

ANNUAL REPORT 2002
Dutch Polymer Institute

**Creating value in
key technology areas**

ANNUAL REPORT 2002

Dutch Polymer Institute

Annual report 2002

Dutch Polymer Institute

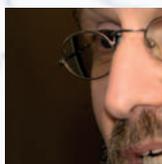
Preface

Pre-competitive research a driver for innovation	5
--	---



Chapter one

Making knowledge applicable	6
Highlights of 2002	6
Summary of financial data 2002	9
Performance Indicators	10



Chapter two

Polymer characterisation cuts to the core	12
<i>An interview with Prof. Peter Schoenmakers (University of Amsterdam) and Dr Brian Dickie (Dow Benelux).</i>	



Chapter three

Catalysis has become an interdisciplinary business	14
<i>An interview with Prof. Jan Teuben (University of Groningen) and Dr Jan-Dirk van Loon (Basell).</i>	



Chapter four

In search of the ultimate properties	16
<i>An interview with Rob Kirschbaum (DSM) and Prof. Oren Regev (TU/e).</i>	



Chapter five

Sustainability covered by coatings	18
<i>An interview with Prof. Rolf van Benthem (TU/e/DSM).</i>	



Chapter six

Future of TPVs is sealed	20
<i>An interview with Kinsuk Naskar M.Sc. (University Twente) and Dr Jernej Jelenic (Akzo Nobel).</i>	



Chapter seven

Bright future for polymer electronics	22
<i>An interview with Cristina Tanase M.Sc. (RUG) and Dr Dago de Leeuw (Philips).</i>	

Appendices

DPI organisation	24
Technology Area factsheets	
Core Programme	25
Polyolefins	28
Engineering Plastics	30
Coating Technology	33
Rubber Technology	35
Functional Polymer Systems	38
High-Throughput Experimentation	42

Acknowledgements

44

About the cover

A historic primitive cave painting or what? Actually it is a state of the art SEM-picture of nanotubes in a polystyrene film. Nanotubes could very well be the next hot thing in polymers. They are stronger than steel and they can also conduct electricity. Nanotubes are a fashionable topic verging on hype. The picture nicely shows how the nanotubes form networks (see also chapter 4).

Pre-competitive research a driver for innovation

The Dutch Polymer Institute was set up in 1997 as one of the four Leading Technology Institutes, following an initiative of the Minister of Economic Affairs, Hans Wijers.

The initial form chosen for DPI was a public-private alliance for pre-competitive research in the area of polymer materials. Its key stakeholders are the Dutch academia, the Dutch government and the Dutch polymer industry. The funding formula is as follows: the government contributes 50%, the industry 25% and the academia 25%.

Today, the institute is still largely based on the same principles, although both the research programme and industry and academic participation have grown significantly in scale while becoming increasingly international.

DPI's initial five years (1997-2002) can be seen largely as a development stage in which the research programme, the organisation and the relationship with the key stakeholders have matured, thanks to the investments made by the stakeholders in academia, industry and government. The research programme has diversified over this period in two major directions: in the number of polymer technology areas and by the introduction of science-driven and innovation-driven programme areas.

The 2002 Annual Report gives a flavour of the scope and diversity of today's DPI research programme in the form of interviews with researchers and industrial partners involved in the various programme areas. DPI facts and figures are added in separate appendices.

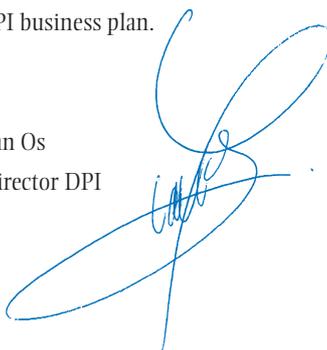
Looking forward to the next five years (2003-2008), it is time to ask ourselves the following questions: is this what we intended at the start and how should DPI look like in 2008? The answers to these questions will show us what path to take to turn the DPI into a technological institute that makes the most effective use of available national and international scientific resources while contributing fully to industrial innovation in polymer materials in the widest sense imaginable.

In 2003, DPI management and the key stakeholders intend to find the appropriate answers to these questions and present them in the form of a stakeholders survey.

A special task force will evaluate the various options for further development of DPI.

Both the stakeholders survey and the task force results will provide the basis for the next five years DPI business plan.

Ir George van Os
Managing Director DPI



Making knowledge applicable

DPI is not “science pour science”, if it is up to George van Os, who took over as DPI’s general manager in 2002. He wants DPI to be staffed by scientists who are driven by innovation. DPI aims at leading research with a focus on innovations, patents, applications and so on. In 2002, DPI took the first initiatives to expand its horizons. The aim is to create more multiformity and to extend DPI’s activities towards Europe. DPI is worried about the continuity of Dutch governmental funding. An interview with George van Os, managing director DPI.

The year 2002 has been one marked by change. To start with, George van Os succeeded Leen Struik as managing director. The number of partner companies has doubled since DPI’s inception in 1997. The activities of the Core Programme, that was formed at the end of 2001, came into full swing. A new Technology Area was set up: High Throughput Experimentation/Combinatorial Material Research. Inside DPI, a magazine for the polymer community, was launched. DPI started a series of workshops on High Throughput Combinatorial Material Research to be held biannually. Finally, the DPI Golden Thesis Award was introduced to honour outstanding DPI research with industrial application potential. These are all signs that DPI is on the right track.

Generating and exploiting knowledge

In the view of Van Os, DPI should be the motor of polymer-related innovation. “Europe, and the Netherlands in particular, have plenty of good scientists and good ideas. However, the resulting innovative power is poor.” His beliefs are backed by a recent assessment by the CER (the Centre of European Reform) of the Lisbon programme of economic and social policy reforms. Concerning innovation, the CER states that “Europe’s record on generating new ideas is strong, but it has had less success in commercialising innovation for the international markets.” Van Os: “DPI invests in research programmes with the objective of exploiting the knowledge generated, whereas much academic research seems to be more about generating knowledge only. Take patents, for example. Whenever DPI research leads to patents, they can be licensed by our partner companies or eventually be transferred and in doing so to create innovation.”

Highlights of 2002

The highlights of 2002 include 12 patents, 12 theses, 6 new partners, a new DPI magazine, the DPI Golden Thesis Award, a new series of workshops on Combinatorial Material Research and a positive evaluation of the research of DPI by an international committee.

January 1

Two new partners join DPI: Fasson/Avery Denisson and Kraton

January 22

The first DPI thesis of 2002: Polymer-solvent compounds: a route to make new polymer structures by Hooy-Corstjens

February 21

Patent application filed for the use of tetra-amides as copolymers

March 5

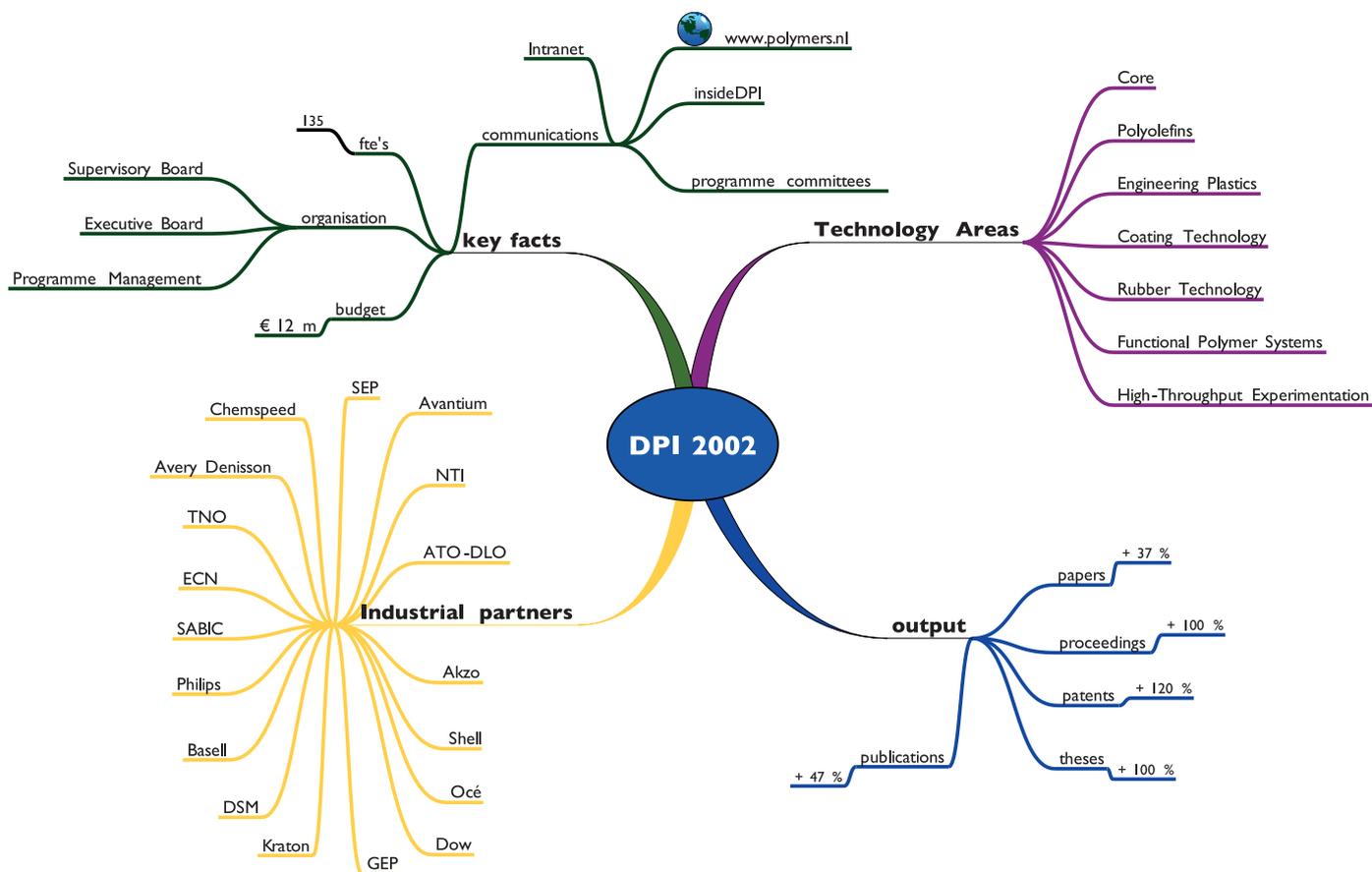
Patent application ‘Olefin polymerisation catalyst component and catalyst system and polymerisation process using such a catalyst system’.

March 7

Monitoring Committee approves DPI

March 20

A new solid state process for chemical modification of PET for crystallisation rate enhancement is patented.



The 4 C's of innovation

“What you need for innovation are creativity, capital, consistency and continuity. Creativity in research, capital, consistency and continuity in management policy, strategy and funding. To be frank, I am a little concerned about the Dutch policy of funding when it comes to continuity. The Leading Technological Institutes were initiated by the former Minister of Economic Affairs, Hans Wijers, as a way of strengthening the Dutch knowledge infrastructure and boosting innovation. For these investments to be successful, continuity and consistency are needed. One has to bear in mind the time frame of research. A PhD study, for example, takes four years. And very often it takes many times as long to be really successful in innovation. Mind you, the Dutch funding commitments in Leading Technological Institutes covers, all in all, two and a half PhD studies. Just as we are beginning to pluck the fruits of investing in public-private research, the Dutch Ministry of Economic Affairs is in the process of designing a new strategy in “Koers op innovatie”,

April 24

Patent application filed concerning synthesis of copolymers of acrylates and α -olefins

April 25

DPI thesis on transmissive and emissive polymer waveguides for communication and illumination by De Graaf

May 19

Patent application filed concerning polarised light emitting backlights and frontlights

June 6

Thesis of Segeren on microparticle adhesion in xerography

June 12

The first in a series of DPI workshops on Combinatorial Material Research is held

July 1

Three new partners join DPI: Chemspeed, Avantium and NTI Europe

focusing on four key technologies, as they are called. What worries me is how these key technologies are to be chosen. Will this new policy be led by the issues of the day or will it be based on the continuity of insight and experience?”

Multiformity

If the number of new partners joining were the prime indicator, DPI should consider itself a success. Six companies joined DPI in 2002: Fasson/Avery Denison, Kraton, Avantium, Chemspeed, NTI-Europe and ATO/DLO. An almost equal number expressed their intention to join in 2003 (and have indeed since done so): SEP, Microdrop, Analytik Jena, Sabic and Teijin. The majority of the newcomers are global operating companies. The network of academia participating in DPI is growing further. Queen Mary University of London joined in 2002, while the University of Maastricht, Leeds University and the National Technical University of Athens are considering joining DPI in 2003. Van Os: “For a number of reasons this expansion in general and the expansion into Europe in particular, is crucial for DPI. As more companies join, the research basis broadens, so attracting even more companies. Furthermore, the additional participation of outstanding non-Dutch universities will be beneficial to the quality of the research programme. These developments will substantiate the aim of DPI’s management to realise a significant part of the budget outside the Netherlands.”



George van Os,
managing director DPI:

**‘I am a little concerned
about the Dutch policy of funding
when it comes to continuity.’**

July 25

Patent application filed concerning the process of the copolymerisation of α -olefins with vinyl monomers

August 5

DPI researcher Galaktionov obtains doctorate on the subject of optimising distributive mixing

October 1

DPI moves from the TU/e premises to Kennispoort. Queen Mary University of London joins DPI. New DPI thesis “The influence of rheological versus mechanical properties in silicate polyamide nanocomposites”

October 9

InsideDPI, a new magazine for the polymer community, is launched

October 18

George van Os succeeds Leen Struik as managing director of DPI

November 1

ATO/DLO joins DPI. Parlevliet's thesis entitled “study of the fibre-matrix interfacial bonding in continuous glass fibre-reinforced nylon-6 nanocomposites with the single fibre fragmentation method”

Summary of financial data 2002

Income (million euros)

Contributions ex Industrial Partners	3.45	29%
Contribution ex Knowledge Institutes	3.02	25%
Contribution ex Ministry of Economic Affairs	5.49	45%
Interests	0.15	1%
Total income	12.11	100%

Expenditure (million euros)

By nature

Personnel

Research related	9.75	81%
Non-research related	0.73	6%

Depreciation

Research related	0.96	8%
Non-research related	0.01	0%

Other

Research related	0.39	3%
Non-research related	0.25	2%

By Programme Area

Organisation & support	0.84	7%
------------------------	------	----

Core Programme	1.93	16%
----------------	------	-----

Polyolefins	2.44	20%
-------------	------	-----

Engineering Plastics	1.89	16%
----------------------	------	-----

Coatings	0.99	8%
----------	------	----

High Throughput & CMR	0.23	2%
-----------------------	------	----

Rubbers	0.77	6%
---------	------	----

Functional Polymers	3.00	25%
---------------------	------	-----

Total expenditure	12.09	100%
--------------------------	--------------	-------------

Total expenditure	12.09	100%
--------------------------	--------------	-------------

November 6

Rastogi's DPI thesis on molecular organisation in homogeneous polyethylene copolymers at elevated pressure-temperature

November 11

Patent application filed "reversible addition-fragmentation chain transfer photo-polymerisation using visible light obtaining small MWD polymers"

November 20

Eighth DPI thesis of 2002: "Crystallisation of isotactic polypropylene, the influence of stereo defects" by Van der Burgt

November 28

Annual DPI meeting attracts record number of attendees. Henri Jagt receives the first Golden Thesis Award

December 23

Patent application filed for the use of RAFT agents for simultaneous reversible addition-fragmentation chain transfer polymerisation and ring opening polymerisation

Key Performance Indicators

Number of Industrial Partners

End 2001	10
End 2002	18

Number of Partner Knowledge Institutes (universities, etc.)

End 2001	14
End 2002	15

Industrial contribution (cash and in-kind)*

End 2001	25%
End 2002	29%

Number of patents filed by DPI

In 2001	5
In 2002	12

Number of patents licensed or transferred to industrial partners

In 2001	1 (license)
In 2002	5 (transferred applications)

Number of spin-off companies

In 2001	0
In 2002	0

Industrial follow-up

Subject to the outcome of the stakeholder survey to be conducted in the 2nd half of 2003

Track record former DPI researchers until 2002

Departed in total	114
Employed by partner knowledge institute	41
Employed by non-partner knowledge institutes	5
Employed by industrial partner company	13
Employed by industrial non-partner company	2
Returned to native country or moved abroad	11
Retired	2
Unknown (still under investigation)	40

European governmental funding (% of total funding)

In 2002	0%
In 2002 (two proposals submitted for EEC Framework VI)	0%

Participation of Foreign Knowledge Institutes*

In 2001	1%
In 2002	1%

Research output

	2001	2002
Scientific publications	71	104
Ph.D theses	6	12

Overhead costs*

In 2001	8%
In 2002	8%

Expenditure for knowledge transfer

In 2002	€ 164,105
---------	-----------

* % of total expenditure

Polymer characterisation cuts to the core

In 2001 DPI developed the concept of the Core Programme. Core activities came into full swing in 2002.

One of them, polymer characterisation, is exemplary for the Core's philosophy. An interview with two analytical chemists: Brian Dickie (Dow Benelux BV) and Peter Schoenmakers (University of Amsterdam).



Peter Schoenmakers (UvA, DPI):

'Chemists and physicists who do not usually speak the same language, are teaming up in the projects and learning to communicate with each other.'

The industry's focus is more and more shifting towards making better materials rather than to develop new ones. For this analytical chemistry can be of great help, at least according to Prof. Peter Schoenmakers and Dr Brian Dickie. They both should know. Schoenmakers is Professor of Polymer Analysis at the University of Amsterdam and coordinator of the newly formed DPI Core programme polymer analysis and characterisation (PAC). Dickie focuses on polymer characterisation in Analytical Sciences Corporate R&D of Dow and is industrial contact person for Dow. Schoenmakers: "What does it mean, for example, that you have a polymer system with an average of two functional groups? If the specifications of the material are not too critical, this type of knowledge is quite satisfactory. However, if you want materials with better performance, you will need a much better understanding of the real behaviour of the molecules. One needs to answer questions like how many molecules are there with one, two or three functional groups. In other words, the functionality type distribution determines how many molecules will crosslink during polymerisation. Brian Dickie: "I agree. A better analysis can be a competitive advantage. It will also tell us why a material works today and does not work tomorrow."

Analysis is not a product

It has taken some time to find the most suitable place for polymer analysis within DPI. Initially when there was talk of starting analytical service activities, it was met by little enthusiasm of the partner companies. When the Core Programme was created in 2001 as a facilitating science support for the Technology Areas, an ideal platform was created for a serious analytical effort within DPI. Schoenmakers: "Analysis is not a product. Our partners do not have a business unit Analysis." Dickie adds: "DPI with the Technology Areas and Core Programme resembles the partner companies in a much better way. That's what I like about DPI." And so do the other companies. When the first official meeting of the Polymer Analysis and Characterisation (PAC) cluster was held in March 2002, 12 partner companies were present. Dickie can see a number of reasons for this changed mindset. "The PAC programme leads to a pool of skilled people and a higher level of expertise. That is beneficial to all partners involved."

Problems initiate projects

The PAC programme is not about developing esoteric new techniques or methodologies. Projects, or work packages as they are called, are focused on real problems within the Technology Areas of DPI. Schoenmakers: “What we strive for is that a TA-related problem is tackled, analysed and then made accessible to all TAs.” Dickie: “That’s of course the interesting thing about this approach. Once a polymer analysis is developed it can become part of the analytical toolbox.” Obviously, PAC can’t solve all problems of all TAs. Schoenmakers: “That would be overambitious. Our aim is that at least each TA should find something of interest in PAC.”

Currently, three work packages are running: polymer distributions (TNO and University of Amsterdam, UvA), polymer networks (UvA and TU/e) and polymer surface characterisation (University of Twente, AMOLF).

Communication

Schoenmakers: “What is phenomenal about the programme is that people are working together who had not done so previously. Chemists and physicists who do not usually speak the same language, are teaming up in the projects and learning to communicate with each other.” Dickie: “The secret of real understanding is to know both sides of the story.”

Another strong asset of the programme is the fact that several knowledge centres, with complementary areas of expertise, are working together to solve analytical problems. At the same time it becomes possible to focus this expertise on new areas, at least for some of the institutes. Schoenmakers: “AMOLF is a reputed mass spectrometry centre. Until now, however, they have focused their attention on research into proteins. If we can shift their focus to the area of polymers, DPI can benefit greatly from the existing mass spectrometry knowledge.”



Brian Dickie (Dow):

‘A better analysis can be a competitive advantage.’

Catalysis has become an interdisciplinary business

An important part of the Polyolefins Technology Area involves catalysis. Part of this research is based at the University of Groningen, at the Centre for Catalytic Olefin Polymerisation. It is here that Prof. Jan Teuben's group came up with two significant patents regarding the use of organometallobenes in olefins polymerisation. Jan Teuben (RUG/DPI) and Jan-Dirk van Loon of DPI's partner Basell discuss whether the industry is still interested in catalysis research at all.



Jan Teuben (RUG, DPI):

'The trimerisation of ethene to hexene-1 is a kind of serendipitous finding.'

The chemistry of organometallobenes goes back a long time, and it had become clear as early as the 1950s that they could be used for polymerisation. Prof. Teuben, of the 'Molecular Inorganic Chemistry' unit of the University of Groningen, who is involved in many of DPI's programmes in the Polyolefins Technology Area, remarks: "In fact very little has been done with that knowledge since." Teuben is considered to be the first among Dutch academics to seriously devote research time to applying the metallobenes successfully in the area of polymers. Metallobenes, when used as catalysts, allow unprecedented control over the properties of the polymer.

Catalysing interdisciplinary answers

This is precisely why metallobenes are being used increasingly in the industry as catalysts. Yet Teuben is worried. "While the economic weather forecasts are grey, certainly for the chemical industry, and the number of companies producing polyolefins decline, industry will be less interested in catalysts for olefin polymerisation." Jan-Dirk van Loon thinks differently. Van Loon is a project leader in Basell's Catalysts business unit and a member of the Programme Committee of the Polyolefins Technology Area. He is currently involved in the quality improvement programme Six Sigma, but previously he was responsible for marketing metallobene catalysts. "For some considerable time, the companies in the polyolefins business have been in the process of consolidating. But having said that, I would like to stress that catalysts are of the utmost importance to the industry. Not only as a means of improving the plant's economy, but also of improving the performance of the products." What has changed with respect to metallobenes, he says, is that a set of different questions arose within this industry's segment. Van Loon: "In the 1980s, companies were particularly active in exploring the potential scope of metallobene catalysts. Now they are much more focused on commercialising the existing set of catalysts. This leads to different questions that need to be addressed, from catalyst's support to scaling-up. Most of the time, the answers to these questions can be found only at the interface of various disciplines. For example, in the case of scaling-up supported catalysts, you have to deal with both solid state chemistry and process technology. It is exactly here that the role of DPI is crucial. DPI's research provides a platform for a multidisciplinary approach."

Trimerisation

Much of research is painstakingly cumbersome. You know you are following the right track, but despite all the efforts the research obstinately refuses to bear the expected fruits. And then, suddenly, there is a result, precisely when you least expect it. This is just what happened to Teuben's group. They were delving into pathways of polymerising ethene using single site catalysts, and suddenly hit upon the trimerisation of ethene to hexene-1. Teuben: "All in all, this is still a polymerisation of ethene, only it stops at three units. However, I agree it is a kind of serendipitous finding." Hexene-1 is an important raw material that is used in the many polyethylene resins for improving the (elastic) properties of the final product. The trimerisation of ethene was patented in 2001, and Teuben considers it to be one of the highlights of his group's research.

Elevated temperatures

One of the other highlights refers to a patent application filed in 2002. It involves the work of Winfried Kretschmer, who did a great deal of research into optimising a catalyst system for high molecular ethylene or α -olefin polymerisation. Teuben: "This titanium catalyst is not a metallocene, but contains in addition to a cyclopentadienyl another specific active ligand. What has now been proven is that the system works very nicely for ethylene at elevated temperatures." Van Loon: "First of all, of course, the industry is always interested in DPI patents. What is nice about the DPI research in Groningen is that in essence it is very fundamental research, but at the same time addresses the questions that are relevant for the industry." Both Teuben and Van Loon agree that that sums up DPI in a nutshell.



Jan-Dirk van Loon (Basell):

'Catalysts are of the utmost importance to the industry.'

In search of the ultimate properties

Nanotubes could very well be the next hot thing in Engineering Plastics. They are much stronger than steel and even stronger than Dyneema. But, besides the strength, they have many other valuable properties, e.g. they can also conduct electricity. Although the first commercial applications are entering the market, the current cost of producing nanotubes is standing in the way of a stream of new applications for the time being. Research on nanotubes is taking place within DPI. DSM, DPI's partner company and one of its founding fathers, is very interested.



Rob Kirschbaum (DSM):

‘The price for nanotubes is prohibitively high if nanotube-based products are to become commercially interesting.’

Rob Kirschbaum is Director of Innovation at DSM Venturing & Business Development, and for obvious reasons nanotubes have his interest. “Like genomics, bio-inspired materials, self-cleaning surfaces and so on”, says Kirschbaum. “A company like DSM is in constant search of materials that have the ultimate properties. Here we have a material that is the strongest and stiffest known to man. A big improvement on the materials available until now, such as Dyneema.” Nanotubes are a fashionable topic verging on hype. Typing the word into a search engine returns hundreds of thousands of results. There are numerous nanotube websites. CNN produced a feature on new fuel cells based on nanotubes. DSM recently announced a strategic alliance with Carbon Nanotechnologies (CNI), the company started by Nobel prize winner Richard Smalley. The greatest evidence of hype is the price that the material can fetch. Very pure single-wall nanotubes can easily set you back € 500 a gram. Kirschbaum: “This is absolutely crazy. As long as people are prepared to buy them for these prices, the situation will not change. However, I would estimate that, five years from now, the price will be close to € 100 a kilo. By the way, I recently visited a Chinese university that was producing nanotubes. They charge \$ 1000 for a kilo and the first kilo is given away free. But even this price is prohibitively high if nanotube-based products are to become commercially interesting.” Oren Regev works on nanotubes for DPI with Prof. Cor Koning and Dr Joachim Loos. He is a professor at the Ben-Gurion University of the Negev in Israel, and is currently on sabbatical at the TU/e: “It takes skill to make them and the process is not highly commercialised as yet.” Regev uses pure single-wall nanotubes for which he pays € 200 a gram. “We are working with model systems, which demands absolute cleanliness. I don’t want to have to worry about changing too many parameters at the same time. For most of the experiments we use only milligrams.”

Ultimate reinforcement

Nanotubes are fullerene-related carbon structures that consist of graphene cylinders closed at both ends with caps containing pentagonal rings. Just like fullerenes, they were discovered by accident. Japanese electron microscopist Sumio Iijima found them on the cathode during the arc-evaporation synthesis of fullerenes in 1991. It quickly became clear that a very promising material had been discovered. An extremely high elastic modulus coupled with a tensile strength an order of magnitude higher than conventional carbon fibres make carbon nanotubes the ultimate reinforcement in polymer and other composite materials. Kirschbaum: “Nanotubes seem to survive contact with molten aluminium, which

means that aluminium could be directly reinforced with carbon nanotubes, resulting in stronger and thinner materials. Imagine what that could mean in the aerospace sector, for instance in terms of fuel savings.” Regev: “I remain unconvinced that the first commercial application will be based on the mechanical strength of the nanotubes. Individual single wall nanotubes may well be very strong indeed, but as soon as they are integrated in a matrix, the mechanical properties are less impressive than we expected.”

Soccer field

Nanotubes, however, are versatile materials. Not only are they immensely strong, they can also conduct both heat and electricity, and their hollow geometry could allow them to be used for storing gas or liquid. Kirschbaum: “At a recent exhibition in Tokyo, they had a computer running on methanol. The fuel cell used is based on nanotubes that deliver the necessary specific surface area. Three grams of nanotubes is enough to provide a surface area the size of a soccer field.” Another recent announcement was made by Samsung, of the first TFT display based on nanotubes. Regev: “There are plenty of opportunities for nanotubes in the automotive industry. There is a demand for conductive coatings for electrical equipment with low loading of additives. Nanotubes could do the job.”

However promising, numerous and versatile the applications, there are still many problems to solve. Kirschbaum: “For example interfacial problems when reinforcing polymer materials and the tendency of single-wall nanotubes to form bundles, to name but a few.”

Patent

In that sense, Regev's work within DPI appears to be something of a breakthrough. A patent application has been filed, so at the time of publication of this annual report Regev is unable to go into details. Regev: “What we have done is to disperse nanotubes in a polymer matrix that we then make into a film by compression moulding. This results in a polymer film that we can study with scanning and transmission electron microscopy at room temperatures and cryogenic temperatures. As far as we know now, the process we have chosen leads to better performance with respect to electrical conductivity.”

Innovation

Both Regev and Kirschbaum think highly of DPI. Regev: “I have not seen a concept of this kind anywhere before. In most countries, the ties between industry and academia are loose, if not to say nonexistent. Kirschbaum thinks that DPI serves as a good intermediary between industrial research and academic research. “In the last decade, corporate R&D has shifted more to the business units, so putting longer-term research subjects under great pressure. This means that the gap between industrial research and academic research has become wider. Moreover, at a time of downturn in the chemical industries, the horizon is being shortened from many years ahead to no more than a quarter of a year. In an environment like this, DPI is a particularly effective instrument for safeguarding continuity.” A critical success factor, according to Kirschbaum, is for partner companies to attract good people into the DPI programmes. “It is my experience that DSM programmes will fit properly onto DPI programmes only if DSM deploys the right scientists and interface managers.”



Oren Regev (the Ben-Gurion University of the Negev, TU/e, DPI):

‘I am not convinced that the first commercial application will be based on the mechanical strength of the nanotubes.’

Sustainability covered by coatings

Coatings are omnipresent. Nine out of ten items in our everyday life are coated. In Europe alone, sales of paints amount to some € 16 billion. These data make it clear that coatings industries have to face the issue of sustainability. A great deal of research is needed to decrease the environmental footprint of coatings.

The chair in coatings at the TU/e is dedicated to this subject. An interview with the new professor of coatings, Dr Rolf van Benthem.



Rolf van Benthem (DSM, TU/e, DPI):

‘Coatings in itself is an example of sustainability avant-la-lettre.’

The chair in coatings has many colours. The succession of Professor Rob van der Linde was urged vigorously by DPI; it is hosted by the TU/e and partially financed by DSM. Rolf van Benthem has occupied the only chair in coatings in the Netherlands since October 2002. The professorship is part time, and for the rest of the time he is Competence Network Manager at DSM, including programme manager for Coatings Resins. Van Benthem has put sustainability high on the scientific agenda. Van Benthem: “I am always explaining to people that a coating in itself is an example of sustainability *avant-la-lettre*. The function of the coating is to extend the lifetime of the product that is coated, not forgetting the decorative aspect, of course.” But naturally, sustainability requires more. As Research Commissioner Philippe Busquin states in respect to Framework VI: “Tremendous opportunities are offered by research to optimise the life cycle of materials and products and to break the link between environmental impact and economic growth. This is one of the major objectives of European research, which should be pursued for many years to come.” The classic definition of sustainable development is: “meeting the needs of the present without compromising the ability of future generations to meet their own needs”.

Alternatives

There are many alternatives to the traditional solvent-borne coatings, for example water-borne coatings and powder coating systems. They are solvent-free, easier to recycle and produce fewer waste products. On the other hand, powder coatings are restricted primarily to industrial use. It is unfair to expect anyone at home to start using powder coatings to paint window frames. Yet there is a more fundamental problem. Van Benthem: “In order to really boost the alternative coatings systems, solvent-free coatings should match the performance of solvent-borne coatings. Reaching this state will require considerable research.” One of the DPI projects is about overcoming the temperature problem of powder coatings. Van Benthem: “The drawback of powder coatings is that they need high temperatures, up to 200 °C, for flowout and cure. The DPI project *Low temperature curable powder coatings by encapsulated crosslinkers* aims at lower curing temperatures and the associated energy savings. This may be done by encapsulating the crosslinkers in the paint and unleashing them with a highly temperature-sensitive trigger mechanism.”

Self-healing

Many roads, however, lead to sustainability. Maintenance, an important aspect of coatings, is not inherently a sustainable effort. It uses energy and produces waste. The Van Benthem's group have successfully researched fluor-containing coatings to reduce the need for maintenance. Fluor from the polymer migrates to the surface where it appears to have an antifouling effect. But questions arose as to whether the effect is lasting. What happens if such a coating is brushed during cleaning? If the fluor-containing top layer is removed in the process, the water and soil-repellent properties will be lost. One project within DPI's Coating Technology area is addressing this very problem. Van Benthem: "The obvious route to self-healing or self-replenishing is to try to get the fluor throughout the entire coating during crosslinking. When the fluorinated fragments gradually migrate to the surface, the coating would have the ability to recover its repellency after being damaged."

Green coatings

The ultimate dream for a research group aiming at sustainability would be to use raw materials from natural resources instead of materials based on petrochemicals. One such project is on its way in cooperation with DPI's newest partner, ATO-DLO. One of the options could be to use sugar-based diols. But, because the project has yet to be approved by the Programme Committee of Coating Technology, Van Benthem is reluctant to say very much about it.

Smart versus sustainable

On the same day as the interview, The Walt Disney Company announced that it is to use flexible play DVD technology to make movies available to consumers for a limited time. After 48 hours, the DVD will no longer be readable by the DVD player and can then be recycled. The DVD, based on a newly patented resin co-polymer from GE Plastics, has a special coating that turns from red (readable) to black (non-readable) within 48 hours. Van Benthem: "That is in principle the direction coatings will take. Coatings need to protect and at the same time be decorative and preferably smart as well. But we have to bear in mind that smart and sustainable do not always go together. And if forced to choose, I would go for sustainability."



**"Coatings need to protect,
be decorative, sustainable and
preferably smart as well."**

Future of TPVs is sealed

Thermoplastic elastomers are gradually replacing classical crosslinked rubbers, because they are easier to process and recycle, among other reasons. The market for thermoplastic vulcanisates is growing at an annual rate of 13 %. This class of elastomers is especially useful in under-the-bonnet applications in cars and they have great potential in automotive weatherseals, e.g. in door and boot seals. DPI research into rubber technology focuses on optimising the peroxide systems used as the basis for vulcanisates. An interview with DPI researcher Kinsuk Naskar and Akzo Nobel's senior application scientist Jernej Jelenic.



Jernej Jelenic (Akzo Nobel):

‘That is the strength of DPI, doing scientific research that addresses industrial needs.’

“The use of peroxides in thermoplastic vulcanisates is a fine example of the neat concept of DPI”, says Jernej Jelenic, senior application scientist in the R&D team ‘crosslinking peroxides & polymer additives’ and industrial contact person in DPI for rubber technology. Jelenic adds: “There are two types of curing systems for thermoplastic vulcanisates. The traditional phenol-formaldehyde resins and the more recent organic peroxides. The disadvantages of the phenolic resins created an industrial demand for alternatives.” Kinsuk Naskar, a PhD student in Prof. Jacques Noordermeer's group, speedily sums them up. “Phenolic resin cured TPVs are difficult to colour and can easily absorb water. On the other hand, thermoplastic vulcanisates based on peroxides are easier to process without showing any colouring problem.” Thermoplastic vulcanisates (TPVs) are the result of mixing and crosslinking a rubber in a thermoplastic polymer. Microparticles of fully vulcanised EPDM rubber are dispersed in a polypropylene matrix. Because of this chemical structure, TPVs resemble vulcanised EPDM in mechanical properties. Naskar: “We are trying to optimise the peroxide-based curing system for PP-EPDM TPVs, resulting in a maximum curing yield of EPDM (ethylene-propylene-diene terpolymer) and a minimum degradation of polypropylene.”

Optimising properties

The solubility parameter of the peroxides and that of the polymers, the decomposition mechanism of the various peroxides and the kinetic aspects determine the final properties of TPVs. Naskar's research focuses on selecting the optimum peroxide-coagent combination. Naskar: “We examined five different types of peroxides at a fixed PP/EPDM blend ratio. The results show that dicumyl peroxide, DCP, yields the best overall properties.” Naskar also investigated the influence of peroxides at various PP/EPDM blend ratios. As the quantity of PP increases, the tensile strength, Young's modulus and hardness of TPVs increase and compression set properties deteriorate. This, of course, is a logical consequence of the increased thermoplastic component (hard phase) in the blend. Once again, DCP proved that, irrespective of the blend composition, it is the best peroxide system for delivering TPVs with the finest balance of properties.

Opportunities

Jelenic: “That is the strength of DPI, doing scientific research that addresses industrial needs. DCP may be the best peroxide to produce TPVs, but a major disadvantage of some peroxides is that they decompose and give rise to smelly by-products. Kinsuk’s research has found alternatives that avoid this effect.” Naskar: “What we did was to use multifunctional peroxides. That is to say, peroxides that combine both peroxide and co-agent functionality in one single molecule. We found that multifunctional peroxides give TPVs with properties that are more or less comparable with TPVs where ‘normal’ peroxides were used. However, the multifunctional ones do not provide smelly by-products.”

All this will add to the potential fit for TPVs as a substitute for vulcanised EPDM rubber. Jelenic: “We are committed to continuing the developments initiated by DPI together with our customers in specific applications. I believe that our crosslinking technology with peroxides will significantly contribute to the further market growth of TPVs.”



Kinsuk Naskar (DPI):

‘We found that multifunctional peroxides give TPVs with properties that are comparable with TPVs where ‘normal’ peroxides were used. However, the multifunctional ones do not provide smelly by-products.’

Bright future for polymer electronics

Traditionally, polymers have been used in applications where their mechanical properties are paramount. Since the discovery that polymers can conduct electricity, they have quickly started to appear in optical and electronic devices. Initially they were used as photoconductors in photocopiers, but more recently they have become crucial as active components, for example in polymerLED displays and polymeric integrated circuits. The first shavers with polyLED displays are now commercially available. The semiconducting polymers used in photocopiers, transistors and displays are usually based on different types of materials, but what they have in common is the importance of the charge transport. Various publications have proposed different models for the different materials. DPI research in the Functional Polymer Systems Technology Area has revealed that a single model is able to describe the charge transport for all three applications for all three classes of semiconductors in common use. An interview with DPI researcher Cristina Tanase (RUG) and Industrial Contact Person Dago de Leeuw (Philips).



Dago de Leeuw (Philips):

‘Polymers are entering the world of high-tech applications.’

“Did you know that the first 17-inch polyLED display has now been fabricated in a research environment?”, Dago de Leeuw (Philips) asks Cristina Tanase (DPI) at the start of the interview before adding pensively, apparently to no one in particular: “Plastics are associated with insulating. Indeed, they are very good insulators, which is why copper wires are encased in plastic. So it comes as a surprise to many people that plastics can be conductors or semiconductors. For that matter, people also associate plastics with cheap or low-tech products. The stuff you have in the garden if you cannot afford the wooden garden furniture. But suddenly, polymers are entering the world of high-tech applications.”

From transistors to flexible displays

The research on polymers for use in ICs and displays has rocketed in recent years. In the mid 1970s it was discovered that conjugated double bonds in polymers make it possible for electrons to jump from one molecule to another. As early as the mid 1980s, polymers were being used as photoconductors in copiers. The next milestone was transistors or even ICs made entirely from polymers. De Leeuw: “The idea arose that it would be great not to have to unload the shopping cart full of products at the checkout, but just walk through and leave the shop. This would require transponders and small IC tags on the products, which would be feasible only if the ICs were low cost. This led to the development of polymer transistors and eventually all-polymer integrated circuits.”

However, the most exciting developments in the area of polymer electronics are in polymer-based displays. Interest in this area started after the discovery that certain polymers are also able to emit light. The benefits of polymer displays are so numerous that the next generation of displays is likely to be based on them. Tanase: “PolyLEDs have great

advantages. They are light, thin, flexible and require no backlight. PolyLED displays have a high contrast, high brightness and require less power." PolyLED displays are already being used in mobile phones, personal digital assistants and shavers. Philips introduced the first polyLED display in the Sensotec men's shaver, which gained celebrity status after its appearance in a James Bond film.

Hopping of electrons

In principle, polymers are characterised by low charge carrier mobility, which is a measure of how easily electric charge moves through the material. The higher the mobility, the greater the number of applications that become possible. As polymers are often tangled up like spaghetti, a limit is imposed by the ability of electrons to hop from one chain to another. Conductivities of 10^5 S/cm have been realised so far, but polymers with such high values are still very unstable. De Leeuw: "For all applications mentioned, the charge transport in the polymers is an important parameter."

Predictive value

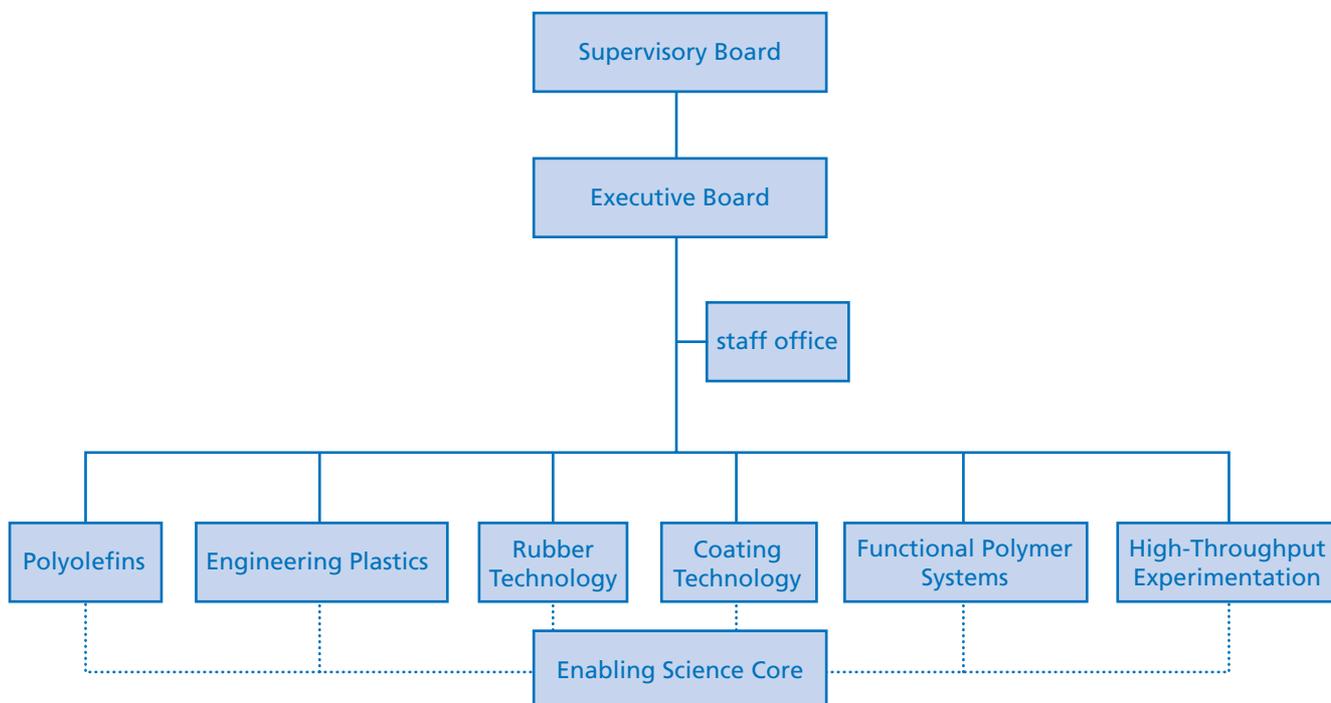
Anyone reading Tanase's latest article to be published on hole mobility in hole-only diodes and field-effect transistors, might be tempted to jump to the conclusion that her research is about pure physics with no direct value to applications. Tanase: "We used two polymers, OC₁C₁₀-PPV (poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) and P3HT (poly(3-hexyl thiophene)) to make both LEDs and FETs. The experimental mobilities in both systems were determined from the transfer characteristics of these devices. The large mobility differences obtained between LEDs and FETs is determined by the strong dependence of the hole mobility on the charge carrier." Dago de Leeuw is quick to stress the importance of basis research of this kind. "Conjugated conductive polymers are used in transistors, LEDs and photocopiers. Models have been proposed in numerous papers to describe the charge transport in materials of this type. The problem is that no two different applications use the same type of polymer. So you have as many models as polymers used. The importance of Cristina's research is that she came up with one model that unifies previous models in LEDs and FETs. This obviously has great predictive value, and that in turn will benefit the improvement of materials."



Cristina Tanase (RUG, DPI):

'One model can describe the charge transport in transport in transistors, LEDs and photocopiers.'

DPI organisation



Members of the Supervisory Board

Dr Ir H.G.J. de Wilt, chairman
 Prof. Dr E. Meijer, DSM Research BV, vice chairman
 Prof. Dr L. Boehm, Basell Polyolefine GmbH
 Ir A.C.G. de Kok, Dow Benelux NV
 Drs N.P.J. Kuin, Océ Technologies
 Mr. Dr P.W. Kwant, Shell International BV
 Prof. Ir K.C.A.M. Luyben Technical University Delft
 Ir J.H.J. Mengelers, TNO Institute of Industrial Technology (Eindhoven)
 Dr Ir J.A. Pals, Philips Research
 Prof. Dr R.A. van Santen, TU/e
 Prof. Dr W.C. Sinke, ECN - Energy Research Centre of the Netherlands
 Prof. Dr Ir H. Tijdeman, University Twente
 Dr Ir J.A.J.M. Vincent, Sabc EuroPetrochemicals BV
 Prof. Dr D.A. Wiersma, University of Groningen
 Prof. Dr J. de Wit, Akzo Nobel NV

Members of the Executive Board

Ir G. van Os, Managing Director
 Prof. Dr P.J. Lemstra, Scientific Director
 Drs J.P. Bakker, Financial Director

Programme Management Technology Areas

Dr B.C. Roest, Polyolefins
 Ir R.P.A. van den Hof, Engineering Plastics
 F. Thys, Coating Technology
 Prof. Dr Ir J.W.M. Noordermeer, Rubber Technology
 Prof. Dr M.A.J. Michels, Functional Polymer Systems
 Prof. Dr U.S. Schubert, High-Throughput Experimentation
 Prof. Dr P.J. Lemstra, Core

Staff Organisation

Dr J.A.K.M. Buskes, communications manager (a.i.)
 Drs. M.C.A van Egmond, management assistant
 Ir. S.K. de Vries, programme officer
 Drs. A.M.L. Noordzij, secretarial support
 F.B.C. Drouvin, secretarial support

Core Programme factsheet

Overview

At the end of phase 1 (1997-2001), DPI made strategic adjustments in the organisation for phase II (2002-2008). This led to an enabling science Core Programme connected to and serving all Technology Areas. The need for the restructuring was that by late 2001 many of the partner companies found themselves no longer able to participate actively in the full spectrum of DPI activities. For example, some were prevented by reorganisations and the sale of certain activities from making their staff available to serve on the various Programme Committees.

In the first half of 2002, the DPI Management Team made strenuous efforts to start the development of the Core Programme. The first step that they undertook was to analyse all projects within DPI. Non-TA-specific projects were transferred to the DPI Core Programme, most notably the projects that originated in the former “Mesoscopic Chemistry/Physics” subcluster. Next to Mesoscopic Chemistry/Physics, four new activities were formulated for the future Core Programme: polymer characterisation, high-throughput experimentation/combinatorial chemistry, bio-related polymers and polymers in medicine and structure vs. performance & solid-fluid mechanics of polymers

Mission

The DPI Core Programme was initiated as an enabling science activity supporting research in the various TAs. The objectives are twofold:

- fostering advanced characterisation techniques and modelling activities to support research programmes in the various Technology Areas, and
- incubating new research activities, which are fostered for some time within the DPI Core but may in due course develop into a new Technology Area with new and/or existing industrial partners.

In addition to this twofold purpose, the Core Programme acts as ‘cement’ between the various TAs. The goal of the DPI Core Programmes is full integration with the five Technology Areas. The mission is for the DPI Core Programme to connect to national and European programmes, for example within Framework VI, thereby providing a funnel of basic knowledge into the DPI community and feeding targeted research programmes: TAs and future IPs (Integrated Projects in the EU Framework VI terminology).

Partners

The activities on Polymer Characterisation are concentrated at the Universities of Amsterdam (Schoenmakers and partners), Twente (Vancso and partners) and Eindhoven (Goossens and partners). The DPI Executive Board decided at the end of 2002 to support the chair at the UvA (Schoenmakers) with 0.25 FTE starting in 2003, to enable Prof. Schoenmakers to coordinate the polymer characterisation activities in the Netherlands in a virtual organisation of researchers from the DPI partner companies.

In 2002, the programme on High-Throughput-Experimentation (HTE) and Combinatorial Chemistry took off almost exponentially at the TU/e, thanks to the supreme effort put in by Prof. U. Schubert, (see highlights 2002).

Although activities on bio-related polymers and polymers in medicine did not start in 2002, numerous proposals were received, notably from ATO (Dr Eggink and partners). Modelling activities (solid/fluid mechanics etc.) are concentrated in Eindhoven (Profs. Meijer, Baaijens and Michels).

Budget

The budget for the Core activities in 2003 is approximately € 2.4 million (16% of the total annual DPI budget). The number of allocated FTEs at the end of 2002 was close to 20, but a marked increase is expected in 2003 (when projects are due to start up in the “bio-related polymers” subarea).

Communications

The Programme Committee for the Core Programme consists of the five Programme Managers, with the DPI scientific director acting as chairman. In 2003, this committee will be augmented with academic experts.

In view of the recent start-up of the Core Programme activities, meetings were organised on an ad-hoc basis in 2002. For the “Polymer Characterisation” topic, many meetings were organised with industrial representatives to get the programme under way. For the “high-throughput experimentation/combinatorial chemistry” topic, a dedicated workshop was organised with industry in the spring of 2002. For the “modelling, solid/fluid mechanics of polymers” topic, meetings were held with industrial contact persons. All these meetings will be streamlined in 2003.

The aim is to link the DPI Core Programme to the “outside academic world”. The underlying idea is to funnel basic knowledge via the Core into the various DPI Technology Areas.

Highlights of 2002

- The DPI Core Programme was installed and the budget allocated (16% of total budget);
- the activities in the high-throughput experimentation subarea took off almost exponentially, including three new dedicated industrial partners (NTI, Avantium and Chemspeed);
- a nucleus was created for a nationwide activity on polymer characterisation, serving the DPI community;
- the modelling activities, backed up by experimental validation, on the “toughness” topic reached a breakthrough status.

Projects

Products of controlled/living polymerisation

(Ten Brinke-RUG; Klumperman-TU/e)

New copolymers will be made aiming at unique morphologies and properties of the tapered/gradient type. The objective is to gain the most complete control possible on copolymerisation techniques in order to produce tailor-made (co)polymers, leading to unique copolymer structures that can be used as compatibilisers in blends or in functional devices.

New materials from polymer-ceramic nanocomposites (Fischer-TNO)

Exploring engineering possibilities based on nanoclay additives will lead to polymeric materials with enhanced barrier and thermal properties.

New living polymers (Fleer, Cohen Stuart-Wageningen University)

Making polymer chains based on association rather than covalent bonds and to develop a new class of living polymers that self-associate into long chains. The deliverables will be a new class of polymers with controlled solution and melt-viscosity.

Colloidal LC reinforced composites (Picken-TU Delft)

The objective is to make composite materials with the properties of fibre-reinforced composites and the ease of processing of unfilled systems or TLCPs.

Polymer characterisation (coordinator Schoenmakers UvA)

Characterisation tools are advancing rapidly, and DPI aims to be at the forefront with available techniques, also at prototype level, and dedicated personnel. The objective is to establish a platform within DPI for the characterisation of polymer systems, both the molecular structure and physical properties, including morphology at various length scales. This platform will deliver up-to-date analytical tools and well-trained personnel to enable the DPI community to make use of state-of-the-art polymer analysis.

High-throughput experimentation/combinatorial chemistry

(coordinator Schubert TU/e)

Combinatorial techniques are set to revolutionise how R&D is performed in the area of synthetic polymers (as in the past in pharmaceuticals). The aim is to explore in depth the possibilities of combinatorial techniques in the field of synthetic polymers, offering DPI partners the possibilities of combinatorial chemistry, including the training of PhD students, who are potential future personnel for partner companies.

Bio-related polymers & polymers in medicine (no projects in 2002)

Biotechnological routes may provide novel ways of making specific (co)polymers; the use of “plastics” in the human body will be the key issue for the coming years.

The project’s objective is to explore the possibilities of biotechnology for making specific (co)polymers (e.g. enzymatic polymerisations) and to make use of the know-how within DPI for specific projects in the “Polymers in Medicine” area, or, more specifically, implants. This will lead to novel routes for making specific (co)polymers and novel products for medical implants

Modelling, solid/fluid mechanics of polymers

(coordinator Meijer (HEH)-TU/e)

The aim is to better understand and generalise experimental results as well as reducing the number of experiments significantly, placing an emphasis on modelling validated by experiments. A basic understanding of polymer properties, notably fluid dynamics (rheology) and solid-state properties, e.g. toughness, will deliver a strong knowledge base for the DPI community and a high profile and visibility in the academic world.

Targets 2003

- To expand the polymer characterisation subarea with more physical analysis. In this respect, the new activities on cryomicroscopy at the TU/e is already an asset.
- To integrate the High-Throughput Experimentation/Combinatorial Chemistry subarea with the various Technology Areas and/or to establish a separate (new) TA in this area;
- To start challenging projects in the bio-related polymers and polymers in medicine subarea;
- To connect modelling with experimental validation and input to the various TAs.

Output 2002

Theses

Galaktionov, O.S., Optimization of distributive mixing: From prototype flows to industrial devices, 2002.

Scientific Papers

Grillet, A.M., A.C.B. Bogaerds, G. W.M. Peters, F.P.T. Baaijens, Numerical analysis of flow mark surface defects in injection molding flow, *Journal of Rheology*, 2002, 46, 651-670.

Tyagi, S., A.K. Ghosh, P. Montanari, G.W.M. Peters, H.E.H. Meijer, Linear viscoelastic and transient behavior of polypropylene and ethylene vinyl acetate blends: An evaluation of the linear palierne and a nonlinear viscoelastic model for dispersive mixtures, 2002, 42(11), 2107-2119.

Verbeeten, W.M.H., G.W.M. Peters, F.P.T. Baaijens, Viscoelastic analysis of complex polymer melt flows using the extended pom-pom model, *Journal of Non-Newtonian Fluid Mechanics*, 2002, 108(1-3), 301-326.

Anderson, P.D., O.S. Galaktionov, G.W.M. Peters, H.E.H. Meijer, C.L. Tucker, Material stretching in laminar mixing flows: extended mapping technique applied to the journal bearing flow, *International Journal for Numerical Methods in Fluids*, 2002, 40, 189-196.

Bogaerds, A.C.B., A.M. Grillet, G.W.M. Peters, F.P.T. Baaijens, Stability analysis of polymer shear flows using the extended pom-pom constitutive equations, *Journal of Non-Newtonian Fluid Mechanics*, 2002, 108, 187-208.

Grillet, A.M., A.C.B. Bogaerds, G.W.M. Peters, F.P.T. Baaijens, Stability analysis of constitutive equations for polymer melts in viscometric flows, *Journal of Non-Newtonian Fluid Mechanics*, 2002, 103, 221-250.

Peters, G.W.M., F.H.M. Swartjes, H.E.H. Meijer, A recoverable strain based model for flow-induced crystallization, *Macromolecular Symposia*, 2002, 185, 277-292.

Schrauwen, B.A.G., L.E. Govaert, G.W.M. Peters, H.E.H. Meijer, The influence of flow-induced crystallization on the impact toughness of high-density polyethylene, *Macromolecular Symposia*, 2002, 185, 89-102.

Melick, H.G.M. van, A. van Dijken, J.M.J. den Toonder, L.E. Govaert, H.E.H. Meijer, Near-surface mechanical properties of amorphous polymers, *Philosophical Magazine B*, 2002, 10, 2093-2102.

Galaktionov, O.S., P.D. Anderson, G.W.M. Peters, C.L. Tucker III, A global, multi-scale simulation of laminar fluid mixing: the extended mapping method, *International Journal of Multiphase Flow*, 2002, 28(3), 497-523.

Galaktionov, O.S., P.D. Anderson, G.W.M. Peters, H.E.H. Meijer, Mapping approach for 3D laminar mixing simulations: application to industrial flows, *International Journal for Numerical Methods in Fluids*, 2002, 40(3-4), 345-351.

Anderson, P.D., O.S. Galaktionov, G.W.M. Peters, H.E.H. Meijer, C.L. Tucker III, Material stretching in laminar mixing flows: extended mapping technique applied to the journal bearing flow, *International Journal for Numerical Methods in Fluids*, 2002, 40(1-2), 189-196.

Galaktionov, O.S., P.D. Anderson, G.W.M. Peters, H.E.H. Meijer, morphology development in kenics static mixers (application of the extended mapping method), 2002, 80, tbd-tbd.

Galaktionov, O.S., P.D. Anderson, G. W. M. Peters, Structure development during chaotic mixing in the journal bearing flow, *Physics of Fluids*, 2002, 14(9), 3009-3017.

Lyulin, A.V., N.K. Balabaev, M.A.J. Michels, Correlated segmental dynamics in amorphous atactic polystyrene: a molecular dynamics simulation study, *Macromolecules*, 2002, 35(25), 9595-9604.

Lyulin, A.V., J.J. de Groot, M.A.J. Michels, Computer simulation study of bulk atactic polystyrene in the vicinity of the glass transition, *Macromolecular Symposia*, 2002.

P. van der Schoot, Scaling theory of chemically activated living polymerization in a good solvent, *Macromolecules*, 2002, 35, 2845-2850.

Lyulin, A.V., M.A.J. Michels, Large-scale computer simulation of local segmental dynamics in amorphous atactic polystyrene, *Computer Physics Communications*, 2002, 147, 298-302.

Lyulin, A.V., M.A.J. Michels, Molecular dynamics of bulk amorphous Polystyrene in the vicinity of T_g, *Macromolecules*, 2002, 35, 1463-1472.

Schoot, P. van der, Self-Assembly of globular particles in a nematic dispersion of colloidal rods, *Journal of Chemical Physics*, 2002, 117, 3537-3540.

Gucht, J. van der, N.A.M. Besseling, G.J. Flier, Statistical thermodynamics of equilibrium polymers at interfaces, *Physical Review E - Statistical, Nonlinear and Soft Matter Physics*, 2002, 65, 051801.

Gucht, J. van der, N.A.M. Besseling, M.A. Cohen Stuart, Surface forces, supramolecular polymers and inversion symmetry, *Journal of the American Chemical Society*, 2002, 124, 6202-6205.

Gucht, J. van der, N.A.M. Besseling, G.J. Flier, The chain-length dependence of polymer chains at a surface near the adsorption/depletion transition, *Macromolecules*, 2002, 35, 2810-2816.

Gucht, J. van der, N.A.M. Besseling, G.J. Flier, Surface segregation in polydisperse polymer melts, *Macromolecules*, 2002, 35, 6732-6738.

Hoogenboom, R., M.W.M. Fijten, U.S. Schubert, Living cationic polymerizations utilizing an automated synthesizer, 2002, 43(2), 969-970.

H. Zhang, R. Hoogenboom, M.W.M. Fijten, U.S. Schubert, Screening and application of ATRP catalysts utilizing an automated synthesizer, 2002, 43(2), 17-18.

Polyolefins factsheet

Overview

The Polyolefins Technology Area seized every available opportunity in 2002 to grow to maturity. In many cases, a stage was reached where it was possible to harvest the results of the projects launched in 1998-1999, leading to a number of high-quality publications. New projects based on these results were started. The Technology Area also co-sponsored third parties on a significant scale, examples of which were an impressive conference in Sorrento, initiated and chaired by Prof. Busico, and a symposium on catalysis in Eindhoven, organised by Prof. Niemantsverdriet's group and Dr Chadwick's team.

SABIC's decision to take over a number of tickets from DSM, and DSM's simultaneous decision to stay, have meant that our platform has grown significantly.

Partners

Industry

The partners in this Technology Area in 2002 were Basell, SABIC, DSM, Dow, Akzo Nobel and Shell.

Academia

Eight institutes participated in the programme: the COP centre (University of Groningen), TU/e and the Universities of Twente, Utrecht, Amsterdam (UvA), Nijmegen, Naples and Hamburg.

Budget

The budget spent in 2002 was € 2.44 million. The number of FTEs allocated at the end of 2002 was approximately 30.

Communications

The organisation is now well established. Three meetings of the Programme Committee have been held, as well as three polyolefin days, which are open to scientific and industrial cluster members. These days were held at RUG, UTwente and TU/e. Regular meetings are held with the main scientists to coordinate organisational issues and – preferably – scientific actions. Four of these scientists have been appointed as Programme Coordinators, and we are now establishing the details of the practical implementation of this position.

Highlights of 2002

- Scientifically, important results were achieved in the metal-organic groups of RUG and Utrecht, both leading to new

insights into structures, a patentable process to produce 1-hexene by trimerisation of ethene and a very productive study on the role of MAO (or the like) as cocatalyst. The KUN made an interesting modelling contribution.

- At the TU/e, significant progress was made in the immobilisation of single-site catalysts. The filing of a patent application is in progress.
- Also at the TU/e, a new way of preparing UHMWPE with a narrow MWD was invented, which will be patented.
- A study of the initial stages of the polymerisation of ethene with Cr, located on small SiO₂ wafers, attracted much attention and was published in *Macromolecules*.
- The Chadwick group made a welcome addition to our studies by focusing on the “classical” Ziegler-Natta catalysts, which, especially in PP, are still unbeatable in general performance. A contribution was written for an encyclopaedia.
- The grain-free sintering of UHMWPE was developed further, leading to additional patents and a broader application range. Besides prostheses, other applications have not been ruled out. The basic theory, which comprises a method of controlling entanglement and disentanglement, is becoming increasingly clear as an important instrument in practice.
- The University of Hamburg completed a research project on polypropylene structures in relation to the metallocene structures used as a catalyst.
- The University of Naples is still making impressive progress on mechanistic studies, mainly for the propene polymerisation and the ethene-propene block copolymerisation. The relationship between active sites, their environment and the tacticities are becoming increasingly clear, thanks to very skilled workers and high-class NMR equipment.
- The Chemical Technology department of the UvA (Prof. Iedema) is working on an interesting modelling system of the polymerisation of ethene under high pressure (LDPE) giving a direct connection to rheological values.
- The broadening of PP molecular weight distributions was studied successfully using a unique new reactor-calorimeter (Prof. Weickert). Highly precise and reproducible polymerisation rate profiles can be measured in gas, liquid, and slurry phases. Based on these measurements, the hydrogen response in both polymerisation rate and average molecular weight was measured using Ziegler-Natta catalysts, and a completely new mathematical model has been developed.

- Within the “riser-downer project” the miniplant has now entered the test phase and new methods have been developed to model the plug-flow behaviour. This extended “fluidization” model was combined with a comprehensive kinetic study, and a new predictive reactor model was suggested for describing the behaviour of this new reactor type.
- The LLDPE miniplant of the High Pressure Laboratories was completed and is used by several DPI groups (Chadwick, Hessen, Loos) for testing new catalysts and supporting techniques.
- The preparation phase of two more reactor setups - tubular reactor and hollow shaft reactor - is complete. Completion of these facilities depends on future financing.

Output 2002

Patents

Kretschmer, W.P., Olefin polymerization catalyst component, catalyst system and process using such a catalyst system, 5 March 2002.

Theses

Deckers, P.J.W., Non Flory-Schultz ethene oligomerisation with titanium-based catalysts, Groningen, 2002.

Hopf, A., Homo- und Copolymerisation von Propen/Ethen mit Cs-symmetrischen Metallocen/MAO-Katalysatoren, Hamburg, 2002.

Bogaerds, A.C.B., Stability of viscoelastic flows, 2002.

Rastogi, A., Molecular organization in homogeneous polyethylene copolymers at elevated pressure-temperature, Molecular organization in homogeneous polyethylene copolymers at elevated pressure-temperature, 2002.

Proceedings

T.J.J. Sciarone, C.A. Nijhuis, A. Meetsma, B. Hessen and J.H. Teuben, Electron deficient iron benzyl complexes and the weak interactions of derived cations with fluorinated arylborate anions, Noordwijkerhout, 2002.

I.C. Van Puten, A.G.J. Van der Ham, Hydrodynamics of a tubular slugging reactor for olefin polymerization, Circulating Fluidized Bed Technology 7, 2002.

Parasu Veera, U., G. Weickert, Y. Banat, The effects of temperature, pressure, and particle size on the equilibrium sorption of propylene in semi-crystalline polypropylene and comparison between liquid and gas phase propylene polymerization with a highly active Ziegler-Natta catalyst, 2nd European Conference on Reaction Engineering of Polyolefins (ECOREPID), Lyon (France), 2002.

Parasu Veera, U., G. Weickert, U.S. Agarwal, Simulation of the multi-grain model via fixed boundary transformation, 2nd European Conference on Reaction Engineering of Polyolefins (ECOREPID), July 1-4 2002, Lyon (France), 2002.

Scientific papers

Pater, J.T.M., G. Weickert and W.P.M. van Swaaij, Polymerisation of liquid propylene with a 4th generation Ziegler-Natta catalyst—influence of

temperature, hydrogen and monomer concentration and prepolymerisation method on polymerization kinetics, Chemical Engineering Science, 2002, 57 (16), 3461-3477.

Kretschmer, W.P.; C. Dijkhuis; A. Meetsma; B. Hessen; J.H. Teuben, A highly efficient titanium-based olefin polymerisation catalyst with a monoanionic imidoimidazolidide p-donor ancillary ligand, Chemical Communications, 2002, 608-609.

Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G., A bis (ortho-amine)aryl-gold(I) compound as an efficient, nontoxic, arylating reagent, Organometallics, 2002, 21(21), 4556-4559.

Zhang, X. B. Hessen, Polyethylene with Pendant 3-Thienyl Functionalities, Chemical Communications, 2002, 23, 2862-2863.

Busico, V., R. Cipullo, G. Talarico, W.P. Kretschmer, V. van Axel Castelli, M. Vacatello, Oscillating metallocene catalysts: how do they oscillate?, Angewandte Chemie-international Edition, 2002, 41, 505-508.

Loos, J., M. Arndt-Rosenau, U. Weingarten, W. Kaminsky, P.J. Lemstra, Melting behavior of nascent polyolefins, Polymer Bulletin, 2002, 48(2), 191-198.

Severn, J.R., R. Duchateau, R.A. van Santen, D.D. Ellis, A.L. Spek, Homogeneous Models for Chemically Tethered Silica-Supported Olefin Polymerization Catalysts, Organometallics, 2002, 21(1), 4-6.

Busico, V., R. Cipullo, W. Kretschmer, G. Talarico, M. Vacatello, V. van Axel Castelli, The strange case of the "oscillating" catalysts, Macromolecular Symposia, 2002, 189, 127-141.

Beekmans, L.G.M.; D.W. van der Meer; G.J. Vancso, Crystal melting and its kinetics of poly(ethylene oxide) by in-situ atomic force microscopy, Polymer, 2002, 43(6), 1887-1895.

Meer, D.W. van der, B. Pukanszky, G.J. Vancso, On the dependence of impact behavior on the crystalline morphology in polypropylenes, Journal Of Macromolecular Science-physics, 2002, B41 (4-6), 1105-1119.

Iedema, P.D., Grcev, S., Hoefsloot, H.C.J., Molecular Weight Distribution Modeling of Radical Polymerization in a CSTR with Long Chain Branching through Transfer to Polymer and Terminal Double Bond (TDB) Propagation, Macromolecules, 2002, 11(4), 410-428.

Iedema, P.D., Hoefsloot, H.C.J., Molecular weight distribution modelling of radical polymerization in batch and continuous reactors with transfer to polymer leading to gel formation, Macromolecular Theory and Simulations, Weinheim, 2002, 11(4).

Parasu Veera, U.; G. Weickert; U.S. Agarwal, Modeling monomer transport by convection during olefin polymerization, Aiche Journal, 2002, 48(5), 1062-1070.

Loos, J., M. Arndt-rosenau, U. Weingarten, W. Kaminsky, P.J. Lemstra, Melting behavior of nascent polyolefins synthesized at various polymerization conditions, Polymer Bulletin, 2002, 48, 191-198.

Rastogi, S., P.T.J. van der Burgt, J.G. Chadwick, B. Rieger, Influence of thermal treatments on the polymorphism in stereoirregular isotactic polypropylene: effect of stereo-defect distribution, Journal Of Macromolecular Science-physics, 2002, B41, 1091-1104.

Parasu Veera, U.; G. Weickert; U.S. Agarwal, Modeling monomer transport by convection during olefin polymerization, Aiche Journal, 2002, 48(5), 1062-1070.

Agarwal, U.S., Simulation of bubble growth and collapse in linear and pom-pom polymers, e-Polymers, 2002, 014.

Ming, W., M. Tian, R.D. van de Grampel, F. Melis, X. Jia, J. Loos, R. van der Linde, Low surface energy polymeric films from solventless liquid oligoesters and partially fluorinated isocyanates, Macromolecules, 2002, 35(18), 6920-6929.

Tian, S.W., J. Loos, Low voltage scanning electron microscopy (LVSEM) and atomic force microscopy (AFM): state-of-art microscopy techniques for investigations of polymer single crystals, e-Polymers, 2002, 036.

Engineering Plastics Factsheet

Overview

The traditional view of engineering plastics puts them somewhere between the bulk polymers (polyolefins, PS, PVC) and specialty polymers (“specialty” primarily in the sense of their very high temperature resistance). This ‘in-between situation’ is thought to reflect their better than bulk-polymer properties at higher added value and their lower cost compared with the specialty polymers. This is indeed true for the current polymer producers. A producer of nylons, polyesters or polycarbonate faces the challenge of continuously improving the properties of the materials and opening up new application areas and markets. This demands

incremental improvements in the polymer processes and composition of formulation. After all, every engineering plastic on the market is a composition of the polymer in question plus various products that are added to enhance properties: fibre reinforcement, flame retardants, impact modifiers, mineral fillers, pigments, and so on.

Another view on engineering plastics sees them as the solution provider for a particular application, with the specific choice of polymer and formulation providing the right material for the job, in terms of both properties and costs. This still demands

Olefin copolymerisation via controlled radical polymerisation

Free radical polymerisation is a well-established synthetic technique for producing polymers such as low-density polyethylene (LDPE), polystyrene (PSTY), and polymethyl methacrylate (PMMA, plexiglass). Copolymers of alpha-olefins and (meth)acrylates or styrene, when manufactured in a controlled way with respect to composition and structure, could open interesting application areas. However, it is difficult to produce copolymers of this kind in the usual way. The large differences in reactivity mean that one of the monomers needs to be recovered and fed back into the process, which pushes up the costs, and it is impossible to avoid a broad chemical composition distribution. Side reactions (especially chain transfer to the alpha-olefin) lead to poor control over molar mass distribution. In other words, the control over structure is very poor, which has hampered economically viable development, and only a few commercial applications exist, most notably in the area of “bulk” polymers, ethylene-vinyl acetate copolymer, or EVA.

Radical polymerisation

Atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerisation create opportunities for producing copolymers of (meth)acrylates or styrene with alpha-olefins with a well-controlled structure and without the negative effects associated with other technologies on structure control, reactivity and purity. This is no straightforward matter, and many “road blocks” had to be

removed in order to find the right initiators, catalysts, etc. and to understand the underlying mechanism. This has now led to considerable progress in making copolymers of methyl acrylate, methyl methacrylate or styrene with 1-octene. Except for a reduction in the rate of polymerisation, the incorporation of the alpha-olefin showed no negative effect on the usual reaction schemes of ATRP and RAFT. Conventional free radical polymerisations as reference experiments showed clearly that it would not be possible to produce copolymers in this way. As well as the copolymers, a block copolymer of PMMA and a poly(MMA-co-1-octene) copolymer were also made.

Patents

Two patent applications were filed on this work, and although there is still a long way to go to reach commercialisation, we are identifying a number of good leads towards this end. It goes without saying that the strengths and weaknesses of the ATRP and RAFT technologies have to be kept in mind when considering potential future applications. Until now, the molecular weights where good control is obtained have been low to moderate. There is no intention to make inroads into large bulk polymers. However, because of the controlled molecular structure, and the ease of adding functional groups, the following areas are of interest:

block copolymer impact modifiers and/or compatibilizers for use in engineering plastic blends and composites; encapsulation of drugs for controlled release; additives in hair gel and other personal care products (commercial examples in this field are starting to evolve); functionalised coatings; and functionalised oligomers for grafting onto engineering polymers.

incremental improvement, which is becoming increasingly sophisticated now that the big step improvements have all been discovered and applied. A thorough understanding of the relationships between polymer structure and the final properties is necessary in order to bring about valuable improvements while avoiding an expensive process of trial and error. Here lies an interesting scientific challenge for DPI because the demand for knowledge is clearly present in industry. A number of projects within the EP TA are clearly related to this need, for instance in the area of new catalysts for current polyesters, improved catalysis for controlled propane oxide polymerisation and fibre reinforcement mechanisms.

Solution providing, however, creates far more extra added value for polymeric materials when new technologies are applied to create new properties and functions within the materials. This “technology push” provides new opportunities and creates new markets. It will, however, always be difficult to predict which of the

new technologies will be the big winner. Developing new technologies based on existing, known and expressed market needs is only a small part of the whole story. Here too lies an important scientific challenge for DPI: developing new technologies based on scientific principles and with the best possible chance of future use in industry. Projects within the EP TA in this category include new routes to polyamides, polyester-amides and polycarbonates with (fast) crystallisable units, controlled radical polymerisation to create high impact-resistant vinyl copolymers with olefins, new concepts to disperse carbon nanotubes in polymers and unravelling the mechanism of reinforcement with nanofibres.

Partners

Industry

Dow, DSM, GEP, Océ Technologies, Shell, TNO participate in the Engineering Plastics Technology Area. Teijin and ATO-DLO joined the Technology Area at the end of 2002.

Breakthrough: One simple test predicts lifetime behaviour

Ever seen cellars full of pressurized tubes, kept under well-controlled temperatures to investigate long-term behaviour of polymers? How tedious this type of experiments can be is visible on the Internet (<http://www.physics.uq.edu.au/pitchdrop/pitchdrop.shtml>). In 1927 Professor Parnell heated a sample of pitch and poured it into glass funnel with a sealed stem. Three years were allowed for the pitch to settle, and then the sealed stem was cut. From that date on the pitch has slowly dripped out of the funnel - so slowly that now, 72 years later, the eighth drop is only just about to fall.

Constitutive modelling, heavily based on mathematics, is very often considered to be a non-sexy topic in polymer science and technology. It is, however, very useful, mainly because it makes it possible to predict mechanical long-term behaviour. Why should this annual report highlight a topic in solid-state rheology, originating from constitutive modelling? An area where only few people are active in, including a few DPI researchers?

The reason is that DPI made a breakthrough in predicting the long-term mechanical behaviour of polymeric materials. It took more than 15 years of combined experimental and theoretical work to arrive at a proper constitutive equation for amorphous

polymers, based on the polymers intrinsic behaviour as can be measured for instance under superposed pressure or in compression, both eliminating catastrophic localization. Subsequently, it took some years to really exploit the possibilities of investigating mechanically rejuvenated materials, making for instance polystyrene completely ductile in tensile (no crazes occur), focusing on how they change in time. Right now the rejuvenated state is taken as the starting point for the real mechanical behaviour of polymeric materials. The polymers response on ageing is described, via the single demobility state parameter D, as influenced by temperature and stress, basically increasing the yield stress in time, and loading. Yield, softening and subsequent hardening are the keywords in explaining materials behaviour and providing guidelines for their improvement.

As a consequence a single test, either tensile, compression or indentation, is now sufficient to determine the present age state of polymeric materials by simply measuring their yield stress. Subsequently their long-term (ductile) fracture behaviour can be predicted using shift factors for temperature and stress and integrals over time, even after years of loading under changing conditions. This work, however, so far has concentrated on amorphous polymers. The real challenge yet is to extend it to semi-crystalline polymers.

Academia

Research takes places at the TU/e, TUD, UT, RUG, TNO, ATO-DLO, Queen Mary and Westfield College London and Stellenbosch University South Africa.

Budget

The budget spent was approximately € 1.9 million. 24 researchers are involved in EP related projects.

Highlights of 2002

- Two new companies joined the TA in 2002: Teijin and ATO-DLO
- Four patent applications were filed in 2002, concerning the process of the copolymerisation of α -olefins with vinyl monomers, high Tg (>120 °C) segmented copolymers with crystallisable amide units, a new solid state process for chemical modification of PET for crystallisation rate enhancement and the synthesis of copolymers of acrylates and α -olefins
- EP symposium on Polymer Chemistry was held in June 2002.

Output 2002

Patents

Gaymans, R.J., J. Krijgsman, High Tg (>120 °C) segmented copolymers with crystallisable amide units, 2002.

Gaymans, R.J., Krijgsman, J., Husken, D., Segmented copolymer containing amide segments, 2002.

Theses

Hooy-Corstjens, C.S.J. van, Polymer-Solvent Compounds: a route to make new polymer structures, Eindhoven, 2002.

Jong, M. de, The influence of rheological versus mechanical properties in silicate polyamide nanocomposites, Delft, 2002.

Parlevliet, P.P., Study of the fibre-matrix interfacial bonding in continuous glass fibre-reinforced nylon-6 nanocomposites with the single fibre fragmentation method, Delft, 2002.

Krijgsman, J., Engineering polymers with uniform crystallisable units, Enschede, 2002.

Proceedings

Dommelen, J.A.W. van, W.A.M. Brekelmans, F.P.T. Baaijens, Micromechanics of particle-modified semicrystalline materials, Proceedings of the Eighteenth Annual Meeting of the Polymer Processing Society, Guimaraes, Portugal, 2002.

Schaake, R.P., W.P. Vellinga, H.E.H. Meijer, Friction on polymers: from single- to multi-asperity, The Physics Congress, Brighton (UK), 2002.

Dommelen, J.A.W. van, W.A.M. Brekelmans, F.P.T. Baaijens, Micromechanical modeling of finite elastoviscoplastic deformation in semi-crystalline polymers, Abstract book of the PMSE 2002 Spring National Meeting, 223rd ACS National Meeting, Orlando, Florida, 2002.

Mergler, Y.J., A.J. Huis in 't Veld, Micro-abrasive wear of semi-crystalline polymers, 29th Leeds-Lyon Symposium on Tribology: "Tribological Research and design for Engineering Systems", Leeds (UK), 2002.

Dommelen, J.A.W. van, W.A.M. Brekelmans, F.P.T. Baaijens, Micromechanics of particle-modified semi-crystalline materials, Fifth World Conference on Computational Mechanics, 7-12 July 2002, Vienna (Austria), 2002.

Scientific papers

Sijbesma, R.P., B.J.B. Folmer et al, Supramolecular polymers by chain extension of polar telechelics, 2002, 43(2), 375.

El-ghayoury, A., A.P.H.J. Schenning, P.A. van Hal, C.H. Weidl, J.L.J. van Dongen, R.A.J. Janssen, U.S. Schubert, E.W. Meijer, Metallo-supramolecular oligo (p phenylene vinylene)y w 60 x fullerene architectures: towards functional materials, Thin Solid Films, 2002, 403-404, 97-101.

Ten Cate, A.T., R.P. Sijbesma, Coils, rods and rings in hydrogenbonded supramolecular polymers, 2002, 23(18), 1094-1112.

Kemmere, M.F., T.J. de Vries, M.A. Jacobs, M. van Schilt, J. Keurentjes, Application of supercritical carbon dioxide in polymer processes, 2002, 1, 37-53.

Jacobs, M.A., T.J. de Vries, M.F. Kemmere, T. de Loos and J.T.F. Keurentjes, Antisolvent effect of carbon dioxide in ethylene-PEP systems, SAFT and Sanchez-Lacombe modeling, 2002, 1, 171-188.

Bosman, A.W., B.J.B. Folmer, Supramolecular polymers in action, 2002, 43(1), 322.

Ten Cate, A.T., R.P. Sijbesma, et al., Tuning supramolecular ringopening polymerization by conformational design, 2002, 43(2), 333.

Brunsveld, L., J.A.J.M. Vekemans, et al., Hierarchical formation of helical supramolecular polymers via stacking of hydrogen-bonded pairs in water, 2002, 99(8), 4977-4982.

Gorp, J.J. van, J.A.J.M. Vekemans, E.W. Meijer, C3-Symmetrical Supramolecular Architectures: Fibers and Organic Gels from Discotic Trisamides and Trisureas, Journal Of The American Chemical Society, 2002, 124(49), 14759-14769.

Meijer, E.W., A.P.H.J. Schenning, Material marriage in electronics, Nature, 2002, 419, 353-354.

Lou, X., J.L.J. van Dongen, H.M. Janssen, R.F.M. Lange, Characterization of poly(butylene terephthalate) by size-exclusion chromatography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, Journal Of Chromatography A, 2002, 976 (1,2), 145-154.

Van Melick, H.G.H., A. van Dijken, J.M.J. Den Toonder, L.E. Govaert, H.E.H. Meijer, Near-surface mechanical properties of amorphous polymers, Philosophical Magazine B, 2002, 82 (10), 2093-2102.

Schrauwen, B.A.G., L.E. Govaert, G.W.M. Peters, H.E.H. Meijer, Influence of flow induced crystallisation on impact properties of HDPE, Macromolecular Symposia, 2002, 185 (1), 89-102.

Coating Technology factsheet

Overview

Among the major drivers in the coating industry are the increasing demand for the environmental, health and safety aspects of coatings and improved performance. In addition, new functions of coatings are being called for. These aspects are reflected in the Coating Technology research programme.

Powder coatings and UV coatings give the least emission in application. The use of these coatings for new substrates is an important issue for this Technology Area.

The major drawbacks of powder coatings are the high curing temperature and the relatively poor flow. The Coating Technology programme is tackling both problems by looking at new interactions in the powders to increase stability.

UV curing is another environmental friendly way of applying coatings without using solvents. UV curing systems suffer in general from unsatisfactory mechanical properties, e.g. in coil coatings, where the coating is exposed to significant stress after curing. To avoid this problem, a UV dual cure has been introduced, where curing takes place partly before and partly after the final deformation of the coils.

The durability of coatings will be an important focus in the near future. The primary determinant of the life cycle of an object is frequently the lifecycle of its coating. In the past, new and innovative coatings have contributed significantly to the lifecycle of passenger cars. We intend to launch a project for predicting, and ultimately improving, the lifetime of a polyester coating.

Mission

The aim of the Coating Technology Area is to supply the coatings industry with concepts and tools for the development of future coatings. DPI projects in this area are focused on pioneering polymer research combined with application-oriented material research.

Partners

Industry

Akzo Nobel, DSM, Dow, Shell, Océ and TNO participate in the Coating Technology programme. SEP joined the Technology Area at the end of 2002. SEP is an industrial liaison group surrounding the TU/e polymer chemistry laboratory.

In the course of 2002, NTI and Chemspeed became temporary members of the Coating Technology Area. In 2003, they will move to the newly formed "High Throughput Experimentation" Technology Area. Partner companies represent the entire chain of knowledge, from raw material suppliers, resin producers and coatings producers to end users.

Academia

Research takes place at the TU/e, the University of Wageningen, the University of Amsterdam and TNO Eindhoven.

Budget

The budget spent in 2002 was € 0.99 million.

Communications

The programme committee met 4 times in 2002. Focal points for future research projects have been defined.

Eight meetings, mostly on combined projects, were held with industrial consortium members.

Highlights of 2002

- A new programme manager was appointed for Coating Technology, Mr. Thys, who started in May 2002.
- SEP joined Coating Technology
- Coating Technology served temporarily (together with Functional Polymer Systems) as a host for high throughput experimentation.
- A new UV curing monomer was developed. This monomer allowed a two-step UV curing system to be developed. It was also shown that such a system could be incorporated in supramolecular associating systems.
- Ionomeric polyesters are showing promise as a material for powder coating polyesters.
- Telechelic material with controlled molecular weight has been prepared and separated according to functionality. Two patents on radical addition fragmentation polymerisation have been filed.
- The combination of non-covalent crosslinking based on complexation with UV crosslinking has been shown to be feasible.

Output 2002

Theses

Segeren, L.H.G.J., Microparticle Adhesion in Xerography- a combined atomic force microscopy and inverse gas chromatography, June 2002.

Proceedings

Wouters, M.E.L., B. de Ruiter, Contact-angle development of polymer melts, 2002 Athens Conference on Coatings Science and Technology, Athens (Greece), 2002.

Scientific Papers

Trofimov, S.Y., E.L.F. Nies, M.A.J. Michels, Thermodynamic consistency in dissipative particle dynamics simulations of strongly nonideal liquids and liquid mixtures, *Journal of Chemical Physics*, 2002, 117(20), 9383-9394.

Ghayoury, A. El. C. Boukaftane, B. de Ruiter, R. van der Linde, Ultraviolet dual-cure process based on acrylate oxetane monomers, *Journal of Polymer Science Part B-polymer Physics*, 2002.

Ghayoury, a. El. C. Boukaftane, B. de Ruiter, R. van der Linde, Dual-cure processes: Towards deformable cross-linked coatings, *Macromolecular Symposia*, 2002, 187(1), 553-561.

Segeren, L.H.G.J., M.E.L. Wouters, M. Bos, J. W. A. van den Berg, G.J. Vancso, Surface energy characteristics of toner particles by automated inverse gas chromatography, *Journal of Chromatography A*, 2002, 969(1), 215-227.

Jiang, X., A. van der Horst, P.J. Schoenmakers, Breakthrough of polymers in interactive liquid chromatography, *Journal Of Chromatography A*, 2002, 982(1), 55-68.

Andersson, G.G., W.J.H. van Gennip, J.W. Niemantsverdriet, H.H. Brongersma, Calcium Induced Oxidation of PPV Studied with X-ray Photoelectron Spectroscopy and Secondary Ion Mass Spectrometry, *Chemical Physics*, 2002, 278, 159-167.

Gennip, W.J.H. van, J.K.J. van Duren, P.C. Thuene, R.A.J. Janssen, J.W. Niemantsverdriet, The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF studied by secondary ion mass spectroscopy and X-ray photoelectron spectroscopy: Formation of AlF₃ disproved, *Journal of Chemical Physics*, 2002, 117, 5.

Wouters, D., C. Eschbaumer, U.S. Schubert, Melting and crystallization behavior of metallo-supramolecular polymers studied by scanning probe microscopy techniques, 2002, 43, 1045-1046.

Singha, N.K., B. de Ruiter, U.S. Schubert, Atom transfer radical copolymerization (atrcp) of a monomer bearing an oxetane group, 2002, 43, 165-166.

Zhang, H., R. Hoogenboom, M.W.M. Fijten, U.S. Schubert, Screening and application of atp catalysts utilizing an automated synthesizer, 2002, 43, 17-18.

Schmatloch, S., M. Fernandez-Gonzalez, U.S. Schubert, Metallo-supramolecular Di(ethylene glycol): Water-soluble reversible polymers, *Macromolecular Rapid Communications*, 2002, 23, 957-961.

Schubert, U.S., S. Schmatloch, A.A. Precup, Access to supramolecular polymers: Large scale synthesis of 4'-chloro-2,2':6',2''-terpyridine and an application to poly(propylenoxide) telechelics, 2002, 5, 211-221.

Rubber Technology

Overview

The Rubber Technology Area was formed in 2001. The main activities in 2002 were focused on establishing the participants in the TA, formulating projects and finding personnel to get the projects under way. It is important to keep in mind that most projects are in their start-up phase. With nearly all vacancies filled in 2002, activities in all the projects will get into full swing in 2003.

It was envisaged in 2002 that once Acordis and Teijin had joined, a subcluster 'Fibres and Composites' would be formed together with the Engineering Plastics Technology Area. However, the membership of Acordis did not materialise, and although Teijin did join DPI, it bought a ticket in the Engineering Plastics TA. How the two TAs will deal with the rubber interest of Teijin between them will be a subject of discussion in 2003.

Mission

- To establish a chain-of-knowledge in the field of rubber technology, aiming at research subjects at the forefront of the area.
- To act as an academic training ground for students and scientists working in the area of rubber technology.

Partners

Industry

The partners in this Technology Area in 2002 were Akzo Nobel, DSM, Kraton Polymers, TNO Industry and Océ Technologies. Negotiations with other partners are pending. They will be joining later than originally expected as a result of the current financial situation of this industrial segment.

Academia

Three institutes participated in the programme: TUD, TU/e and UT.

Budget

The budget spent in 2002 was € 0.8 million. The number of FTEs allocated at the end of 2002 was approximately 10.

Communications

The Programme Committee of this TA met three times in 2002: to formulate its mission, decide upon the projects and get the research started.

Three progress meetings with representatives of the partner companies involved were held for the projects 'Thermoplastic elastomers by dynamic crosslinking using radical curing agents' and 'Morphology and structure-rheological property relations for saturated olefinic thermoplastic elastomer compounds'. Informal contacts between academia and industry take place frequently, as the need arises. Contacts with the outside scientific world are taking off. Parts of the work on the two projects mentioned above were presented at the International Rubber Conference (1-4 June 2002 in Prague), the American Chemical Society, Rubber Division Meeting (1 November 2002 in Pittsburgh, USA), the Asia Rubber Techn. Expo (28-30 November 2002 in New Delhi), and the Polymer Processing Society Meeting (16-20 June 2002 in Guimaraes).

The first thesis will appear in 2004.

Highlights of 2002

- The rubber activities within DPI have doubled from 4% in 2001 to approximately 8% in 2002.
- Kraton Polymers joined the Technology Area in January 2002.
- Focal points of interest have been defined, on the basis of which a variety of projects have been launched.
- Much of 2002 was used in hiring the necessary candidates and acquiring equipment. With two exceptions, all projects are now running.
- By the end of 2002, the Rubber Technology TA was fully operational.
- Six presentations were given at international conferences.
- The first scientific paper was submitted and accepted for publication.

Projects

Structure – property relationships

This topic focuses particularly on blends of rubbers and rubbers/thermoplastics in the vulcanised state. Thermoplastic elastomers are gradually replacing parts of classical crosslinked rubbers because of their ease of processing and the possibility of

recycling the scrap, among other reasons. Two sorts of thermoplastic elastomers are presently competing against the monopoly of vulcanised EPDM rubber: compounds of saturated styrenic block copolymers with polypropylene and so-called TPVs, dynamically cured compounds of EPDM rubber and polypropylene.

The project 'Morphology and structure-rheological property relations for saturated olefinic thermoplastic elastomer compounds' became fully operational in 2002. Its objective is to develop a descriptive rheological model for two-phase systems in relation to their morphological structure.

A Brabender internal mixer and a co-rotating twin screw extruder were used to prepare different compositions of the two blends referred to above. Transmission electron microscopy and low voltage scanning electron microscopy were used for characterisation. Electron tomography made it possible to construct a three dimensional model of the blends. Blends prepared in the two types of preparation equipment show differences in morphology. The particle size distribution of the dispersed EPDM phase in TPVs made in the twin screw extruder was found to be larger than the one made in the Brabender. For SEBS/PP/oil blends, the PP/oil and SEBS/oil phases were more co-continuous when made in the Brabender. The differences are not yet understood. The stress-strain behaviour of these blends was strongly influenced by their crystallinity and morphology. In general, the blends with higher crystallinity had better properties, except for the SEBS/PP/oil blends, where the degree of co-continuity had a major influence.

The thermal behaviour was investigated using DMA, DSC and dielectric measurements. The oil distribution in TPVs and SEBS blends in the rubbery state and in the melt has been a mystery for decades. To solve this problem, the T_g of the rubber/PP/oil ternary blends and in binary PP/oil and rubber/oil blends were determined using DSC and DMA. However, these measurements were unable to give the T_g of the oil phase, which prompted the synthesis of a fluorescent probe for dielectric measurements. The probe is sensitive to the viscosity and polarity of the surroundings, and for the first time it was possible to measure the change in glass transition of the oil. The measurements performed will form the basis for calculating the oil distribution in the TPV and SEBS/PP/oil blends in future studies.

Melt creep experiments showed that the yield strength of TPVs depends on composition. The SEBS compounds showed no yield stress whatsoever, levelling off to a constant viscosity. The results

of dynamic rheology of the compounds showed interesting correlations with the blend morphology. Further experiments are necessary to gain an understanding of these correlations.

The projects 'Low Surface Energy Rubber Materials Based on (Per)fluorinated Polyethers' and 'Investigations on Blending, Reinforcement and Curing in EPDM/ NR/ BR Rubber Compound for the Tyre Sidewall Application' were started in October 2002.

Reinforcement

All cured rubber articles are reinforced with carbon black or other reinforcing and non-reinforcing agents. A project was started in October 2002 to unravel the physicochemical mechanisms behind reinforcement.

Vulcanisation chemistry

95% of all rubber articles are vulcanised. Vulcanisation with sulphur was started by Goodyear as long ago as 1839, and is still almost universally applied (> 95%), in spite of the lack of understanding of the underlying chemistry. This is largely a result of the solid and insoluble nature of the rubber vulcanisate, which precludes most of the common analytical techniques. The research in this field aims at using alternative curing agents, resulting in products with better properties (good dynamic performance in combination with good ageing characteristics) and allowing easier analysis.

The project 'Thermoplastic elastomers by dynamic crosslinking using radical curing agents' was operational throughout the year. Its objective is to develop a proper peroxide-based curing system for dynamically vulcanised blends of EPDM rubber and polypropylene, which are known as TPVs, with a maximal curing yield of EPDM and a minimum degradation of polypropylene.

The effect of different types of peroxides at a fixed PP/EPDM blend ratio was studied. The solubility parameter of the peroxides and that of the polymers, the decomposition mechanism of the various peroxides and the kinetic aspects determine the final properties of TPVs. In this respect, dicumyl peroxide (DCP) showed the best balance in all three properties. The influence of various peroxides on varied PP/EPDM blend ratio was also investigated. As the proportion of PP increases, the tensile strength, Young's modulus and hardness of TPVs increase while the compression set properties deteriorate due to the increased thermoplastic component (hard phase) in the blend. DCP was again found to give the best balance of properties irrespective of the blend composition.

A graft comb-like copolymer of PP and EPDM was synthesised at DSM in a two-step process. In the first step, an ethylene-propylene-diene terpolymer was prepared using vinyl norbornene (VNB) as diene resulting in unreacted double bonds. In the second step, iPP chains were allowed to grow through these double bonds to form the graft copolymer. Its effects as a compatibiliser in PP/EPDM TPVs, influencing morphology and subsequently the physical properties are being investigated.

A special kind of multifunctional peroxide having co-agent functionality was synthesised at Akzo Nobel. The effects of the latter on properties are still under study.

The projects 'Investigations on Blending, Reinforcement and Curing in EPDM/ NR/ BR Rubber Compound for the Tyre Sidewall

Application' and 'Dynamic Property Improvement of Peroxide-cured Ethylene-based Polyolefinic Rubbers by Sulphur-bridged Co-agents' were started in October/November 2002.

Thermoplastic rubbers

The aim is to develop an entirely new line of thermoplastic rubbers based on block-copolymers of acrylates and saturated olefinic blocks. Another line of projects is focused on morphology-rheology- properties of thermoplastic vulcanisates, in order to find routes to further improve their properties. The latter represent the fastest growing thermoplastic elastomers range, where much attention is still needed to improve their production possibilities and properties.

Output 2002

Proceedings

Debnath, S.C., J.W.M. Noordermeer, Understanding the Chemistry of the Rubber/Silane Reaction for Silica Reinforcement, using model olefins, ACS Rubber Division meeting, Savannah, 2002.

Debnath, S.C., J.W.M. Noordermeer, Reaction of Bis (tri-ethoxy silyl propyl) tetrasulfide in model olefins, International Rubber Conference 2002, Prague - Czech Republic, July 1-4, 2002.

Naskar, K., J.W.M. Noordermeer, Dynamically vulcanised PP/EPDM Blends: Effects of different types of peroxides on the properties, Proceedings of the International Rubber Conference, Prague, 2002.

Naskar, K., J.W.M. Noordermeer, Dynamically vulcanised PP/EPDM blends: Effects of different types of peroxides on the properties, ACS Conference, Rubber Division, American Chemical Society, Pittsburgh (USA), 2002.

Naskar, K., J.W.M. Noordermeer, Effect of different types of peroxides on the properties of dynamically vulcanised PP/EPDM blends, Asia Rub Tech Expo, New Delhi (India), 2002.

Sengupta, P., J. W. M. Noordermeer, A Comparative Study of Different Oil Preblending Methods on the Morphology and Properties of EPDM/PP/oil Thermoplastic Vulcanisates, Asia Rub Tech Expo 2002, New Delhi.

Sengers, W.G.F., P. Sengupta, A.D. Gotsis, J.W.M. Noordermeer, J.J. Elmendorp, Morphology and rheology of saturated olefinic elastomer compounds, 18th International Conference of the Polymer Processing Society, Guimaraes, Portugal, Guimaraes, 2002.

Sengupta, P., J.W.M. Noordermeer, W.G.F. Sengers, A.D. Gotsis, A comparative study of morphology and structure-related properties of saturated olefinic thermoplastic elastomer blends of EPDM/PP/Oil and SEBS/PP/Oil, Proceedings of the International Rubber Conference, Prague 2002.

Functional Polymer Systems factsheet

Overview

The interest in functional polymers and their applications is growing within both industry and academia. This is true both for typical high-tech companies and the traditional polymer producers that are now rapidly entering this domain.

Among the most significant drivers are the steadily increasing demand for information and communication, and for energy efficiency and energy generation. In these respects, functional polymers have great promise, not only as replacements for traditional materials but also as a way of revolutionising the technology and creating large markets. In contrast to traditional polymers, volumes will remain limited, and the added value is generally in the device. Academic developments are also providing a powerful impetus, where the major drivers are new synthetic capabilities, e.g. in supramolecular chemistry, analysis and manipulation possibilities down to the nanometer scale, interdisciplinary developments between the organic and inorganic research world, the increasing power of computational materials science, and the boost in public funding for nanotechnology in general.

The Functional Polymer Systems Technology Area intends to be a major player in the international research on functional polymers for new (breakthrough) technologies, particularly in the areas of information and communication and sustainable energy. DPI wishes to enter into partnership with industries that are at the forefront of technological development. The larger thematic research programmes within DPI provide the best foundation for the most promising of these developments. In this respect, the present major lines of research in the DPI programme - displays and transistors, all-optical applications, and photovoltaic cells - are all very relevant.

While most of the TA research is currently at the prototype level, technological aspects of processing and long-term performance may also have to be considered. However, DPI also has to be alert to possible rapidly evolving interests in new technological options.

To realise this research ambition, DPI seeks to involve internationally leading groups with a track record in multidisciplinary research in the field and with first-hand access to new fundamental developments, in particular in the organic

nanosciences. Scientific developments will continue in the above-mentioned major areas, but may also extend into energy storage and fuel conversion, sensors and actuators, and into medicine and biology, for example.

Mission

The mission of the FPS TA is to perform research on polymers and their prototype devices that are capable of an electrical, optical, magnetic, ionic, or photoswitching function, and have a potential industrial application.

Partners

Industry

In 2002, the following 10 partners contributed to the area: Akzo Nobel, Avantium, Avery Dennison, DSM, Dow, ECN, Océ, Philips, Shell and TNO. Avantium and Avery Dennison entered in 2002. In the current unfavourable international economic climate, existing contacts with three other industries have not yet led to additional partnerships.

Academia

The research is being carried out in 8 institutions: UvA, ECN, LEI, LUW, RUG, TNO, TUD and TU/e. Contacts have been made with leading international groups for exploring the possibility of future research participation.

Budget

The budget spent is a little over € 3 million. The number of FTEs allocated at the end of 2002 was nearly 40. There are a small number of vacancies.

Communications

Programme Committee

The Programme Committee, consisting of the PM, the partner representatives and four academic experts, met four times in the course of 2002.

Themes

Subcluster theme meetings were held on LEDs/FETs (twice, at Philips and TNO), conductive blends (at Akzo Nobel Deventer), all-optical materials (at TU/e) and photovoltaics (four times, at LUW, TU/e, and ECN Amsterdam). Review reports were written on each of the above.

Projects

For individual research projects, bilateral meetings were held with the relevant partner industries when necessary, and on an informal basis.

Academia

DPI FPS researchers frequently attended scientific conferences and regularly submitted papers to academic journals.

Highlights of 2002

- Avantium and Avery Dennison joined as new industrial partners.
- Trends observed in dye performance in polymer/dye LEDs could be explained by ab-initio quantum-mechanical calculations based on the dye and polymer electronic structures. This may open the way to predictive band-gap engineering of LED materials.
- Several new matrix-related factors have been identified that strongly influence the level of volume conductivity and the type of conductive network formed in conductive polymer blends, including in cured phthalocyanine/polyurethane and phthalocyanine/epoxy, at filler levels well below 10%. Threshold levels appear to be controllable.
- A new method was successfully explored for enhancing the aspect ratio of photo-embossed relief structures while improving their accuracy. This opens the possibility of novel diffusors and wire grid polars for LCDs. A proposal for IP protection has been submitted.
- A combination of n-/p-type polymers were synthesised and processed into an all-polymer bulk heterojunction device, with a 0.5 % power conversion. Although this efficiency is still low compared with devices of other types, it nevertheless shows early in the project that the ideas put forward in the project plans offer a promising route to polymer PV technology.
- A combinatorial approach involving atomic-force microscopy and conductivity measurement was applied to functional films of carbon-black in silicone rubber, with varying CB loadings and curing rates. The method succeeds in rapidly identifying trends in surface morphology and level of conductivity in relation to these parameters, thus showing the power of high-throughput evaluation methods, not only in new synthesis but also in structure-process property studies.

Projects

General

The research programme in 2002 was organised as six subclusters: programme management, polymer LEDs and transistors,

conducting polymer blends, polymers for fuel cell and battery applications, polymers for all-optical applications, and polymer photovoltaics and high-throughput evaluation.

The high-throughput evaluation was a joint activity with the Coatings Technology TA, and has since become a separate TA. The fuel cell/battery activity was split off in 2003 to form a separate cluster.

LEDs and transistors

In this theme, the main object of study is the dye-filled LED for multicolour display applications, where charge transport is provided by a layer of conjugated polymer in a multilayer device, and colour emission is provided by the dispersed dyes. Secondary studies investigate the related phenomena of charge transport and device performance in polymeric field-effect transistors for plastic electronics.

Although the proof of principle already exists, obstacles still remain for the industry in the barriers to charge injection, interface degradation, level of mobility, and transfer of energy from polymer to dye.

The industry's main objective is to gain a better understanding of the limiting factors for device performance, and all these factors are addressed in five well-integrated projects. Patentable findings may well emerge, but they are not the primary aim in this case. Half of the effort is made by PhD students, which will ensure a significant output in terms of scientific papers and theses to the academic community.

Conductive blends

This theme aims at methods of making nonconducting polymers conductive in a controlled way by percolating networks of a dispersed second component.

In commercial products, the filler fraction has to be relatively high to ensure a reasonable conductivity, which has a detrimental effect on other properties. Therefore, one of the aims is to significantly lower the critical filler fraction. Other objectives are an increased level of conductivity and the introduction of attractive alternatives to carbon-black filler.

Work is being undertaken to gain the necessary understanding and technological leads for making highly conductive carbon-black/rubber composites with good mechanical performance, especially for copier applications, to improve the outlet chances for

polymer additives such as carbon-black and to define routes to making thermoset polymers conductive in a controlled way using phthalocyanine salts, with patent options. Academic publications and one thesis are foreseen, in particular on percolation aspects.

Fuel cells and batteries

In this area, the objective is to develop and demonstrate new polymer-electrolyte materials for PEM fuel cells and batteries. There is a need for alternatives to the current commercial PEM-fuel cell material and, more generally, for polymeric ion conductors with good high-temperature stability for energy applications.

It is hoped to develop proofs of principle for imidazole-containing anhydrous proton-conducting polymer membranes as an attractive alternative to Nafion in fuel-cell applications, and for LC polyimide as a high-strength, corrosion resistant and thermally stable electrolyte in Li batteries. In both cases there may be patent options, and one PhD thesis will emerge.

All-optical applications

The intention is to develop new types of functionalised phase gratings by photopolymerisation for use in LCDs, LEDs and PV cells and to develop new patterning and printing techniques for optical films with submicron orientation layers engineered towards the application needs in LCDs and possibly LEDs.

There is much room for performance improvement (brightness, colour, energy and efficiency) of LCD, LED and PV devices by manipulation of the device optics through external micro-structured optical films.

This programme has already generated much IP, and additional prototypes and concepts are expected on smart optical films with the potential to improve electro-optical and optical devices, with further patent options. In addition, scientific publications and three PhD theses are foreseen.

Photovoltaics

The PV programme is aimed at finding new concepts for polymeric photovoltaic cells, in particular for third-generation (after polycrystalline Si and amorphous thin-film Si) solar-cell technology.

For the mass introduction of the use of solar energy, production technology based on polymers will be indispensable, but prototypes with sufficient efficiency have yet to be realised. As a spin-off, new photodetection technology may be developed.

The focus of this programme is very long term, and the first aim is to realise working devices with some degree of efficiency along two lines: hybrid inorganic/organic solid heterojunction systems, and all-polymer n-p heterojunction devices. Given the large size, integrated structure and long-term focus of the programme, much of the new scientific insight generated will spin off into the polymer-LED area, and through many scientific publications and theses will have an impact on the academic field.

High-throughput methods

The aims are to introduce high-throughput methods in the evaluation of functional thin-film materials and to use these methods in the current DPI FPS programme.

The high-throughput techniques are developing rapidly, and will offer much faster screening of functional properties and fast feedback to synthesis and processing.

The methods include automated fast surface-analysis techniques, with local information on chemical composition, morphology and functional properties.

Output 2002

Theses

Leeuwis, C.M., Formation of Mesoscopic Polymer structures for Optical Devices, 2002.

Graaf, M.A. de, Transmissive and emissive polymer waveguides for communication and illumination; controlled scattering of light in amorphous polymers, Eindhoven, 2002.

Proceedings

Blom, P.W.M., H.C.F. Martens, H.B. Brom and J.N. Huiberts, Admittance spectroscopy on polymer light-emitting diodes, Mat. Res. Soc. Symposium, 2002, 665, C3.3.1-C3.3.6.

Soloukhin, V., W. Posthumus, J.C.M. Brokken-Zijp, G. de With, Mechanical properties of silica-(meth)acrylate hybrid coatings on polycarbonate substrate, Nanocomposites 2002: Bringing new value to plastics, San Diego, CA, USA, 2002.

Soloukhin, V., W. Posthumus, J.C.M. Brokken-Zijp, G. de With, Mechanical properties of silica-(meth)acrylate hybrid coatings on polycarbonate substrate, Conference Proceedings: Materials Research 2002, Veldhoven, 2002.

Neffati, R., J.C.M. Brokken-Zijp, M.A.J. Michels, P.J. Lemstra, Carbon Black suspension in silicone and percolation concepts, Material Research meeting, Veldhoven, 2002.

Scientific Papers

Wilderbeek, H. T. A., M.G.M. van der Meer, C.W.M. Bastiaansen, D.J. Broer, Photo-Initiated Polymerization of Liquid Crystalline Thiol-Ene Monomers in Isotropic and Anisotropic Solvents, 2002.

Wilderbeek, H. T. A., J.G.P. Goossens, C.W.M. Bastiaansen, D.J. Broer, Photoinitiated Bulk Polymerization of Liquid Crystalline Thiolenes Monomers, 2002, 35(24), 8962-8968.

Janssen, F.J.J., L.J. van IJzendoorn, H.F.M. Schoo, J.M. Sturm, G.G. Andersson, A.W. Denier van der Gon, H.H. Brongersma, M.J.A. de Voigt, Degradation effects in poly para phenylene vinylene derivatives due to controlled oxygen exposure, Synthetic Metals, 2002, 131, 167-174.

Birgerson, J., F. J. J. Janssen, A. W. Denier van der Gon, Y. Tsukahara, K. Kaeriyama and W. R. Salaneck, Doped polymeric cathodes for PPV/Al based LEDs, Synthetic Metals, 2002, 132(1), 57-61.

Horst, J.W. van der, P.A. Bobbert, M.A.J. Michels, Electronic and optical excitations in crystalline conjugated polymers, Physical Review B-condensed Matter, 2002, 66, 035206, 1-7.

Horst, J.W. van der, P.A. Bobbert, W.F. Pasveer, M.A.J. Michels, G. Brocks, P.J. Kelly, Excitons in conjugated polymers from first principles, Computer Physics Communications, 2002, 147, 331.

Woudenbergh, T. van, P. W. M. Blom, J. N. Huiberts, Charge Injection in Polymer Light-Emitting Diodes, 2002, 42, 495-503.

Blom, P.W.M., T. van Woudenbergh, H. Huiberts, Performance of injection-limited polymer light-emitting diodes, 2002, 725, 8.6.1.

Meijer, E.W., C. Tanase, P.W.M. Blom, E. van Veenendaal, B.-H. Huisman, D.M. de Leeuw, T.M. Klapwijk, Switch-on voltage in disordered organic field effect transistors, Applied Physics Letters, 2002, 80(20), 3838-3840.

Soloukhin, V., W. Posthumus, J.C.M. Brokken-Zijp, J. Loos, G. de With, Mechanical properties of silica-(meth)acrylate hybrid coatings on polycarbonate substrate, Polymer, 2002, 43, 6169.

Soloukhin V.A., W. Posthumus, J.C.M. Brokken-Zijp, J. Loos and G. de With, Mechanical properties of silica-(meth)acrylate hybrid coatings on polycarbonate substrate, Polymer, 2002, 43(23), 6169-6181.

High-throughput experimentation factsheet

Overview

Combinatorial and high-throughput techniques have revolutionised research in biochemistry, genetics and pharmaceuticals. It is now impossible to imagine research and product development in these fields without the application of a wide range of automated synthetic procedures and rapid screening techniques. In recent years, a similar development has taken place in the field of material and polymer research. Early 2002 saw the first activities in the area of automated parallel polymerisations within the DPI Core Programme. The rapid initial results provoked intense discussion with CMR/HTE equipment and software manufacturers as well as leading chemical companies, which concluded that successful R&D in the challenging and important combinatorial material research field required a new approach. As a result, a new subcluster was established within the DPI framework: a combination of fundamental scientific (university) approaches with the new tools of high-tech manufacturers and the real needs of the chemical industry.

The Combinatorial Material Research/High-Throughput Experimentation subcluster was formed in 2002 between the Coating Technology and Functional Polymer Systems Technology Areas. Three high-tech companies joined in 2002, with several more expressing an interest. The decision to form a new High-Throughput Experimentation Technology Area was made at the end of 2002.

Mission

The subcluster aims to develop and apply novel strategies and approaches for polymer research. New instruments and software are combined with state-of-the-art “conventional” polymer knowledge, plus statistical and theoretical methods, with the aim of gaining a more detailed understanding of structure-property relationships. The ultimate goal is a real design of materials and a kind of “material informatics”.

Portfolio

DPI's CMR/HTE programme is intrinsically multidisciplinary in nature, combining both scientific and technology aspects. The participation of specialised manufacturers creates a unique mix of science and technology. The first scientific applications were successfully demonstrated for living cationic and controlled radical polymerisations. Moreover, new fast tools for analysing thin film morphologies were developed. In the near future, the portfolio will be expanded to other important aspects of polymer research, such

as thin film preparation methods, data handling and correlation, additional analytical tools and other polymerisation techniques.

Partners

The members of the CMR/HTE subcluster are unlike those of the other DPI clusters, and include high-tech start-up companies with a leading position in the manufacturing of automated synthesisers, characterisation instruments and software platforms. In 2002, Chemspeed/Basel, NT-MDT/Moscow and Avantium/Amsterdam joined up with the TU/e in the programme.

Budget

High-Throughput Experimentation will be a Technology Area from January 2003. The 2003 budget is € 0.93 million.

Communications

The first DPI workshop on Combinatorial Material Research was held at the TU/e on 12 and 13 June 2002. More than 110 scientists from both industry and academia attended this unique event. There were lectures from leading industrial and academic groups (Rhodia, Avantium, Basell and the University of Saarbrücken), as well as from experts from specialised manufacturers (Chemspeed and NTI). PhD students and post-doctoral researchers from TU/e presented state-of-the-art results in combinatorial material research. In addition, hands-on demonstrations gave a direct insight into automated parallel synthesis as well as novel characterisation tools.

Highlights of 2002

- First workshop in a series on CMR/HTE
- Chemspeed, Avantium and NT-MDT joined the programme.
- Two companies expressed their intention to join (and did so in 2003).
- Living cationic ring-opening polymerisations of 2-ethyl-2-oxazoline and controlled radical polymerisations (ATRP) of MMA were performed fully automated up to 40 polymerisations in parallel. Online and offline characterisation techniques such as GPC, GC, MALDI-TOF-MS and NMR were setup.

ACKNOWLEDGEMENTS

Text interviews: Hans Buskes
Editors: Taalcentrum VU Amsterdam
Photos: Maarten van Loosbroek Studios, Grafisch Atelier Wageningen,
Fotodesign Huib de Jong & Kees Hummel
Cover photo: Joachim Loos
Mindmap (page 7): Hans Buskes
Lay-out: Interlink, Oud-Beijerland
Production: Communicabus
Printing: Den Haag Offset

Dutch Polymer Institute

Kennispoort
John F Kennedylaan 2
5612 AB Eindhoven

P.O. Box 902
5600 AX Eindhoven

040-2475629
040-2472462 (fax)
info@polymers.nl

www.polymers.nl

