempt blends with Nylon/malaeic anhydride modified PP compatibilizers with a random polypropylene copolymer and CARILON. Investigate the effect of adding the compatibilizer first to the polypropylene or first to CARILON, etc.. Evaluate different CARILON, polypropylene, compatibilizer concentrations. Evaluate the ratio of Nylon to modified polypropylene. Evaluate different Nylons, i.e., Nylon xy as opposed to Nylon x.

An increase of 20,000 psi in the flexural modulus (195,000 psi vs 175,000 psi) in a medium impact polypropylene copolymer would be considered significant. Current impact copolymers sell for 45 - 55 cents/lb. A high stiffness medium impact copolymer may bring another 5 - 10 cents/lb, depending on the application (the economics would be tight at best for CARILON).

B. Polyamides (Nylon)

Nylons in general possess high stiffness and strength and relatively high melting temperatures. Their impact properties are good at room and low temperatures. A variety of different properties are available depending on the comonomers being used. Due to nature of their comonomers, nylons also possess good chemical functionality which can be an advantage (good for compatibilization) or disadvantage (moisture absorbance). In addition, they possess fair to good chemical and abrasion resistance. Some disadvantages are that nylons absorb moisture, and have poor notched izod (untoughened nylon).

1. CARILON as a toughener for Nylon - Blend in 3 - 20 percent wt CARILON into nylon. Depending on the nylon end groups available, there may be an improvement in notched Izod impact strength if the appropriate graft copolymer is formed. The blends are extrusion reacted to initiated the copolymerization process.

Primary Purpose - To increase the notched Izod of nylon into the regime of Super-Tough Nylon 66. Secondary Purpose - nylon/CARILON blends could act as an adhesive layer between pure CARILON and nylon or toughened Nylon.

Applications - Same as Super-Tough Nylon; see the report on impact modified nylons in the Appendix. Also, coextruded fuel lines where the nylon/CARILON blend would be an adhesive for CARILON on the inside (solvent resistance) and Super Tough Nylon on the outside (low temperature Izod).

Competition - Zytel ST 801 etc. ; see the Appendix for other impact modified Nylons.

Current Volume/Price of Impact Modified Nylon - 50 MM lb/yr @

Approach: Blends of Nylon 6 with CARILON. Investigate different concentrations of CARILON in Nylon 6. Evaluate different extruder temperature conditions and screw configurations. Nylon 6 is terminated with a NH_2 and COOH, therefore there is the possibility that graft copolymers will form but not crosslinks which may form if both end-groups were NH_2 (Nylon 66). It may be worthwhile to evaluate blends of Nylon 6 (major component), Nylon 66, and CARILON.

Testing will involve, notched Izod (room temp., 0 °C and -30 °C), Gardner Impact (room temp., and -30 °C), flexural modulus, photomicrographs, tensile properties, etc. An increase in Izod strength in a Nylon 6/Carilon blend could be due to an increase in molecular weight. High moleculular weight CARILON samples (LVNs of 5 -6) should also be evaluated for Izod strength.

2. Coextrusions (bicomponent fibers) of CARILON and polypropylene or nylon 6 for tufted carpet applications.

Primary Purpose - CARILON would provide good creep and wear resistance to polypropylene and CARILON is dyeable. Polypropylene would provide good UV stability (as a coating) to CARILON as well as resistance to staining. Polypropylene would be softer and could also be a processing aid for CARILON in a coextrusion process. Polyethylene as a coating could provide similar properties as polypropylene. Nylon 6 could be a processing aid (as a coating to CARILON fibers) for nylon/CARILON bicomponent fibers. There should be good adhesion between CARILON and Nylon 6 (unlike a CARILON/polypropylene fiber). In addition, both combinations, CARILON/polyolefin and CARILON/nylon 6, may have a natural crimp due to different crystallization rates and therefore shrink rates.

Applications - Carpet fibers, and possibly clothing

Competition - Nylon 6 and polypropylene, other bicomponent fibers

Current Volume/Price - Huge/cheap. However, the upscale market for polypropylene and Nylon carpet fiber (stain resistant home applications) can and does absorb higher raw material costs.

Approach - Use the bicomponent fiber line at WRC to evaluate CARILON coated polypropylene fibers and polypropylene coated CARILON fibers, i.e., processability, tensile properties, UV stability and dyeability of CARILON coated polypropylene fibers. Try mismatched viscosity, i.e., high and low melt flow polypropylene or CARILON resins. Investigate thick and thin coatings. There may have to be some compatibilization technology developed for a polypropylene/CARILON bicomponent fiber, however, since the extrusion process is continuous, compatibilization may not be necessary.

Similar experiments as above could be carried out with Nylon 6/CARILON combinations. It is worth noting that CARILON EP polymer and Nylon 6 have almost the same melting temperature which could make processing and post drawing and annealing easier.

3. CARILON coated Kevlar® fibers - Use solutions of CARILON, e.g., with water and resorcinol as a solvent [Akzo], as a spin finish for Kevlar. Kevlar and Nomex are both aromatic polyamides. Both materials should have end groups similar to Nylon 66, i.e., NH2, therefore, there may be good compatibility between Kevlar and Nomex with CARILON.

Primary Purpose - A CARILON coated Kevlar may be more compatible (better adhesion) with rubber for tire applications and some epoxy resins for composite applications.

Approach - Evaluate other solvents, i.e., water, water/resorcinol etc., for CARILON. If good, cheap, safe solvents can be found, approach DuPont or Akzo with this technology for further testing. This would be a low volume, value added application for CARILON. Kevlar sells for $6.00 - $10.00/lb.

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Assigned Polymer Systems

A.	Poly(phenylene ether)	PPE (PPO)
B.	Flouroplastics	PTFE, PVF2,
C.	Poly(vinylchloride)	PVC
D.	Polyolefins	PE, PP, etc.

A. Poly(2,6 dimethyl 1,4 phenylene ether) (PPE):

Polyphenylene ether is an amorphous polymer which exhibits outstanding dimensional stability, excellent electrical properties, and low water sorption. PPE is primarily sold as a blend with HIPS (200 MM lbs in 1990) to improve its poor processibility and impact stength (izod impact: 1.2 ft-lb/in). PPE/HIPS blends, called modified PPE, are found in automotive instrument panel frames, wheel covers, and business equipment/appliance/TV housings. Modified PPE resins may be extruded, injection molded, and blow molded without undue difficulty. The PPE/HIPS blends compete primarily with ABS, PC and their blends. The cost of the modified PPE is roughly 1.15 to 1.85 $/lb depending on the PS content.

Blends with PPE

Blends of PPE with Nylon 6 and 6,6 are produced under the trandenames Noryl GTX, Dimension, and Ultranyl. In 1990, 19 MM lbs of PPE/Nylon blends were sold in the U.S. and this is expected to grow to 31 MM lbs by 1995. The primary markets for these blends include automotive exteriors (panels and fenders), equipment housing, and helmets. Typically, equal parts of PPE and Nylon are blended with roughly 5 to 10 % styrene-elastomer and some small level of compatibilization. The materials exhibit notched Izod impact vaues between 5 and 9 ft-lb/in and 264 psi HDT's near 280 C. Low water absorption (0.5 wt%) in the blends also helps to maintain critical mechanical properties at high humidity conditions. The cost of these blends ranges near 2 $/lb.

From the literature, it is apparent that the properties of the PPE/Nylon systems are not satisfactory for many applications. Presently, PPE blends with PBT and PP are being explored in attempt to reduce the level of water sorption in the Nylon systems. PPE/PBT blends are manufactured by GE under the tradename, GEMAX. The heat deflection temperature of unmodified PBT is significantly lower than that of Nylon 66 and it is likely that this translates into a lower HDT for the blend.

Blends of PPE and Carilon Polymer

Carilon^R polymer offers a balance of properties which could provide a more opportune replacement for Nylon. Carilon^R polymer has an equilibrium water uptake of approximately 4 times less than that of Nylon6 and 66. In addition, Carilon^R polymer has demonstrated superior chemical resistance over the nylons while exhibiting a higher heat deflection temperature. For outdoor applications PPE requires some level of UV protection (typically carbon black), thus the UV sensitvity of Carilon^R polymer could also be supressed with only a limited reformulation of the resin.

Primary Purpose:	Improved dimensional stability of Carilon polymer
	Enhanced chemcial resistance of PPE
Applications:	Automotive body panels and exterior hardware, Tool and equipment housing
Competition:	Commercial PPE/Nylon blends
Market Info:	1990 U.S.: 19 MM lb at 41 $MM

Several compatibilization strategies can be outlined for the Carilon^R polymer/PPE blend systems.

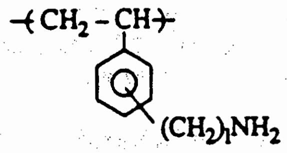
1. Blocks of polystyrene homopolymer are completely miscible with PPE. Thus, block copolymers of PS and another material with compatiblity or miscibility with Carilon polymer are desireable.

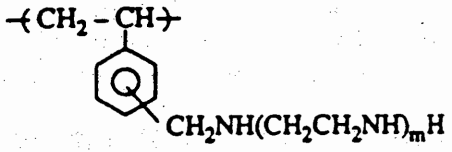
i. Maleated Kraton has been shown to have good compatibility with Carilon polymer as an impact modifier. Kraton FG 1901x may provide sufficient coupling of the PPE and Carilon phases. A starting point for such a blend would have the following composition: 45/45/10 PPE/Carilon/Kraton FG 1901x. If further compatibilization of the Kraton/Carilon interface is necessary, the maleated Kraton could first be modified using diamine chemistry or precompounded with nylon 66. The free primary amines from either of these steps could subsequently react with Carilon polymer to form the pyrrole during compounding.

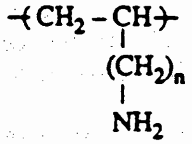
ii. PS-graft-SAN copolymers are available commericially and used to compatibilize PPE/ABS blends. If the AN content of the SAN graft adjusted to 40 to 80 % range, the SAN block would be soluble in the Carilon matrix providing an effective method of compatibilizing the PPE/Carilon interface.

2. Copolymers of styrene and functionalized monomers would be an effective means of compatibilizing the Carilon/PPE interface. Monomers with a primary amine functionallity could provide an avenue for reactive compatibilization of the PPE/CArilon interface.

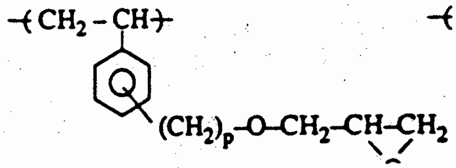
Styrene can be copolymerized with the following monomers using less than 1 mol % reactive monomer.

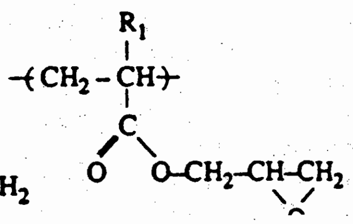


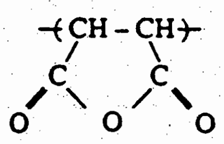




$-(CH_2-CH(-(CH_2)_n-NH_2))-$







3. Maleic anhydride moieties can be incorporated into the PPE backbone (U.S. Patent #: 4,877,847). The PPE could then be reactive compatibilized with Carilon polymer using the diamine chemistry discussed above.

Table I. Current Blends with Poly(phenylene ether) (PPE)

Other Components	Composition	lbs/ year (MM)	Targeted Uses	Cost ($)
High Impact PS	30 to 80% PPE	200	Automotive, Electrical, Business Equipment, Appliances	1.40
Nylon	45% PPE 10% Impact	19	Automotive, Tool Housings	2.15
PBT	45% PPE 10% Impact	<0.1	" "	2.25

B. Flouroplastics

The high thermal stability of the carbon flourine bond has led to considerable interest in flourine containing polymers has heat resistant plastics. The most common of these materials are polytetraflouroethylene (PTFE) and poly(vinylidene flouride) (PVDF) as well as several commercially available copolymers.

In addition to heat resistance, PTFE exhibits outstanding chemical and weather resistance, non-adhesive properties, and a very low coefficient of friction. The poor creep resistance of PTFE is typically combated by incorporating up to 25 % of glass or asbestos fiber. The exceptionally high melt viscosity of PTFE prevents the use of usual melt processing techniques. Typically, parts are sintered or machined. PTFE is copolymerized with monomers such as hexaflouropropylene (FEP) and ethylene (ETFE) to enhance melt processibility. The cost of the PTFE materials is very high: PTFE (6 - 7.50 $/lb), FEP (9 - 10 $/lb), and ETFE (12-15 $/lb).

PVDF is a semicrystalline polymer with a melting point of 171 C and is marketed under the tradename Kynar. PVDF combines melt processibility with many of the desired characteristics of PTFE. The characteristic properties of PVDF are lower cost (6 $/lb), good mechanical strength, flexibility, good chemical and weather resistance, and a continuous use temperature of 150 C. The disadvantages of the material are that it is attacked by some solvents and strong acids and that its dielectric properties are frequency dependent (limiting its use as an electrical insulator). More recent interest in PVDF has focused on its unique piezoelectirc properties. Films of PVDF have been prepared which are 3 to 5 times more piezoelectirc than crystalline quartz.

Blends with Flouroplastics

The most common polymeric blends involving flouroplastics are those where roughly 10 to 15% of PTFE is compounded with a engineering thermoplastic to enhance lubricity. Here, the low coefficient of friction of PTFE is exploited to provide lubricated grades of ETP's such as polycarbonate, acetal, nylon, and poly(butylene terephthalate). In these blends, compatibilization is not a requirement.

Polymeric blends with the major component being PTFE are rare. However, commercial blends of PTFE and polyimides are marketed under the tradename Rulon. Here, the heat stable polyimide at 30 wt% serves to improve the cold flow and poor abrasion characteristics of PTFE. These blends cost roughly 40 to 50 $/lb and are employed in bearings, bushings, and thrust washers.

PVDF is most commonly blended with acrylic polymers to make weather protective films and coatings. The blends are typically sold in film form and subsequently laminated to metal automotive parts and gas station signs. PVDF is miscible with acrylic polymers.

Blends of Flouroplastics with Carilon polymer

1. Lubricated grades of Carilon polymer with PTFE have been compounded. Given Carilon polymer's excellent wear resistance, lubricated grades may not be necessary for many gear and bearing applications.

2. PVDF/Carilon polymer blends have also been produced (U.S. Patent # 4,818,786). PVDF is immiscible, but quite compatible with Carilon polymer. The strength and stiffness of the Carilon polymer are almost fully maintained on addition of up to 40% PVDF. High elongation at break and notched Izod impact values on the order of 3 - 3.5 ft-lb/in demonstrate the good phase coupling of the PVDF/Carilon polymer blends.

3. Compatibilze PTFE lubricated grades of Carilon polymer with PVF2 (Case #: T-3115). Although, compatibilization of PTFE lubricated ETP's is not a strong requirement, the additional coupling of the PTFE particles in the Carilon matrix may have an impact on wear resistance and lubricity.

Primary Purpose:	To improve the wear resistance and lubricity of lubricated grades of Carilon polymer.
Applications:	Gears, bearings, bushings, etc.
Competition:	Metal, lubricated acetal and nylon.
Market Info:	Cost and volumes vary with ETP.

PVDF and the PTFE granules could be blended with Carilon polymer usng a single compounding step. The PVDF cold be incorporated at levels between 1 and 10 wt%, while adjusting the PTFE loading accordingly to avoid additional cost.

CARILON® Blend Strategies
M. Londa

A. Polycarbonate

Polycarbonate exhibits high impact strength, toughness, and high stiffness. It also has good dimensional stability, creep resistance, flame resistance, and thermal endurance (HDT 270-280_F under 264 psi load). Low water absorption is another attractive property. It suffers from reduced impact at low temperatures and on aging at elevated temperature, loss of ductility and impact strength in thicker sections, susceptibility to environmental stress crazing or cracking (especially in the presence of gasoline), and difficult processing due to high melt viscosity. It also has a relatively high price. Polycarbonate has been found to be partially miscible with CARILON polymer (Gergen and Lutz, US patent # 4,880,908).

Blends with Polycarbonate

1. Polycarbonate blends with CARILON polymer and an impact modifier, such as polybutadiene or other elastomer, should have excellent low temperature properties, good mechanical and toughness properties over a wide temperature range, and improved chemical resistance over polycarbonate.

Primary Purpose: To improve toughness and dimensional stability of CARILON polymer and the chemical resistance and thickness sensitivity of polycarbonate.

Applications: Automotive exteriors such as bumpers and panels, equipments housings, and electrical and medical applications which need a balance of chemical, electrical, and physical properties.

Competition: PC/PBT, Xenoy; PPE/Nylon, Noryl GTX

Volume/Price: PC/PBT blends - In 1990 62MM lbs were sold at $1.58/lb; an estimated 81.5MM lbs valued at $2.07/lb will be sold in 1995; PPE/Nylon blends - In 1990 15MM lbs were sold at $2.14/lb; an estimated 24MM lbs will be sold in 1995 at $2.79/lb.

Approach: Polyurethanes may act as a compatibilizer for PC/CARILON blends as they do for PC / POM blends. A blend composition of 45/45/10 CARILON/PC/TPU is probably a good starting point. Depending upon the TPU chosen, various properties may be optimized (see section B).

In addition, polyglutarimide, available from AmeriHaas, is used for compatibilizing Nylon blends with PC or ABS. The use of the compatibilizer in tandem with an impact modifier improves notched Izod performance and heat resistance. It is therefore worthwhile to try as a compatibilizer for CARILON/PC blends.

There are many choices for an impact modifier, as discussed below.

Furthermore, Dexcarb, a commercial PC / Nylon compatibilized blend, might work. The addition of Nylon increases the chemical and fatigue resistance over PC, and the arc resistance is also improved for electronic applications. However, moisture absorption is high and impact strength is low. Specialty nylons can overcome these shortcomings, but at a high price. CARILON polymer should therefore be of benefit, especially in terms of lowering the water sorption. 50/50 blends of CARILON polymer/Dexcarb may not even need additional compatibilization. They may, however, need the addition of an impact modifier so as to optimize impact strength. Polyurethanes could be chosen again, but their relatively high Tg may limit the blend's low temperature performance. Machado and Gingrich (WRC MRS, June 1989 and April 1990), George and Coker (WRC MRS, Feb. 1988), and Waters (WRC MRS, Oct. 1991) have evaluated several impact modifiers in addition to polyurethanes. KRATON® 1901X produced a super tough engineering thermoplastic at low levels (about 5% wt.) of rubber; the addition of Nylon 6,6 allowed the KRATON to continue to exert toughening effects beyond the level where it was ineffective in binary blends. Pebax, a polyamide-ether TPE, and Hytrel, a segmented aromatic polyester, both increased notched Izod impact strength with a corresponding decrease in Gardner impact strength. Paraloid, an acrylic shell-core impact modifier, and Blendex 338, an SAN/ABS shell-core modifier, both increased Izod and Gardner impact strengths while maintaining a balance of good stiffness and strength. The chose of an impact modifier will be very dependent upon the application of interest.

Compatibilized CARILON polymer could be sold as a master batch to be compounded with polycarbonate to ultimately produce injection molded articles. CARILON polymer/PC blends should have several advantages over Xenoy and Noryl GTX type blends. CARILON polymer has increased tensile strength and notched Izod strength, and better chemical resistance than PBT. PBT also has a low HDT (130_F under 264 psi load). These benefits for CARILON polymer could open up opportunities to displace PC/PBT blends. Noryl GTX suffers from Nylon's poor hydrolytic stability; PBT may replace Nylon in PPE blends due to this reason, so again CARILON polymer has a chance to take over these markets.

2. Polycarbonate blends with ABS show improved impact resistance, toughness, and thermal properties over PC. The blends are easier to process than PC, and they have improved low temperature impact resistance over PC. ABS imparts a good balance of properties at a low cost. If AES is substituted for ABS, the blends are more stable to oxidation; AES also retains much of it properties in weathering studies compared to ABS.

CARILON blends with polycarbonate and ABS should have improved impact resistance, toughness, and thermal properties over CARILON polymer or PC. ABS may impart a wider injection molding window, as well as lowering the cost and imparting a good balance of properties to the blends. CARILON polymer would impart chemical resistance to the blends, while polycarbonate would enhance toughness and dimensional stability.

Primary Purpose: To improve processing, thermal properties, and cost of CARILON/PC blends; CARILON polymer may improve tensile strength and chemical resistance to PC/ABS blends, while PC/ABS would impart high impact strength and dimensional stability to CARILON polymer.

Applications: Exterior car body panels, wheel covers, business equipment and computer housings, car instrument panels, electronics, medical parts.

Competition: PC/ABS and PPE/HIPS (Noryl)

Volume/Price: PC/ABS blends - In 1990 36MM lbs were sold at $1.50/lb; an estimated 53.3MM lbs valued at $1.91/lb may be sold in 1995; PPE/HIPS - In 1990 200MM lbs were sold at $1.40/lb; an estimated 258MM lbs will be sold in 1995 at $1.79/lb.

Approach: Equal parts CARILON polymer/PC/ABS could be investigated initially. Since PC and ABS both show affinity for CARILON polymer, a compatibilizer will probably not be needed. The ratio of Acrylonitrile to Butadiene to Styrene could be adjusted so as to increase compatibility of the system. A high Acrylonitrile content would be beneficial for mixing with CARILON polymer, while a high styrene content would be desirable for PC; for impact strength, however, the Butadiene content is important. Finally, the block lengths of the ABS are also critical. Low molecular weights are desirable for diffusion of the ABS to the CARILON polymer/PC interface. But high molecular weights are most effective in terms of interfacial adhesion, i. e., at "gluing" the phases together. So, optimization will obviously take some effort.

B. Thermoplastic Polyurethanes (TPU's)

TPU's are segmented block copolymers consisting of hard and soft domains. The hard block consists of a higher melting polyurethane derived from a diisocyanate, usually MDI, and a chain extender, such as ethylene glycol, butanediol, or hexanediol. The soft block consists of a higher molecular weight (> 1000) polyol, which are either ether or ester based. Since various monomers and ratios can be used in their synthesis, custom tailored properties can be achieved.

TPU's exhibit good impact strength and low temperature properties, superior abrasion resistance, elastic recovery, paintability, and good fuel and chemical resistance. Tensile and tear strength, and a wide range of hardness and modulus are also available. And, products can be formed from many techniques, including injection molding, blow molding, extrusion, vacuum forming, and compression and transfer molding. In addition, reaction injection molding (RIM) has created a large volume potential for thermoset polyurethane elastomers in the automotive industry. They suffer from high moisture absorption and poor heat resistance. CARILON polymer / TPU blends have been investigated by Danforth et al. (US patent # 4,851,482), Machado and Gingrich (WRC MRS April 1990), and Waters (WRC MRS Oct. 1991).

Blends with TPU's

1. Acetal/TPU blends have higher tensile strength, flexural modulus, and a broader useful temperature range than TPU's. Acetal also lowers the moisture absorption of TPU's. While TPU's improve the low notched Izod impact strength of Acetal, Acetal's physical properties decline. CARILON polymer also imparts higher tensile strength and flexural modulus to TPU's. A higher useful temperature range and better fuel and chemical resistance should result from replacing Acetal with CARILON polymer. Additionally, the problem of formaldehyde emission from the processing of Acetal would be overcome.

Primary Purpose: To improve impact strength in CARILON polymer and to increase tensile strength and flex modulus in TPU's.

Applications: Automotive, sporting goods, and footwear

Competition: Acetal/TPU blends

Volume / Price of Acetal/TPU blends: In 1990 0.5MM lbs were sold for $1MM; an estimated 0.6MM lbs will be sold in 1995 for $2.50/lb.

Approach: CARILON polymer and TPU have been shown to be compatible. The final blend morphology, however, will be greatly influenced by processing and the particular TPU chosen. As described above, TPU is a multiphase system itself, which is sensitive to temperature and shearing rate. At the temperatures needed to process CARILON polymers, care should be taken to minimize the time in the melt so as to avoid decomposition of the TPU. Furthermore, Machado and Gingrich observed different results depending upon the type of polyurethane investigated. Estane 58133, a hard (rubber-poor) material with a polyester-based soft block, improved the low temperature Gardner impact strength of CARILON polymer (109 vs 258 in-lb for the neat CARILON polymer and the blend, respectively), although the accompanying improvement in notched Izod impact strength was marginal. On the other hand Estane 58881, a soft (rubber-rich) material with a polyether-based soft segment, caused a substantial loss in Gardner impact energy, but it improved the Izod impact energy (4.1 vs 8.1 ft-lb/in for the neat CARILON polymer and the blend, respectively). The ester-based material, which contains a higher percentage of polar polyurethane hard segments, had a finer dispersion of spherical particles in the polyketone matrix. The -NH groups of the hard segment can hydrogen bond with the ketone groups of CARILON polymer, thereby causing good interfacial adhesion and correspondingly increased Gardner impact strength in the blend. The softer and less polar ether-based elastomer developed elongated rubber particles that were beneficial in terms of Izod impact; but the lower percentage of urethane groups translates to a weaker interface, which is detrimental to Gardner impact. A thorough understanding of the markets in which the blends will be used is therefore critical so that the proper choice of materials can be made.

2. Although the current markets are small, the growth rates of TPU/PC and TPU/ABS blends are expected to be high. TPU/PC blends have high impact strengths, and the addition of TPU overcomes the low critical thickness values for Izod impact of PC. ABS has high flex modulus, good processability, good HDT, and a reasonable cost.

Instead of small quantities of TPU used as a compatibilizer (see section A), Waters (WRC LR# 20240) showed that a 73/25/2 CARILON EP polymer/TPU/PC ternary blend combination resulted in excellent RT Izod impact strength (21.5 ft-lb/in vs 16.2 ft-lb/in for CARILON polymer/TPU). It may be that the PC is surrounded by the TPU in a CARILON polymer matrix, thus forming an *in situ* shell/core impact modifier. It is believed that the phase size of the dispersed phase is very important for impact modification. The small phase size of TPU in CARILON polymer may be increased by the addition of PC, thereby increasing the impact strength. A similar strategy with ABS could be envisioned, and the economics would be better.

Primary Purpose: To improve the impact strength in CARILON polymer.

Applications: Automotive, Medical

Competition: TPU/PC and TPU/ABS blends

Volume/Price: In 1995, an estimated 1MM lbs of TPU/PC blends will be sold at $2.50/lb; about 1MM lbs of TPU/ABS at $1-$2/lb is also estimated.

Approach: CARILON polymer could be compounded with TPU/PC or TPU/ABS in a single step; master batch compounding could also be studied. The type and ratios of TPU and/or ABS should also be investigated.

C. Polysulfone

Polysulfones exhibit good tensile strength and flexural modulus. They are amorphous, transparent polymers with decent chemical and creep resistance, and they are FDA approved. On the down side, they are expensive, have low Izod impact strength, and are not very heat resistant. Blends of CARILON polymer and poly(arylsulfone) (PAS) polymer and oligomer were shown to have improved tensile properties and processability over neat CARILON polymer (US patent # 4,904,744).

Blends with Polysulfones

1. Polysulfone (PSO) blends with PET (Amoco's Mindel B) have greater strength and toughness than PBT, but the temperature and solvent resistance isn't adequate for under-the-hood applications. CARILON polymer could have an advantage here.

Primary Purpose: To improve the solvent resistance and cost while maintaining the strength of polysulfone by blending with CARILON polymer, which should benefit from greater dimensional stability.

Applications: Electrical and electronic applications, such as connectors and switches, and the aerospace market

Competition: Mindel B

Volume / Price of Mindel B: In 1990 1MM lbs were sold for $2.7MM; an estimated 1.8MM lbs will be sold in 1995 for $6.2MM. Larger volumes could be realized by substitution of PET by CARILON polymer due to better solvent resistance, thus opening up under-the-hood applications.

Approach: Compatibilization may not be needed in these blends. Determination of which PSO, such as poly(arylsulfone), poly(ethersulfone), poly(arylethersulfone), or polyphenylene sulfide, is the best for blends with CARILON polymer is needed. Processing of PSO/CARILON polymer blends should be easier than PSO/PET blends since PET has such a slow crystallization rate.

D. <u>Acetal</u>

Acetal is a highly crystalline (80%) thermoplastic with high tensile strength and modulus, excellent fatigue life, and dimensional stability. It also has a low coefficient of friction and high heat resistance for extended use up to 220_F. Its high crystallinity accounts for its low water absorption, good mechanical properties, and predictable long-range performance under load. Although Acetal's abrasion resistance is not as good as that of nylons, it is better than that of many other thermoplastics. Their resistance to organic solvents is notable, but in contact with strong acids Acetals will craze. Furthermore, Acetal has good electrical properties; its dielectric constant and dissipation factor are uniform over a wide frequency range and up to temperatures of 250_F.

There are presently two types of Acetal: a homopolymer, du Pont's Delrin, and a copolymer, Celanese's Celcon. Compounds for injection molding, blow molding, and extrusion are available; care must be taken when processing at elevated temperatures (above 200_C) due to decomposition and subsequent emission of formaldehyde. Glass fiber reinforced (higher stiffness, lower creep, improved dimensional stability) and TFE-fluorocarbon fiber reinforced (improved frictional and wear properties) grades are available. Typical parts include gears, bearings, pump impellers, appliance cases and housings, plumbing components, pipe and fittings, and machinery parts.

Blends with Acetal

1. In addition to TPU (refer to section B, Acetal/TPU blends), other elastomers, such as polybutadiene, EPDM, etc. can be used. Impact-modified acetals typically have notched Izod impact values of 2-5 ft-lb/in. Du Pont's "super tough" grades have significantly higher notched Izod values (17 ft-lb/in) than other impact-modified grades, presumably by grafting the elastomer portion to the acetal resin. For a discussion of impact modification of CARILON polymer, see section A.

2. CARILON polymer/Acetal blends are immiscible. Poly(vinyl phenol) has been used as a compatibilizer for these blends, as it is miscible in the melt and the amorphous phase with both CARILON polymer and Acetal (Machado and Lee, WRC MRS, May 1991). These compatibilized blends had improved tensile strength and a finer domain size, but the ductility and impact strength were poor. Since TPU shows an affinity for both CARILON polymer and Acetal, it could be used instead of poly(vinyl phenol). These blends should show better impact strength, probably at the expense of tensile strength.

Primary Purpose: Decrease CARILON polymer's coefficient of friction and increase Acetal's Izod and Gardner impact strength.

Applications: Appliance cases and housings, gears, bearings, and machinery parts.

Competition: Acetal

Approach: See section B, Acetal/TPU blends.

CARILON Blend Strategies
J. R. Kastelic

A. POLYESTERS: PBT, PET, PETG, PEN and CHDMT

KEY PROPERTIES: Good strength and modulus combine with good solvent resistance in these polymers. Chemical resistance is not exceptional, due mainly to hydrolytic instability, particularly at elevated temperatures, and this restricts used. Only PBT injection molds well due to its relatively good rate of crystallization. The others are too slow to crystallize in molding and actually are maintained in a near amorphous condition which really gives them poor thermal dimensional stability. Crystallization rate is slow particularly in PET and slow to near infinite with optimum levels of CHDM [chclohexyl dimethyl] glycol in what is called "PETG". With the exception of optimum composition PETG, all will eventually crystallize if held above Tg for an extended time. But this frequently leads to some level of shrinkage and part warpage unless the part is mechanically constrained. Alternatively they can be stress crystallized by drawing at or above Tg.

A major limitation of the family is that as crystallinity increases unoriented toughness generally decreases. Orientation fortunately brings impact performance to films and containers of PET. But note that the SBO [stretch blowmold oriented] container neck is still considered too brittle for some demanding chemical packaging applications for hazardous materials. High melting points and high levels of attained crystallinity lead to good high temperature performance in all family members except PETG which approaches a purely amorphous morphology at optimum CHDM co-glycol level. When crystallized or stress crystallized, PET has good water and oxygen barrier. The affordable price of PET, its strength and clarity when stretch blow molded and FDA approvals up to retort temperatures make it one of the higher volume packaging resins.

All members can be oriented into fibers and films and PET films and fibers are widely used commercially around the world. At one time CHDMT [cyclohexyl dimethyl terephthalate] fibers were sold but price proved to not be competitive and it has been dropped. CHDMT is generally copolymerized with other diacids and sold as what is called "PCTA".

BLENDS WITH POLYKETONE:

Primary Purpose: The most important concept is to use PET as a polymeric platelet additive in PK to enhance the WVTR [water vapor transmission rate] of PK containers. Cost dilution is an added benefit if inexpensive polyesters prove workable. Selar analogs of PP and PE in PK have been demonstrated but these tend to fall apart in retorting unless good coupling technology is employed. Here, adhesion of PET platelets to PK matrix resin is expected to be both better than with olefins and less disturbed by exposure to high retorting temperatures. In fact the platelets can be formed to optimum geometry in the compounding step and "frozen in". There should be no need to melt the crystalline PET platelets when fabricating containers with EP polyketone. Higher melting CHDM containing polyesters could be used here to allow the principle to be employed with E polyketones. It appears possible that a polyester micro-fiber phase morphology could also prove attainable. This has the potential to reinforce and improve impact in engineering applications. Alternatively, polyester chopped fiber could be added.

Addition of minor amounts of PK to any of the polyesters has a possibility of nucleating crystallization in injection molding. In PET this could be particularly useful to allow satisfactory crystallization rates to be obtained in injection molding. Toughness might also be improved over pure crystalline polyester. An additional possibility is enhanced bonding of fillers and reinforcements in PET.

Applications: Rigid packaging

Competition: multilayer systems, Barex, Saran coated containers.

Current Volume/Price: estimated at 0.90 to 150 $/lb

Approach: Compound at high temperature and chill in platelet or fiber structure (for packaging or engineering application respectively). Mold or sheet extrude at temperatures which will not melt the polyester phase. In observations of molding machinery transferring from PET to PK and back, the blended purge was observed to remain mechanically intact and ejected from the mold at all blend compositions. It is thus believed possible that compatibilization will not be required. If this proves to be true, PK can be evaluated as a "compatibilizer" for introduction of fillers and reinforcements in various polyesters. Nucleation effects of PK on various polyesters can be screened with DSC. It should be added that Carlton Ash has ideas for compatibilizing PK and various polyesters, but the chemistry is somewhat touchy.

B. ACRYLICS: PMMA and its Copolymers:

KEY PROPERTIES:
Acrylics generally have exceptional transparency, surface hardness and gloss as well as good weatherability and mechanical stability. This makes them suited to outdoor lenses and reflectors as well as household appearance parts and cosmetic items and containers. Materials have high stiffness, low mold shrink and can be readily colored. Toughness is acceptable with some notch sensitivity but can be improved with copolymer addition of methyl acrylate, ethyl acrylate and acrylonitrile. Styrene too can be added. Melt strength is unsuitable for blow molding but other common melt processing techniques are applicable including sheet extrusion. Acrylic sheet is know to have good thermoforming characteristics. Chemical resistance is good but solvents do attack the polymer and allow solvent bonding. HDT [heat deflection temperature] and CUT [continuous use temperature] are average but these are better in imide copolymers. Blends are not common but recent blends with PC, PBT and PET are now marketed. Electricals are good but barriers are unexceptional and even poor. Acylimide and acrylic acid polymers are not considered here due to poor behavior with water and high humidity.

BLENDS WITH POLYKETONE:

Primary Purpose: It is unlikely that PK addition to these polymers would be of value. Many applications require good weatherability and transparency. These would be compromised in blends. However, additions to PK might be valuable to raise it's stiffness and/or weatherability . Gloss, surface hardness and mold shrink might also benefit.

Applications: Outdoor and automotive appearance parts might be made possible by addition of acrylics to PK. Appliance and tool housings would all benefit from increased stiffness and lower mold shrink. Electrical properties should remain very good. However, it is possible that friction and fatigue properties would suffer

Competition: ABS, Nylons and PC are likely key competition.

Current Volume/Price: These polymers range from 0.80 to 2.00 $/lb. Blends would be expected to fall in this range since acrylics are reasonably priced.

Approach: Paraloid acrylic shell-core polymers and Blendex ABS modifiers were found to be very promising additives for improving impact of PK. These produced useful results at concentrations up to about 20%. It can be surmized that both processing compatibility and mechanical integrity with acrylics is good. Maleic anhydride copolymerization with acrylics may be possible to improve phase adhesion. It is conceivable that diamine linking additives (per D.H.W.) might be an adjunct to this. In this light, polyethylene-imines (POLYMIN from BASF) are also worth considering. SMA as an additive might also prove to be of help in compatibilizaton as might KRATON 1901X, Acrylic-Imides (KAMAX) or copolymers of acrylics with oxozoline. It is worth noting that thermoset acrylic purge has never given any stability problems when used with PK. It can be concluded that the chemistry and residual acrylic monomer are not incompatible with PK.

C. STYRENICS: PS, IPS, HIPS, SAN, ASA, ABS and SMA.

KEY PROPERTIES: High stiffness, gloss and colorability are characteristics of the entire family. PS, IPS [impact polystyrene] and SAN [styrene acrylonitrile] are transparent but with addition of rubber in IPS, HIPS [high impact polystyrene] and ABS, clarity disappears and toughness rises to exceptional values. Heat resistance and dimensional stability is good in all members, particularly SMA and SAN. Affordable pricing, potential to tailor properties and outstanding processability lead to a very broad range of uses for the family.

BLENDS WITH POLYKETONE:

Primary Purpose: Addition of PK to these polymers does not appear to present any sure significant opportunities. Solvent resistance might be improved but a more valuable benefit might be compatibilization of fillers and reinforcements. This could lead to even higher stiffness and dimensional stability. With toughness arising from rubber addition, this too can be at least maintained in blends.

A key opportunity is use of impact styrenics to improve toughness and low temperature toughness in PK. There is much precedent for this with other polymer blend systems. IPS, HIPS and ABS are the materials to consider. Depending on the polymer used there may be some cost dilution too. PS by itself might have some benefit in improving stiffness and lowering mold shrink but toughness will likely be inadequate in PS/PK blends. One could expect gloss and appearance to be improved too, but this has negligible value.

Applications: Many and varied

Competition: Nylon, ABS, PBT, Acetal, GE Alloys

Current Volume/Price: 0.80-2.00 $/lb.

Approach: As with acrylic polymers. SMA is likely the most compatible, particularly if diamines are used.

D. NIRILES: PAN and ANS:

KEY PROPERTIES: Oxygen barrier and solvent barrier are the exceptional properties of this family of resins. Water barrier is good but not exceptional. Barex has no FDA approvals but some ANS polymers have approval to hot fill temperatures but not retort.

BLENDS WITH POLYKETONE:

Primary Purpose: No significant opportunity seen. At one time Oxygen barrier was viewed as a possible benefit of nitrile polymer addition to PK. However, recent barrier measurements have demonstrated PK oxygen barrier to be in the same class as Barex and EVOH. Barrier synergy is unlikely in blends. Addition of PK to Nitrile polymers does not present any readily apparent advantages. There is even a good chance that decomposition products in PAN may de stabilize the PK.

Applications: Improved solvent barrier containers, pen barrels ?

Competition: Barex, aluminum

Current Volume/Price 1.35 $/lb.

Approach Not recommended due to suspected chemical incompatibility in melt processing. Luttz reported very high yellowness in ANS / PK blends.