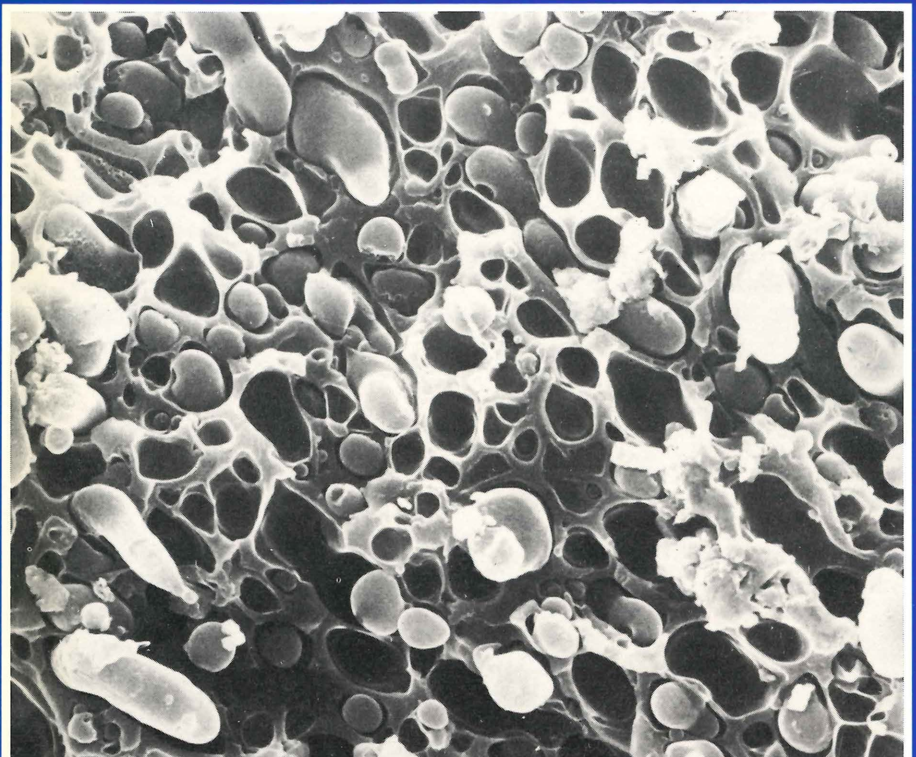
VAMAS



BULLETIN NO. 14
July 1991

Versailles Project on Advanced Materials and Standards
• Canada • France • Germany • Italy • Japan • UK • USA • CEC •

VAMAS

The Versailles Project on Advanced Materials and Standards (VAMAS) supports trade in high technology products through international collaborative projects aimed at providing the technical basis for drafting codes of practice and specifications for advanced materials. The scope of the collaboration embraces all agreed aspects of enabling science and technology - databases, test methods, design methods, and materials technology - which are required as a precursor to the drafting of standards for advanced materials. VAMAS activity emphasises collaboration on pre-standards measurement research, intercomparison of test results, and consolidation of existing views on priorities for standardisation action. Through this activity, VAMAS fosters the development of internationally acceptable standards for advanced materials by the various existing standards agencies.

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Cover: Fracture surfaces of polycarbonate/linear-low-density polyethylene blends.
Photograph by courtesy of School of Industrial Science, Cranfield.

VAMAS

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• Foreword •

The MoU under which VAMAS operates comes to an end in 1992 and discussions are at an advanced stage for extending the Agreement. To aid this process, the CEC requested an independent evaluation of VAMAS and it was agreed to set up an expert panel to assess, inter alia, the scientific and technical achievements of VAMAS, how far VAMAS has met the original objectives, and the effectiveness of its operation.

The Panel, representing the three trading blocks, consisted of Dr R J E Glenny (CEC), Chairman, Mr J A Blair (North America) and Professor R Tanaka (Japan). They produced their report in June 1991 in which they concluded that "VAMAS has made commendable progress since its inception" and operated effectively to produce high quality results. Quite appropriately, the Panel commented that the success of many of the activities is mainly attributable to the enthusiasm and technical competence of its participants and to adequate industrial support.

In view of their findings and the fact that VAMAS is fulfilling a unique role in fostering international collaboration between research organisations, standards bodies and industry on pre-standardisation research in advanced materials, the Panel members have strongly recommended that VAMAS should continue for at least another five years.

For the next phase the Steering Committee has prepared plans for rationalising the TWAs, establishing formal links with international standards organisations and also increasing industrial involvement. By the end of the year I hope the existing MoU will be renewed for five years.

In the meantime it is pleasing to find that VAMAS participants are continuing to move forward positively. Two or three new technical areas are under development and in fact a new activity on Testing of Metal Matrix Composites is due to be launched soon.

Also of interest is an international symposium which the Japanese are organising in Tokyo on 16-18 December 1991. This meeting on Pre-standardisation Research on Advanced Materials will provide good opportunities to discuss past VAMAS work as well as plans for the future.

Kamal Hossain
Chairman

• VAMAS Round Robins •

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AIDE MEMOIRE

Round robins (RRs) are now an integral part of several VAMAS Technical Working Areas. This document is for use as a concise aide memoire for potential RR organisers and participants. A list of more detailed relevant documents is included for additional reference.

1 Preliminary

1.1 Make a clear statement of purpose and objectives. It is necessary to be realistic and set achievable objectives.

1.2 Provide a description of the method, identify likely participants and invite comments on method. Constructive replies will indicate level of participation.

1.3 Lead laboratory should consider field testing the method before going "public".

1.4 Decide on the number of laboratories to be included (5-10?) and number of materials to test (including replication within individual laboratories) - 5-6 laboratories is the minimum for statistical analysis. Allow for 20%-25% dropout. The limiting factor on the number of participants is availability of resources to the organiser (but should be as large as possible).

1.5 Consider the use of familiarisation materials to gain experience; but leave to discretion of participant laboratory.

1.6 Decide on the extent/importance of repeatability and reproducibility prior to tasks.

Repeatability - requires same operator, apparatus, laboratory and materials separated by short intervals of time.
Reproducibility - same material, but different operators, laboratories etc.

1.7 Unless RR is very simple, consider necessity for meetings of representatives.

2 Action Plan

2.1 Aims: Set out the principles and objectives of the RR.

2.2 Management: Identify one person and a deputy responsible for entire programme including correlation of data (it can be useful to delegate sub-tasks). Appoint laboratory coordinators. Inform everyone who they are and circulate information on subsequent changes promptly. Define responsibilities and reporting criteria. Assign a period of time to perform tests; try to be realistic and not too short. Allow laboratories time to raise queries before tests begin, and ask specifically for rapid verbal or written comments on initial document.

2.3 Materials: Specify, make/obtain more material than is required. Allow for loss, breakages. Choose sample size. Characterise sample homogeneity (very important). Keep reserve samples and code before distribution (random/double blind?). Code every sample from earliest point of traceability. Pack and label well for delivery. For international delivery mark 'Laboratory samples - no commercial value'. If hazardous check regulations. Alternatively, consider working with a nominal cost. (It might be preferable for transit of customs - different views exist.) Notify recipients when material mailed. Include return slip (to confirm receipt) and further copy of method.

2.4 Test procedure: Give in imperative as a direct instruction - i.e. avoid conditional. Describe apparatus to be used. Equipment should be calibrated and traceable to standards laboratories, where appropriate. Consider preclusion of participant if cannot comply. Test reference material to ensure compatibility.

2.5 Reporting: Set out obligations in a document. Agree at the outset on a suitable pro-forma for data collection; leave extra space for additional comments. Possibly refuse to accept results if not so represented. Report individual values, not averages unless specified by method. Specify same number of significant figures to be reported by all participants. Try to avoid premature interpretation by participating laboratories (i.e. return raw data). Consider format for computer-based data. Report problems with method. Report preliminary results unofficially. Non-conformable results could be source of useful information.

2.6 Analysis: Consult a statistician (before, as well as after, the RR) to advise, for example, on suitability of sample numbers, rounding off, assumption of normal distributions, etc. Assess degree of agreement between laboratories and replicate tests - use statistical tests. Classify and assess sources of systematic uncertainties/variability - operator, instruments/equipment, calibration, environment, material homogeneity.

2.7 Conclusion: What form should final report take; consider publication. Send draft manuscripts to all participants for checking. Include names and affiliation if agreed. (This should be decided at the beginning - some laboratories may wish to preserve anonymity.) Manuscripts should have tables of all data. Consider subsequent follow-up actions.

3 Comment

3.1 The round robin is a study of the method **not** an individual laboratory assessment. Deviations should be reported but consider carefully the identification of laboratories in question.

3.2 The definition of reproducibility strictly applies to standard test methods. Standardisation experiments provide information on the values of reproducibility and repeatability. Experiments designed to standardise the test method may require fewer laboratories to participate than experiments set up to test the precision of a test method.

3.3 There are a number of relevant documents to consult, indicated by * in the list below, regarding the definitions of systematic error, precision and accuracy in the measurement process. The terminology involved is under constant international review and it is recommended that the appropriate ISO documents are followed.

4 Relevant Documents

BS 0	A standard for standards.
BS 5497: Part 1 1987	Precision of test methods. Part 1. Guide for the determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.
NPL publication* ISBN 0 9504496 0	A code of practice for the detailed statement of accuracy.(P J Campion, J E Burns, A Williams) NPL 1980.
ISO 4259	Methods for determination and application of precision data in relation to methods of test for petroleum products.
IUPAC (Draft 1987-09-04)	Guidelines for collaborative study procedure to validate characteristics of a method of analysis.
LGC 198/OP/001	Guidelines for the development of standard methods by collaborative study. (W D Pocklington) Laboratory of the Government Chemist, London.

ASTM E177-86 *	Standard practice for use of the terms precision and bias in ASTM test methods.
ASTM E691-87	Practice for conducting an interlaboratory test program to determine the precision of test methods.
ASTM Standardisation News July 1988	Round robins. (T W Lashof and J Mandel).
Pure Appl. Chem. 62 (1), 1990, 149-162.	Harmonised protocols for the adoption of standardised analytical methods and for the presentation of their performance characteristics. (W D Pocklington).
ISO, 1984* ISBN 92-67-01032-8	International vocabulary of basic and general terms in metrology. (BS 5233, PD 6461: Part 1, Draft for public comment)

• Technical Note •

THERMAL ANALYSIS OF ORGALLOY R-6000 PP/PA-6 BLEND

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In phase II of the TWA 4 activities on commercial polymer blends the applicability of the test procedures identified in phase I are being examined. To achieve this goal the properties of several commercial polymer blends will be determined. The first of these, a crystalline/crystalline type, is a compatibilised blend of polypropylene and poly-e-caprolactam, PP/PA-6, ORGALLOY R-6000^{TM}, supplied to VAMAS by Atochem. The parent materials investigated in parallel, were i-PP, supplied by Japan Petrochemical, and PA-6, supplied by Allied Signals.

In a cooperative testing programme, 7 laboratories from 4 countries contributed measurements of differential scanning calorimetry (DSC or DTA) and 3 laboratories measurements on thermogravimetric analysis (TGA/DTG). The procedure followed for the DSC/DTA measurements was ISO 3146 Method C; for TGA the Japanese Standard JISK 2120 (1978).

The results of the cooperative tests were summarised at the 7th meeting of the TWA 4 in Hamilton, Ontario in April 1991. A publication containing all the experimental details is in preparation.

The conclusions drawn from the DSC or DTA measurements are:

- The respective temperatures of melting are the same in the blend as in the parent materials, which shows that the components are **immiscible**.

- The values for the enthalpy of melting indicate that the **degree of crystallinity of the components** decreases in the blend, probably because of the presence of a compatibiliser.

- The **blend composition cannot be determined** from DSC or DTA measurements because of the decrease of melting enthalpy in the blend.

The TGA/DTA measurements are of minor importance for the PP/PA blend analysis, because the decomposition temperatures of PP and PA-6 are nearly identical and the blend shows only one decomposition step at the same temperature.

The comparison of the results between the 7 participating laboratories showed good agreement, so that in future blend testing, thermal analysis measurements from one laboratory will be sufficient to characterise the blends. The applied standard ISO 3146, Method C, for DSC measurements is applicable for blends as well as for homogeneous polymers.

• Feature Article •

DYNAMIC-MECHANICAL TESTING OF POLYMER BLENDS

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Abstract

Round robin tests were carried out by the VAMAS Technical Working Area on Polymer Blends, 'Dynamic Mechanical Testing in Solid State' technical group coordinated by Professor Constant Wippler. Fourteen laboratories from five VAMAS member countries participated. Two types of polymer blends: amorphous/crystalline and crystalline/crystalline were examined along with the appropriate homopolymers. In general, the proposed standard test procedure was found to provide results with similar reproducibility for blends as that for single phase polymers. On the other hand, testing of the blends was found to require more rigorous control of all steps along the way, in specimen preparation, testing, and evaluation of data. In particular, the presence of variable blend morphology and crystallinity can seriously affect the results.

1. Introduction

Thermoplastic polymer alloys and blends (PABs) first entered the market in 1944 with the simultaneous invention of polyvinylchloride modified by acrylonitrile rubber (PVC/NBR) and rubber toughened polystyrene (HIPS). These were followed three years later by the terpolymer, acrylonitrile-butadiene-styrene (ABS). Since those early days there has been a rapid expansion in the use of PABs. Suffice it to say that by the end of the 1990s nearly 40% of all polymers will be sold as blends. Blends (along with composites) constitute the fastest growing segment of the plastics industry with a projected annual growth rate of 9% (on average) and 10% to 13% for engineering blends.

By definition, blends are mixtures of homopolymers and/or copolymers. The commercially attractive blends are immiscible, two phase systems, with performance critically dependent on the concentration, size and structure of the dispersed phase [1].

The success of PABs originates in their economic advantage. For example, the development of a new engineering resin (up to pilot production scale) takes 10 to 20 years at a cost of $150 to $200 million whereas the development of a new commercial blend takes two to five years at a cost of $5 million. Furthermore, the technology of PABs allows for several economic advantages, for example, to extend engineering resin performance by diluting it with low cost polymers, to develop materials with a full set of desired properties, to optimise performance at minimal cost to the customer, to develop mixtures with synergistic performance (especially for toughening, chemical resistance and processability), to allow recycling of polymeric waste.

In spite of the widespread use of PABs, their special needs have seldom been recognised by the standardising bodies. For example, ASTM material specifications exist for several of the oldest two-phase systems:

- ABS:D 4673-87 (for ABS), D 3965-88 (for rigid, pipe grade ABS), D 4673-87 (for molding and extrusion grades), D 3464-75 (for compression molding grades);
- HIPS: D 4225-83 (for sheeting materials);
- SBS: D 4474-85 (for styrene-butadiene-styrene);
- SBR: D 3185-88, d 3186-90 and d 33346-90 (for styrene-butadiene-rubber).

These material specifications (sometimes addressing a specific application) have been formulated in terms of traditional test methods, developed for single-phase polymers, which may not be suitable for multiphase systems.

Currently, there are about 500 types and 5000 grades of commercial blends on the market. The approach of formulating material specifications for each of them does not seem to be practical. Instead, one should: (a) examine the applicability of existing test procedures to multiphase systems, and (b) develop a new set of tests focused on what is common to these new materials, but different from the traditional, single-phase polymers.

The principal characteristic of polymer alloys and blends is the presence of two phases. The two-phase nature of PABs engenders several characteristic differences of their behaviour in comparison to single phase polymers. For example, during the flow (while either testing or processing) the morphology may change drastically, resulting in a modification of properties and an introduction of anisotropy. Owing to the presence of the interphase, stress relaxation and physical ageing processes are usually more rapid than in single phase materials. Blending may either increase or decrease the total crystallinity, affecting the mechanical as well as thermal properties and may or may not affect its long term performance.

Since its inception in 1985, the objective of the VAMAS Technical Working Area on Polymer Blends (TWA 4) has been to provide a technical basis for drafting standard test procedures for PABs. The effort is to concentrate on new, high performance materials. The TWA 4 aims to provide data for the functional characterisation of commercial polymer blends. The standardisation of tests for polymer blends was approached from a broad perspective. The members/delegates of the G-7 countries to the TWA 4 unanimously decided to evaluate and identify the test methods applicable to PABs in the following technical areas:

(1) melt flow,
(2) dynamic testing,
(3) thermal properties,
(4) morphology, and
(5) mechanical properties (recently divided into two sub-areas: tensile testing and fracture mechanics).

For each of them a coordinator was appointed and a set of tests (with recommended procedures) was prepared. The tests were to be tried first on a model two-phase blend and then applied to different classes of PABs available on the market. More than 100 laboratories participated in the work. This note will focus on the dynamic mechanical properties of polymer blends in the solid state.

2. Experimental

2.1 Materials

Two types of blends were examined. In Phase I of the programme attention was focused on non-compatibilised mixtures of linear low density polyethylene with polycarbonate (LLDPE/PC), donated respectively by Esso Canada and General Electric Co. Five compositions, containing 0, 25, 50, 75 and 100 wt% PC, were prepared (they will be referred to as blends 1 to 5, respectively). Both pelletised and extruded (2 mm and 6 mm thick sheets) materials were available. The material characteristics and method of blend preparation have been previously described[2,3].

The second, more recently examined blend was ORGALLOY R-6000, donated by Atochem. Preliminary analysis identified the material as compatibilised blend containing about 40 wt% of polypropylene (PP) dispersed in the form of small spherical particles (number average diameter $d_n = 1.1 \pm 0.6$ μm) in a polyamide (PA) matrix. The level of the compatibilising copolymer was found to be 12 ± 2 wt%. The PA was identified as poly-ε-caprolactam and PP as a polypropylene homopolymer. To be able to compare the blend performance with that of its ingredients, matching polymers were obtained from Allied-Signal Inc (PA) and from Nippon Petrochemical Co Ltd (PP). Thus, the tested resins originated from three different sources and while the general response of each ingredient in the blend should be similar to that of the matching neat polymer, a numerical agreement is not to be expected.

2.2 Test procedure

The general procedure recommended for dynamic testing in the solid state reads as follows:

1 The specimens are to be cut from 2 mm thick sheets in the machine and transverse directions (MD and TD, respectively). The size of the specimen is to fit the instrument geometry. The samples are to be conditioned at 23 ±2 °C and relative humidity RH = 50% for at least 4 hours.

2 The reference temperature and frequency are respectively: T_R= 23 °C and $\nu_R = 1$ Hz.

3 Testing is to be done at T = - 100 °C to + 140 °C and ν = 0.01 Hz to 100 Hz.

4 Isothermal frequency scans are to be carried out at $T = T_R$.

5 Single frequency tests are to be done at $\nu = \nu_R$, scanning from the lowest to the highest T.

For hygroscopic blends, such as PP/PA, the performance is expected to depend on the moisture content. In addition, owing to the two-phase nature of blends, the water vapour diffusion rate is anticipated to be slow. Thus, long drying and/or conditioning times should be examined for these materials.

2.3 Testing

Several types of test instrument have been used. These operated either in extension/compression, in flexure (single and dual cantilever) or in shear mode. The results from twelve collaborating laboratories (listed in Table 1) have been compared. When necessary, the original data have been recomputed and expressed as dynamic storage (E′) and loss (E″) tensile moduli.

3. Results and Discussion

3.1 LLDPE/PC blends [2,3]

In these blends, compositions 1 and 5 represent single phase neat polymers whereas 2 to 4 represent antagonistically immiscible two-phase systems. The mean values of E′ at 3.5 Hz along with the standard deviation (σ_n) are listed in Table 2.

For dynamic testing the reproducibility of **single laboratory** data was found to be reasonable, ($\sigma_1 \leq 10\%$). As the data in Table 2 illustrate the **interlaboratory** reproducibility was surprisingly good ($\sigma_n \leq 27\%$) considering the different instruments and methods of testing involved. Moreover, the average values of σ_n for samples 1 to 5 were computed as 18%, 17%, 20%, 19% and 27%, respectively. Thus, the standard deviation of two-phase blends 2 to 4 was found to be comparable to that of LLDPE homopolymer and significantly better than that of PC. At constant temperature the concentration dependence of E′ followed the Takayanagi equation:

$$E/E_1 = [\phi_1 E_1 + (\alpha + \phi_2)E_2]/[(1 + \alpha\phi_2)E_1 + \alpha\phi_1 E_2] \qquad (1)$$

where subscripts 1 and 2 refer to the two respective phases, ϕ is the volume fraction and α is the 'coupling' parameter [5]. For example the LLDPE/PC data at T = 50 °C were well represented by Equation 1 using $\alpha = 0.0912$. Since according to the theoretical model α solely depends on blend morphology, in the solid state its value should be independent of temperature. However, this was not the case for the investigated blends.

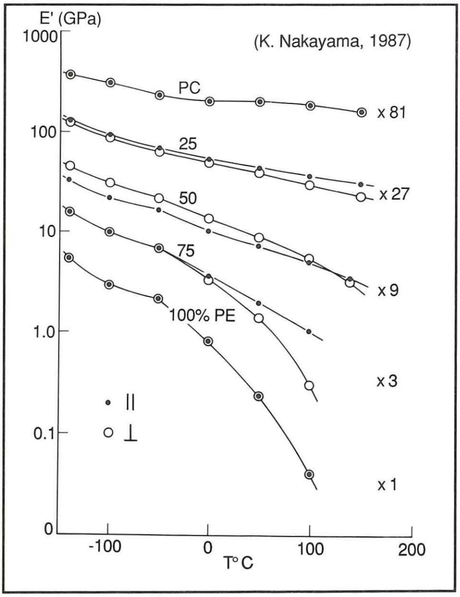

Figure 1. Storage tensile modulus versus temperature for LLDPE/PC blends at frequencies of 3.5 Hz, tested in the machine and transverse directions [3].

During extrusion of the LLDPE/PC blends the dispersed phase became elongated in the machine direction. The resulting anisotropy of morphology engineered a different dynamic response in the machine direction when compared to the transverse direction. An example is shown in Figure 1. One may define the anisotropy ratio as:

$$R \equiv E'_{MD} / E'_{TD} \tag{2}$$

For homopolymers a value R = 1 ± 0.05 was found. A similar value was obtained for blends at $T \leq 0$ °C. The largest value, R = 1.94, was obtained at the highest temperature, T = 100 °C, for the blend containing 25% PC. The effect probably originates in initial structure formation of an oriented PC matrix in which (at a lower temperature) the LLDPE has to crystallise.

3.2 PP/PA blend [6,7]

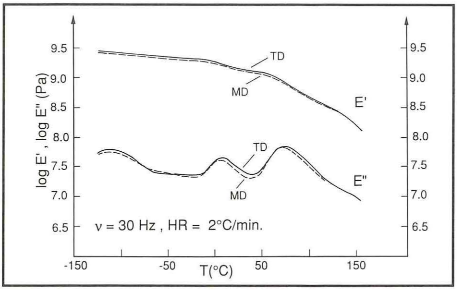

Figure 2. Comparison of dynamic data for ORGALLOY R-6000 specimens cut in machine and transverse directions (MD and TD, respectively) at frequency 30 Hz [7,8].

The commercial alloy, ORGALLOY R-6000, as well as PP and PA homopolymers were tested. In Figure 2 the temperature dependence of the storage and loss tensile moduli is shown for ORGALLOY R-6000 at a frequency of 30 Hz and a heating rate 2 °C/min. As before, the specimens cut in the machine direction and the transverse direction were evaluated. It is evident that the anisotropy is less than that in LLDPE/PC blends.

Similarly for LLDPE/PC and also for PP/PA, Takayanagi's Equation 1 could be used to calculate the tensile moduli using the component homopolymer data. However, as before, the values of α were found to be temperature dependent, in conflict with the fundamental assumption of the theory. Considering that Equation 1 expresses the interrelation between complex moduli, it can easily be resolved into appropriate forms for the real and imaginary parts, E' and E'' [1]. The use of these dependencies did not improve the constancy for the computed α-parameter values.

One of the problems specific to polyamide blends is moisture absorption. These materials are known to be hygroscopic. On the other hand, polyolefins are good barrier materials against moisture penetration. Blending these two resulted in a material with slow absorption/desorption kinetics. As illustrated in Figure 3, it takes at least seven days to dry ORGALLOY R-6000 at 90 °C under dynamic vacuum [7]. Similar drying time was found from the melt rheology data [8].

The round robin test results [6] produced good agreement for the absolute value of the transition temperature of the three peaks evident in Figures 2 and 3. On the other hand, the absolute values of the moduli varied significantly. This variation could only partially be attributed to the moisture content. Problems associated with local variation of blend morphology (phase size and shape as well as the total crystallinity), sample geometry, methods of specimen preparation as well as the test procedure and evaluation of the results, all contributed to the observed error. The tests should be repeated under more stringent control.

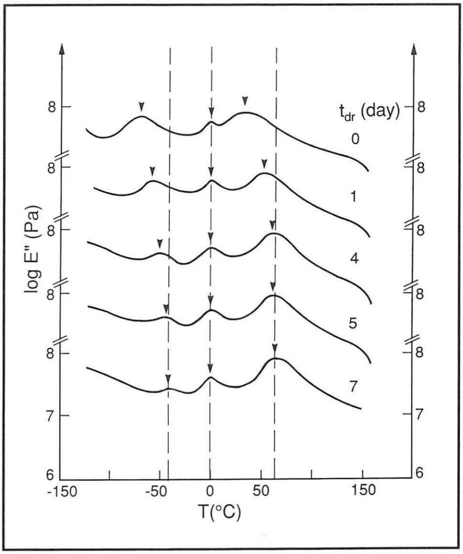

Figure 3. Temperature dependence of loss tensile modulus for ORGALLOY R-6000 after t = 0, 1, 4, 5, and 7 days of drying at T = 90 °C under dynamic vacuum.

4. Conclusions

On the basis of the round robin tests carried out on two types of polymer blends: crystalline/amorphous (LLDPE/PC) and crystalline/crystalline (PP/PA) the following conclusions can be drawn:

- The dynamic-mechanical tests are valuable for evaluating polymer blend behaviour.
- The proposed test procedure can provide a good basis for testing a wide variety of polymers including single and multiphase materials.
- Using specimens prepared under well controlled conditions the reproducibility of polymer blend data was found to be comparable to that of homopolymers.
- Testing polymer blends is inherently more difficult as the sources of error originating in specimen preparation, test procedure, and interpretation/correction of the measured values are more numerous and their magnitude is usually larger.
- There is a need for additional tests on other types of polymer blends before the method can be submitted for consideration by a standardising organisation.

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TABLE 1

Laboratory	Researchers
National Research Council of Canada, Industrial Materials Institute, Boucherville, Canada	L A Utracki, P Sammut
Polysar, Sarnia, Canada	H May
Ecole Supérieure de Physique et de Chimie de la Ville de Paris, Paris, France	J L Halary, E Rouyer
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Government Industrial Research Institute of Osaka, Osaka, Japan	K Tanaka
Japan Synthetic Rubber Co., Japan	K Ito, E Maekawa, M Niimoni
Research Institute for Polymers and Textiles, Tsukuba, Japan	K Nakayama
Toray Research Center, Shiga, Japan	M Todomi, R Hoshino, K Kitamura
Birmingham University, Birmingham, United Kingdom	F Biddlestone, J Hay
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Liverpool University, Liverpool, United Kingdom	G Eastmond
National Physical Laboratory, Teddington, United Kingdom	J K Arthur, J C Duncan, J L Lesniarek-Hamid, B E Read, P E Tomlins

TABLE 2

Mean Values of E′ (in Extrusion Direction at 3.5 Hz) and Standard Deviation (n = 6 for Blends 1, 3, 5 and n = 4 for Blends 2, 3 and 4); in GPa

	Blend 1 (LLDPE)		Blend 2 (25% PC)		Blend 3 (50% PC)		Blend 4 (75% PC)		Blend 5 (PC)	
T °C	E′	σ_n	E′	σ_n	E′	σ_n	E′	σ_n	E′	σ_n
-140	3.96	1.2	4.25	1.05	3.73	0.75	3.62	1.23	3.74	1.14
-100	2.60	0.55	2.84	0.39	2.82	0.57	2.75	0.82	3.25	0.95
-50	1.84	0.37	2.01	0.27	2.03	0.38	2.11	0.55	2.48	0.66
0	0.76	0.11	1.06	0.16	1.31	0.24	1.64	0.41	2.15	0.55
50	0.245	0.04	0.56	0.136	0.89	0.19	1.34	0.37	1.94	0.50
100	0.032	0.06	0.27	0.087	0.59	0.20	1.10	0.34	1.77	0.45
140	-	-	0.0065	0.0012	0.40	0.17	0.92	0.34	1.59	0.36

• Technical Working Areas •

Technical Working Area 1

WEAR TEST METHODS

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Objectives

- To develop internationally agreed wear test methodologies for advanced materials, initially ceramics and inorganic coatings
- To improve reproducibility and comparability of wear test methods
- To characterise wear behaviour of advanced materials.

At the April 9, 1991 meeting of the TWA1 twelve proposed projects were discussed and evaluated with respect to the goals of VAMAS. Also at this meeting, several projects that were suggested in a survey by Prof Czichos were discussed. Three new projects were selected unanimously:

(1) uniform format for reporting tribological data for computerised databases
(2) wear volume measurement comparison and
(3) survey of present standard test methods for wear.

The goal of project No 1 is to define a uniform format for organising and reporting wear data with application to computerised databases. This project is very important and timely, because of recent interest in using computer databases for storing materials property data and searching the databases to retrieve data for research, design and material selection. We have seen large differences between the databases being used by different people in US and also in other countries. If a uniform format is developed, then it will be much easier to exchange data among organisations interested in the same type of data. In fact, recent international efforts on data exchange (PDES) is an excellent example, indicating the need for a standardised database format. Other benefits of the proposed project include agreements on important variables and units, as well as methods for reporting data precision. At the completion of this project a VAMAS report will be issued, which will contain recommendations for a uniform format for reporting of wear data.

The goal of project No 2 is to evaluate and compare different methods used for wear volume measurements. Several specimens worn under different loads will be prepared to produce a range of wear volumes. These specimens will then be circulated among the participating laboratories with instructions for wear volume measurements by two or three different techniques.

The purpose of project No 3 is to gather and disseminate a listing of currently available standards for wear testing. This project has received a preliminary approval by the VAMAS Steering Committee. A questionnaire has been prepared for distribution to the participating laboratories. The results of this project will be compiled in a VAMAS report.

Projects No 1 and 2 are awaiting final approval by the Steering Committee. We plan to hold the next meeting of our Group in conjunction with the Tribology Conference in Lyon, France, September 3-6, 1991. The purpose of this meeting is to review the status of our projects and discuss other potential activities of our group. Particularly, we plan to re-examine the survey that was undertaken by Prof Czichos, which contains recommendations for several further interlaboratory testing programmes.

Technical Working Area 2

SURFACE CHEMICAL ANALYSIS

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Objectives

- To provide the measurement infrastructure required for setting standard methods of specifying surface chemical analysis
- To develop an agreed base for principles, definitions and equations for relevant aspects of surface analysis techniques
- To identify reference procedures for materials, data, instrumentation and measurement methods

Progress continues very strongly in this programme, particularly with the electron spectroscopies. The projects begin to crystallise more clearly into those defining the relevant aspects of basic theory of the process (projects 3, 7, 11, 14, 16, 17, 20, 25, 26, 28, 31), the calibration of instruments (2, 4, 9, 22, 23), the development and validation of software and transport vehicles (10, 13, 18, 21, 24, 29, 30), the development of reference materials (1, 5, 6, 12, 27) and the determination of reference data (8, 15, 19). Recent surveys of industrial requirements highlight quantification as a major problem still for AES, XPS, SIMS (both static and dynamic) and SNMS. The above projects largely focus on this major problem for AES and XPS but less strongly for SIMS and SNMS.

In terms of the theoretical developments it is useful to highlight projects 17, 20, 25 and 28 which seek to confirm, at the most basic level, how we should take accurate measures for bulk homogeneous materials in AES and XPS. Project 14 will define how best to make a peak area measurement consistent with our knowledge of electron excitation and transport and further will allow a good estimate of composition depth profiles in the surface region to a depth of 5 nm. By a different approach this is the objective of project 3 which is partly coordinated with project 14 and partly with project 26. Project 3 now appears to have attracted all of the major players in ARXPS so that some very clear and definitive work may be done. The problem of modelling the whole emission spectrum, including both the cascade secondary electrons and the reflected and diffused primary electrons in project 7, is proceeding well using an analytical approach which compares well with the Monte Carlo methods used in project 26. The angle resolved measurements are further being correlated with sputter depth profiling in thin oxide films on aluminium in projects 17 and 31. None of these methods give data with zero uncertainties. All give compositions over the important outer 5 nm at the surface and it is the purpose of part of this programme to define, with clear uncertainties, what is the best that can be done using the best theoretically based procedures in each of the three approaches. Project 31 is nearing completion; several laboratories have performed careful ARXPS on a new single sample of Al_2O_3 on Al sent sequentially from laboratory to laboratory as well as on the previous sample, sputter cleaned and then oxygen exposed for a well defined time. This latter experiment is performed individually. Results are currently being collated.

Within this first group of basic projects is also project 11 concerning the factors giving rise to charging in insulators. This major problem needs to be solved for all techniques including AES, XPS, SIMS and SNMS. It is a problem that may be alleviated more in some techniques than in others and more in some instruments than others. Project 6 also addresses this problem with reference materials currently undergoing pilot testing in a few laboratories. Project 6 will seek to give confidence for those attempting to give correct peak shapes for polymers with a calibration of energy position traceable to project 2. This latter project is nearing finalisation as the new data for high accuracy determination of the Al and Mg Kα X-ray energies become available from NIST.

The calibration of electron spectrometers proceeds towards its later stages in projects 2, 9, 22, 23 with extensive round robins involving all Member States. These calibrations should put all instruments, everywhere, on an identical quantitative footing. The problems which may once have been thought of as differences between manufacturer and manufacturer occur almost as much between machine and machine and the different operating conditions within one machine. This is why individual machines need calibration.

The vehicle of interchangeability of data was initiated with the data transfer format of project 10. This, on its own was of little immediate value until one could output data from commercial instruments in this format. Project 29 provides this crucial link in its file format translation system. This system is a key component that will catalyse future activities. In future real spectra may be analysed fairly readily with new types of analytical routines by transferring the data out into the standard format. This will allow new methods to be tested for eventual inclusion in commercial systems. To reduce all of the general handling problems we have, in project 30, the Common Data Processing System. Manuals and software for this, currently available in Japanese, are being translated into English. A less developed approach but involving the powerful mathematical tools of MATLAB is being considered in conjunction with projects 3 and 6. MATLAB is particularly powerful for matrix operations such as those in factor analysis being listed in project 13. The reverse problem of testing commercial software by injecting known synthetic data is an objective of project 21. Here the difficult problem of formatting becomes very severe but very necessary.

The above work attempts to place surface analysis on an absolute and traceable footing. Industrial laboratories often circumvent these problems by comparing good and bad samples - in a sense establishing a local standard each time and slowly accumulating an ill-defined in-house expert folk-lore associated with particular individuals. This has to be done as industry has to solve its problems today and not tomorrow. As the VAMAS work matures these in-house databases would be more effective with a centrally compiled and validated spectral database. In order to do this, certain information needs to be filed with the spectra. Project 24 is addressing this problem with considerable energy and urgency in conjunction with the ASTM E-49 committee on Computerisation of Material Property Data. This committee works closely with Technical Working Area 10: Materials Databanks.

Where absolute calibrations are difficult or where it is useful to confirm them under working conditions, the use of reference materials is a convenient and effective procedure. For sputter depth profiling, reference materials have been certified in project 1. For SIMS a very extensive and thorough infrastructure of reference materials with full traceability of calibration, is being established in project 5 which may or may not later be compared with project 19. Further reference materials are being developed in projects 6 and 27 to establish the correct operator and instrument procedures for work in XPS on polymers and for the calibration of the intensity scale in differentiated AES instruments, respectively. In order to describe depth profile shapes accurately with few parameters the LOGIT function is currently being tested in a range of laboratories in project 18. One of the most difficult calibration problems concerns that of adsorbed overlayers. The nuclear scattering techniques which are surface sensitive but not surface specific do provide such a calibration as the cross-sections may be known from other work. This is the objective of project 12. In terms of both sensitivity and quantification, SNMS must be used to bridge the gap between SIMS and AES/XPS. A small effort has now started in project 15.

In view of the considerable potentials for SIMS and SNMS and the very clear problem in their implementations it would be useful for national representatives to consider what work is in progress in their member states and to determine if there are viable projects which could benefit from VAMAS sponsorship or coordination. Although the VAMAS AES/XPS programme is not complete and does not cover every issue it is clearly further down the road to international agreements and confidence than the SIMS/SNMS area.

VAMAS SCA PROJECT LIST (1 MAY 1991)

Project No:

1 Development of thin oxide films as reference materials (M P Seah).

2 Development of calibration data for the energy scales of Auger-electron spectrometers (M P Seah, C J Powell).

3 Procedures for quantitative X-ray photoelectron spectroscopy (C J Powell, J E Fulghum for Phase 1).

4 Measurement of spatial resolution in AES.

5 Development of reference materials prepared by ion implantation (W H Gries, D Gould).

6 XPS intensity calibration and stabilisation with polymeric reference materials (C E Bryson).

7 Correction methods for backscattering in AES (J P Langeron).

8 Reference data for sputtering rates in oxides (H J Grabke).

9 Intercomparison of Auger-electron energy and intensity measurements (M P Seah).

10 Development of a standard data transfer format (W A Dench).

11 Multitechnique characterisation of vacancies in alumina (C Le Gressus).

12 Calibration of surface layers by nuclear reaction analysis (I V Mitchell).

13 Tests of algorithms for data processing in AES - Factor analysis and intensity (P R Underhill).

14 (a) Tests of algorithms for background subtraction in XPS (S Tougaard).

(b) Tests of algorithms for background subtraction in AES (S Tougaard).

(c) Tests of algorithms for quantitative XPS by peak and peak background shape analysis (S Tougaard).

15 Evaluation of SNMS sensitivity factors (M Anderle).

16 Intercomparison of surface analysis of thin aluminium oxide films (P Marcus).

17 Quantitative AES of Au-Cu alloys (R Shimizu).

18 Evaluation of LOGIT, an algorithm for fitting sputter-depth-profile data, for the measurement of interface widths of an NBS thin-film reference material (J Fine).

19 Round Robin SIMS study of impurities in GaAs crystals (S Kurosawa).

20 Round Robin AES study of Co-Ni alloys (K Yoshihara).

21 Tests of algorithms for the analysis of multicomponent spectra in XPS (A F Carley).

22 Calibration of channel electron multiplier detection efficiency stabilities (M P Seah).

23 Absolute calibration of XPS instrument intensity scales (M P Seah).

24 Conventions for spectral databases (R N Lee).

25 Quantitative XPS of Au-Cu alloys (K Yoshihara).

26 Theoretical assessment of escape depth (R Shimizu).

27 Multiline reference material for differential AES intensity calibration (M P Seah).

28 Quantitative XPS of Co-Ni alloys (K Yoshihara).

29 Development of a File Format Translation System (K Yoshihara).

30 Development of a Common Data Processing System for AES and XPS (K Yoshihara).

31 Intercomparison of the Effects of Al on the Determination of Thin Oxide Film Thicknesses (P Marcus).

Technical Working Area 3

CERAMICS

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Objectives

- To undertake pre-standardisation research on the reliability and reproducibility of test procedures for advanced technical ceramics

A round robin exercise is currently underway to measure the fracture toughness of advanced ceramics at high temperature. The round robin is coordinated by the Japan Fine Ceramics Center. The exercise builds upon the recently completed room temperature fracture toughness round robin which utilised the indentation fracture, indentation strength in bending, and single edge notch beam test methods on a silicon nitride and zirconia toughened alumina. The new project also uses the single edge notch beam, but includes chevron notch and the relatively new single edge "V" notch beam methods. A sintered silicon nitride is used. Twelve laboratories are participating:

Belgium	CRIBC
CEC	JRC Petten
France	Rhône-Poulenc
Germany	BAM
	Universität Karlsruhe
Japan	GIRIN
	JFCC
	NIRIM
	NRIM
UK	AEA Technology
	NPL
USA	NIST

The successful hardness round robin has led to a set of guidelines for the use of hardness measurements on ceramics. These guidelines are the first step towards a standard test method and are now being discussed within the CEN TC 184 WG3.

A meeting is scheduled for TWA 3 at the European Ceramic Society Conference in Augsburg in September. The meeting will review progress on the high temperature toughness round robin and will contemplate future projects that TWA 3 may undertake. Fractography and/or quantitative microscopy projects have been suggested. It is projected that a final report on the dynamic fatigue project coordinated by NIST will be ready by the time of this meeting. The USA room-temperature fracture toughness round robin results may be available by then as well.

The topic of how best to publish the results of the activities in TWA 3 will be brought up at the Augsburg meeting. The available fracture toughness findings have been well documented by JFCC.

Similarly, NPL has done a commendable job in documenting the hardness results and has gone one step further by preparing guidelines which could form the basis of a standard test method. This epitomises the VAMAS mission of internationally cooperative pre-standardisation research.

Technical Working Area 4

POLYMER BLENDS

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Objectives

- To provide the technical basis for drafting standard test procedures for new, high performance polymer alloys and blends in 5 complementary technical areas: melt flows, dynamic testing, thermal properties, morphology, mechanical properties

1. Introduction

The aim of Phase II is to examine the applicability of test procedures identified in Phase I and to develop the technical basis for their adoption by the Standardising Organisations. To achieve these goals, the properties of several commercial polymer alloys need to be examined. The first of these is a compatibilised blend of polypropylene and poly-ε-caprolactam (ORGALLOY R-6000^{TM} from Atochem) and the second a compatibilised blend of polyphenylene-ether and polyamide-6 6 (ULTRANYL^{TM} from BASF). Both alloys were supplied by the manufacturer free of charge.

2. The 7th Annual Meeting of TWA-4

It was held in Hamilton, Ontario, Canada on 28-29 April 1991. During the first day the test results on ORGALLOY R-6000^{TM} were presented by the technical area coordinators.

2.1 (M G Rogers): Melt flow properties

The properties were studied by nine laboratories at 230 °C and 250 °C. Drying conditions were critical to reproducibility. It was found that to a large extent flow behaviour is determined by polypropylene, PP. At low deformation rates (in the dynamic shear field) the variation of data suggested the presence of an apparent yield stress. The dynamic test results were reproducible ($\sigma = \pm 3\%$). The inter-laboratory data were within ± 6%. On the other hand, the steady state (capillary) data were erratic ($\sigma = \pm 10\%$). The difference in material response to a small strain oscillatory deformation and that to a large strain in the steady state flow originated in a modification of the blend morphology. The structure of the material under large strains was found to change irreproducibly.

The elongational properties of molten ORGALLOY R-6000 were examined from the entrance-exit pressure drop and from direct tests. In both cases strain hardening was observed, yielding values more than one decade higher than predicted by the Trouton rule.

2.2 (C Wippler): Viscoelastic properties of solids

The properties were examined in six laboratories at T = - 120 °C to + 200 °C and frequencies ν = 0.01 Hz to 80 Hz. The storage and loss tensile moduli of ORGALLOY R-6000 as well as parent polymers were determined. The greatest difficulties were due to the moisture content upon drying at 90 °C under dynamic vacuum; the polyamide (PA) loss peak positions changed by more than 30 °C; systematic changes were observed for up to seven days of drying. The reproducibilities were found similar for the alloy as for the parent polymers. In principle, the sources of an error for blends are more numerous (eg originating in specimen preparation, test procedures and interpretation/corrections) and their magnitude may be larger. However, on the whole, good agreement was observed between data from different laboratories. A preliminary report summarising these results, entitled *Dynamic Mechanical Properties of Poly-ε-caprolactam/Polypropylene Alloy* (by C Wippler) was submitted for publication in *Polymer Engineering and Sciences*. There is a need for additional data.

2.3 (I K Partridge): Mechanical properties

The properties of ORGALLOY R-6000 sheets were examined in twelve laboratories. The data show that the blend has unstable structure and its behaviour is sensitive to deformation rate and moisture level. The impact performance at T = 25 °C, relative humidity RH = 50%, and at the hammer impact speed 3 m/s was examined; the fracture was brittle with the fracture energy $G_c = 5.9\ \mathrm{kJ/m^2}$ and $10\ \mathrm{kJ/m^2}$, for MD and TD specimens, respectively (the literature value for PA-6, $G_c = 8.2\ \mathrm{kJ/m^2}$). Using injection moulded plaques in a Charpy configuration the critical fracture energy parameters were calculated as $G_c = 6.7\ \mathrm{kJ/m^2}$ and $K_c = 3.67\ \mathrm{MN/m^{1.5}}$. The tensile tests were also conducted. The tensile and yield strength decreased with temperature, while the ultimate elongation increased. Yield stress followed Eyring kinetics. The blend properties were similar to those of PP. The most important observation was that the unstable morphology of the alloy resulted in variation of its mechanical behaviour.

2.4 (W Mielke): Thermal Analysis

ORGALLOY R-6000 and the two homopolymers were analysed in a differential scanning calorimeter. Two peaks in ORGALLOY R-6000 were found to correspond to the melting point of PP (T_m = 165.6 °C) and PA (T_m = 223.2 °C). By comparing the heat of fusion, ΔH, of the three polymers it was discovered that in ORGALLOY there is a significant amount of excess material which does not participate in the crystallisation process. Furthermore, on scanning it increased from 13% to 21% from the first to the third scan, respectively. The infrared spectroscopy identified it as an amorphous mixture of PA-6 with PP acting as compatibiliser. The interlaboratory data were in agreement within $T_m \pm 2$ °C and $\Delta H \pm 5\%$. (See Technical Note in this Bulletin.)

2.5 Morphology

Owing to absence of an identifiably responsible organisation for these activities this aspect of the blend behaviour was not reviewed.

3. Recent Events

3.1 New Blend

BASF (Dr F Ramsteiner) offered 1 tonne of ULTRANYL^{TM} to the VAMAS TWA 4 (Dr I K Partridge). The same test specimens were supplied to members of ESIS. Thus, for the first time the same material will be used by the two organisations for mechanical and fracture (J-integral) testing.

3.2 Organisational Changes

In view of the increased emphasis on mechanical testing the responsibilities for these activities have been divided. Dr K Akkapeddi (USA) offered to coordinate the tensile tests while the fracture tests will continue to be coordinated by Dr I K Partridge (UK). The responsibility for coordinating the morphological characterisation is being transferred to Japan.

Technical Working Area 5

POLYMER COMPOSITES

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Objectives

- To assess and refine fracture toughness measurements for delamination crack growth
- To develop test procedures, data presentation and failure criteria for fatigue of continuous fibre composites using flexural and tensile test conditions
- To develop creep test procedures for continuous multidirectional composites

Fatigue Round Robin

Additional tests have been conducted to check the variability of the ultimate strengths reported, and hence the fatigue stresses used in the programme. The tests used unidirectional glass-fibre/epoxy specimens from the same batch as used previously. In this series of tests the tabs made from ±45° glass-fibre fabric/epoxy laminate, as supplied to participants previously, were applied by NPL prior to distribution of the specimens. Preliminary analysis suggests that although there have been some changes in the data, an unsatisfactory wide range of values still exists. Laboratories previously recording low values have again recorded the lowest values. As this series of tests used randomised specimens all produced by the coordinator it is necessary to examine further non-specimen parameters such as type of grip (e.g. hydraulic, manual, wedge etc.), grip face texture, grip pressure, machine and specimen alignment. It is essential that the ultimate strength can be measured consistently by participants if subsequent fatigue testing is to produce worthwhile results.

Delamination Test Methods

Work is expected to be completed by the three UK laboratories involved in measuring delamination crack growth under fatigue conditions by the end of this year. In addition to the French laboratory results reported in the last Bulletin, results are now available from one Japanese laboratory.

Technical Working Area 6

SUPERCONDUCTING AND CRYOGENIC STRUCTURAL MATERIALS

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Objectives

- To establish reliable measurement techniques for superconducting materials, initially through the use of round robins on critical current and AC loss measurements in multifilamentary wires
- To establish reliable measurement techniques for cryogenic structural materials, initially through the use of round robins on tensile and fracture toughness measurements

The 7th TWA meeting was held, on 10 June 1991, at the University of Alabama, Huntsville, USA associated with the 1991 International Cryogenic Materials Conference. In total 31 participants from 9 different countries attended the TWA meeting.

The result of the 2nd intercomparison on the critical current (I_C) measurement in a Nb_3Sn superconducting wire was reported. The result of the first intercomparison indicated that the main origin of the scatter in I_C was the strain effect in the Nb_3Sn wires. The scatter in I_C was much reduced in the second intercomparison which was performed under more refined conditions than the first intercomparison; e.g. the standard deviation/average I_C (SD/Av I_C) was reduced from 8.3% to 2.2% at 12 Tesla. The SD/Av I_C of the reference Nb-Ti wire which is much less sensitive to strain was 2.1% at 8 Tesla and 1.2% at 6 Tesla. There was general agreement that the recommendation of the TWA for the standardisation of I_C measurement should be based on the procedure of the second intercomparison.

The guideline of the second intercomparison of the AC loss measurement in ultra-thin filamentary Nb-Ti wire, which relates to the electrical application of superconductivity, was also agreed at the 7th TWA meeting. The wires, with systematic changes in filament diameter, will be distributed to participant laboratories in August, and the measurements will be finished by March, 1992.

After the second intercomparison of tensile and fracture toughness measurements at 4.2 K using SUS 316LN steel and more specified conditions, the scatter in the data was much reduced compared to the first intercomparison; e.g. SD/Av yield strength was reduced to 1.4%. The same tests using a Ti alloy will be started from this August. Meanwhile, the intercomparison of the strain gauge calibration at cryogenic temperatures is in progress, and the interim report has been presented at the TWA meeting.

In the 7th TWA meeting the chairman presented his expectation that the final report of the TWA will consist of 5 volumes; volume 1 = critical current measurement, volume 2 = AC loss measurement, volume 3 = terminology, volume 4 = tensile and fracture toughness measurements, and volume 5 = strain gauge calibration at cryogenic temperatures. These reports will be published during the Japanese fiscal year of 1992.

The future possible technical subjects of this TWA were discussed. These will be high magnetic field calibration (H_{C2} measurement), T_C and I_C measurements on high-T_C oxide superconductors, tensile and fracture toughness measurements on Al alloys and shear strength characteristics of non-metallic composites, and fatigue and Charpy tests at cryogenic temperatures. The VAMAS TWA will maintain close contacts with the newly established IEC TC-90, and will effectively contribute to the standardisation activities in the IEC TC-90.

Technical Working Area 7

BIOENGINEERING MATERIALS

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Objectives

- To establish internationally agreed procedures for biocompatibility testing of bioengineering materials using cell culture methods

Report on International Round Robin Tests in 1990

1. Introduction

The present constitution of the TWA steering group is:
Chairman: Dr T Tateishi
Members: Professor P Christel, Professor A E Clark, Professor A Pizzoferrato, Professor G Stookey, Professor D F Williams

Many kinds of materials have been implanted into the human body, replacing joints, bones, teeth, vessels, etc. It is natural to test strictly 'biocompatibility' of these materials before use, because they must be safe for human use.

Test materials are generally implanted into animals for the biocompatibility test. However, this kind of test (*in vivo* test) is expensive, time-consuming and not quantitative. Moreover, the *in vivo* test is likley to be restricted from the point of view of the prevention of cruelty to animals.

On the contrary, *in vitro* testing such as tests by cell culture method gives quantitative evaluation with a short period of experiments, although it could not perfectly reflect *in vivo* conditions. Therefore, *in vitro* testing is expected to be promoted for biocompatibility evaluation and to be ameliorated so that it could take the place of *in vivo* tests as much as possible.

There are two concepts concerning biocompatibility in the cell culture method, namely cytotoxicity and cytocompatibility. Cytotoxicity and cytocompatibility must be classified into two separate categories. Cytotoxicity is concerned mainly with leaching of toxic chemicals from materials while cytocompatibility is concerned with electrochemical, micromorphological and physical characteristics of material surfaces, including at the same time the meaning that the materials are free from toxic chemicals.

In TWA 7 of VAMAS, tentative procedures of cell growth and cell adhesion tests by cell culture method have been prepared. According to the procedures, round robin tests in Japan were done in 1989 by a sub-group of the VAMAS TWA 7 reported in Bulletin 13. The procedures tested in the VAMAS/TWA 7 were focused on the cytocompatibility, wholly evaluating compatibility (including toxicity) of test materials by making cultured cells directly contacting test materials. On the other hand, the procedures prepared in the ISO/TC194 are focused on the cytotoxicity, evaluating toxicity of leaching chemicals from test materials. VAMAS TWA 7 continues to maintain contacts with ISO/TC194 so that the procedures will not overlap.

2. Objective

VAMAS TWA 7 promotes international round robin tests in order to establish procedures for *in vitro* biocompatibility testing of bioengineering materials such as artificial joint materials, by cell culture method so that the tests can replace animal tests.

We aim to verify through international round robin tests the procedures where cell growth rate and cell adhesion rate are adopted as parameters for evaluating the biocompatibility of materials.

3. International Round Robin Tests

3.1 Materials

Hydroxyapatite, zirconia, Ti-6Al-4V

3.2 Test Conditions

(i) Cell	L-929
(ii) Control	ϕ 30 mm culture dish (polystyrene dish)
(iii) Experiments	Each experiment was independently repeated 3 times in every research institute.

3.3 Participants of the Tests

(France)
Professor Pascal Christel,
Ms G Guillemin
Laboratoire de Recherches
Orthopédiques
University of Paris

(Italy)
Professor Arturo Pizzoferrato
Department of Clinical Pathology
Faculty of Medicine
University of Bologna

(USA)
Professor Buddy Clark,
Dr Arthur F Hefti
Department of Dental Biomaterials
College of Dentistry
University of Florida

Professor George Stookey,
Dr Yiming Li
Oral Health Research Institute
School of Dentistry
Indiana University

(Japan)
Dr Tetsuya Tateishi,
Dr Takashi Ushida, Dr Atsuo Ito
Biomechanical Engineering Section
Mechanical Engineering Laboratory
Agency of Industrial Science and
Technology

3.4 Results and Discussion

3.4.1 Relative cell growth rate

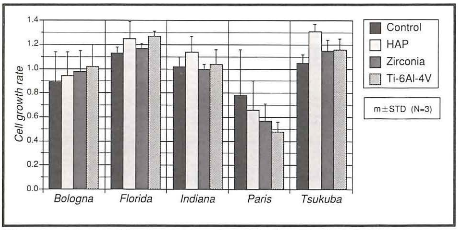

Figure 1. Means and standard deviations of cell growth

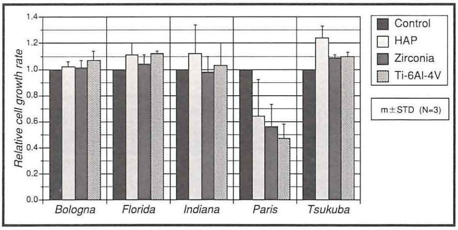

Figure 2. Means and standard deviations of relative cell growth rates

Figures 1 and 2 show means and standard deviations of cell growth rates and those of relative cell growth rates in every research institute. It would be natural that cell growth rates might vary with research institutes, because the research institutes use their own foetal bovine serum from different rots, which the culture medium contains at the rate of 10% v/v. Therefore, it would be appropriate to discuss the ratio of cell growth rate on test materials to that on the standard material (polystyrene dish), namely relative cell adhesion rate.

As shown in Figure 2, the relative cell growth rates did not scatter among the institutes and materials. According to the F-tests, there was no significant difference at 95% of probability among cell growth rates of four tested materials in any single research institute, except hydroxyapatite vs other materials in Tsukuba. There was at 95% of probability also no significant difference of relative cell growth rates of each material among the institutes, except Paris vs Tsukuba about hydroxyapatite, Paris vs other institutes about zirconia and Ti-6Al-4V. Generally speaking, the round robin tests proved that the procedures could yield reproducible results for relative cell growth rate.

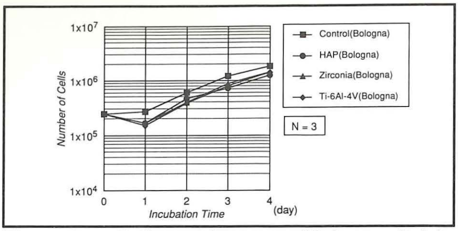

Figure 3. Cell growth curves (Bologna, Italy)

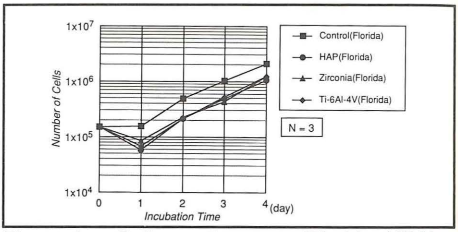

Figure 4. Cell growth curves (Florida, USA)

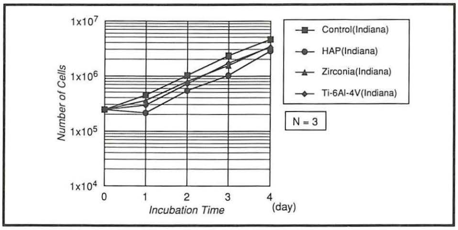

Figure 5. Cell growth curves (Indiana, USA)

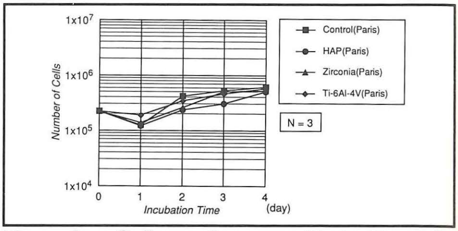

Figure 6. Cell growth curves (Paris, France)

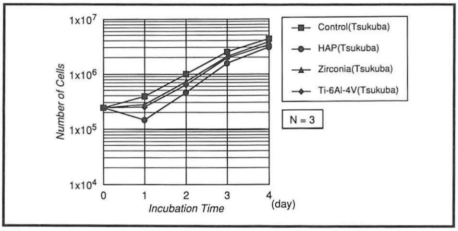

Figure 7. Cell growth curves (Tsukuba, Japan)

Figures 3 - 7 show cell growth curves in each research institute. The cell growth curves show that control, hydroxyapatite and Ti-6Al-4V have no cytotoxicity, and also show the exponential phase of growth from first day to the fourth day of the incubation.

(ii) Relative Cell Adhesion Rate

Figures 8 and 9 show means and standard deviations of cell growth rates and those of relative cell growth rates in every research institute. As shown in Figure 8, there were, in every institute, significant differences of cell adhesion rates between control and other materials. According to the F-tests, the differences were significant at 95% of probability, except for control vs zirconia in Indiana, and control vs zirconia and Ti-6Al-4V in Paris. On the other hand, there was not found any significant difference of cell adhesion rates at 95% of probability among hydroxyapatite, zirconia and Ti-6Al-4V in every institute also according to the F-tests.

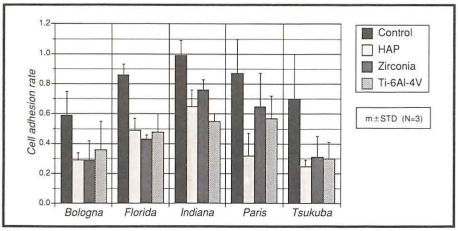

Figure 8. Means and standard deviations of cell adhesion rates

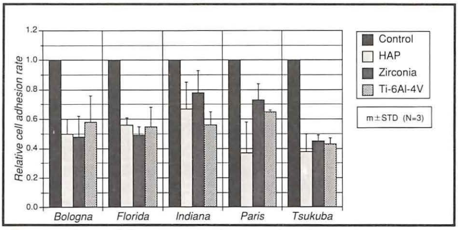

Figure 9. Means and standard deviations of relative cell adhesion rates

The standard deviations of the cell adhesion rates were, however, relatively large compared to those of cell growth rates. It is possible that some factors which were not described in the procedures influenced the results. One of the factors might concern the pipetting process. When washing materials' surfaces with PBS(-2), whether cells are peeled off by pipetting or not would depend on the strength of the pipetting if the cells do not tightly adhere on materials after 6 hours from seeding. As the strength of the pipetting is difficult to prescribe in the procedures, it should be adequate to make the incubation time longer.

Concerning methods for counting the number of cells, several kinds of methods were taken among the institutes such as a method using a hemocytometer which is the method described in the procedures, a method using a Coulter counter, and a photocytometric method. It is also possible that this difference caused the deviations of the data among the institutes.

4. Conclusions

1 The round robin test proved that the procedures yielded reproducible results concerning the cell growth test.

2 It is necessary to develop a procedure which can strictly cancel personal deviations of cell manipulations concerning the cell adhesion test.

5. Future Plan

The procedures verified in the round robin tests are to be discussed through liaison with ISO/TC194.

TWA 7 plans as the next step international round robin tests concerning 'biodegradation' of bioengineering materials, which includes degradation *in vivo* and resorption *in vivo*. The details will be discussed at the meeting of the TWA 7 which is to be held at Chester, UK in September 1991.

Technical Working Area 8

HOT SALT CORROSION RESISTANCE

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Objectives

- To develop unified procedures for assessing the hot salt corrosion resistance of superalloys in burner-rig tests

The majority of participants in Europe and the USA are now conducting hot salt corrosion tests using the specified materials and test conditions. Results have already been received from the Japanese participants and from one European laboratory. The aim is to complete the test programme by the end of 1991 and the work of evaluation will follow.

The draft Guideline Document already produced will be modified in the light of the experimental results.

Technical Working Area 10

MATERIALS DATABANKS

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Objectives

- To assess the role of standards in the flow of computerised materials information
- To identify needs, problem areas and options for standardisation activity and coordinate pre-standardisation research

Following a rapid evolution of worldwide activities and discussions during the last half year addressing the field of materials databases, the ongoing and forthcoming activities of this TWA required some reorientation which is being defined in a progressive fashion. The following summary presents the project status and medium-term planning from this point of view.

1. Materials Data Interchange

The forerunner activities for this complex problem area which had essentially been organised by ASTM committee E49 in 1990 had already shown that major efforts were needed by each participating data system to develop translators from their own system language to the agreed standard interchange language and vice-versa. These first experiments were soon abandoned because it had turned out that the required programming efforts were excessive. Simultaneously the STEP (Standards for the Exchange of Product Data) organisation has made significant progress in the development of a materials model which has the potential to provide a basis for implementing a data exchange method using the Express language. All related activities worldwide including ASTM-E49 are now focused on the STEP approach which has the advantage of integrating materials data interchange with the CAD/CAM/CIM area where a more advanced status has already been reached. This integration should ultimately lead to a universal standard for any exchange in computer-aided engineering systems which would then include materials information.

Activities in TWA 10 can not at present contribute to this new development. It is therefore proposed to suspend work in this area for some time until progress in the STEP materials development will allow pre-normative validation testing to start, which should be organised under the VAMAS aegis.

2. Inventory of Methods/Models for Materials Data Analysis and Evaluation

The initial activity on this wide subject area is led by the National Research Institute for Metals (NRIM) at Tokyo with the New Material Center (NMC) at Osaka as the secretariat. An inquiry and call for participation has been issued, and positive responses were received from 20 institutions in VAMAS countries and China, Czechoslovakia, Poland and USSR, supplemented by many additional proposals for candidate participation. Based on these proposals the evaluation work should not only address metals and alloys but also polymers and ceramics.

The organisation of the activity groups is being prepared. In view of the increasing interest in the integration of materials information and databases into industrial CIM concepts, pre-standardisation efforts on materials data analysis and evaluation have come into enhanced demand. TWA 10 can therefore acquire a leading function in this field.

3. Inventory of Materials Designation Systems

A final report under the contract with NPL has been submitted by K W Reynard and is being reviewed. As more data are still coming in (and welcomed) the dBase IV files are being maintained. The form and method of distribution of the report and the database have yet to be determined.

Technical Working Area 11

CREEP CRACK GROWTH

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Objectives

- To develop a unified approach to the measurement and interpretation of creep crack growth data

The draft standard on creep crack growth in the steady-state creep regime has now been agreed by the members of the VAMAS group and is proceeding through the ASTM approval system. A formal standard should be available by the end of 1992.

At a recent meeting in Tokyo the present status of the current work was reviewed with particular emphasis on activities in Japan. The work on large-scale specimens is mainly complete and results for the relatively low ductility superalloy material were evaluated. Some further analysis is required to provide a consistent basis for comparison of data.

A final meeting of the Group is planned for 22 November 1991 at NPL, Teddington.

Technical Working Area 12

EFFICIENT TEST PROCEDURES FOR POLYMER PROPERTIES

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Objectives

- To provide support for standardisation activities in the characterisation of long term properties of viscoelastic polymer materials
- To produce a guide for accelerated durability tests
- To consider the role of standard reference materials in accelerated durability testing

The broad objectives of the TWA are to provide support to standardisation activities in the characterisation of the long term properties of viscoelastic polymer materials. Relevant properties include creep, stress relaxation, fatigue and durability in aggressive environments. In order to avoid prohibitive amounts of testing over long time scales it is common practice to make use of extrapolation, interpolation, interconversion of property data or accelerated tests. Many of the procedures are at best approximate and they often lack standardisation.

A specific area currently being addressed by TWA 12 is that of the durability of polymers in aggressive environments such as heat, light, and liquid chemicals with particular reference to accelerated tests.

Current work is addressing two topics:

1 Provision of a general guide to the use of accelerated durability tests (ADT) is being co-ordinated by R P Brown, Rapra Technology Ltd., Shawbury, SY4 4NR, UK, and could, in due course, provide the basis for a standard.

2 Consideration of the role of standard reference materials (SRM) in ADT is being led by G Zerlaut, DSET Laboratories, Box 1850, Black Canyon State, Phoenix, Arizona, USA. It will provide one or more guides to the use of SRM in ADT.

A broad survey amongst VAMAS participants evaluated their priorities with respect to the different aspects of the general TWA context (ie creep stress relation, durability, etc) and was responsible for the choice of durability as the current specific area.

A detailed survey examined the availability, status and use in VAMAS countries of standard tests for ADT and this led to the selection of the two current work topics identified above. A paper giving broadly the results of the survey has been accepted for publication in *Polymer Testing.*

The Guide to Accelerated Durability Tests has been largely drafted but a few sections are still outstanding. A study of the use of SRMs in ADT has been produced by G Zerlaut and the Guide is being developed. TWA members are participating in an interlaboratory comparison to evaluate SRMs organised by ASTM G3 06 and the practical work is expected to commence shortly. The next meeting to consider and progress these topics is being arranged for October 1991 in conjunction with the ISO TC61 meeting in Madrid, Spain.

It is intended that the Guides being produced will form the basis of guidance standards published by ISO.

Technical Working Area 13

LOW CYCLE FATIGUE

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Objectives

- To identify those aspects of testing procedure that significantly affect the reproducibility of the results of low cycle fatigue tests at high temperatures

This intercomparison programme of high temperature, low cycle fatigue tests was aimed at examining the effects of testing variables and material characteristics on the agreement of results obtained by different laboratories. The programme involved the testing of four materials classified according to their cyclic strain characteristics as strain hardening (AISI 316L), strain softening (9Cr1Mo steel and IN718) and strain stable (Nimonic 101 alloy).

The experimental programme, involving 16 European and 10 Japanese laboratories, was concluded in 1990 but considerable difficulty was encountered in analysing the data. Overall it was shown that for all materials, the within-laboratory variation in lifetimes was significantly less than that between the results of different laboratories, the divergence increasing as the total strain to which the specimens were subjected decreased. Similarly the variation in stress range at half-life at a given strain range was generally 3-4 times greater when considering results from all laboratories as opposed to those from any single laboratory. It was noted that the spread in 9Cr1Mo steel data was slightly less than for AISI 316L, whilst that for IN718 and Nimonic 101 alloy was greater. The use of alternative failure criteria to specimen separation had little effect on the scatter of the data.

Consideration of sub-sets of the data showed that limiting the analysis to data from smooth specimens tested with axial strain control reduced the scatter marginally because of the generally shorter lifetimes of ridged specimens.

Overall it was concluded that the primary causes of differences were measurement uncertainties in the control and traceability of the strain range and rate, temperature and the alignment of the test assembly. Experiments to explain some of the conflicting data by determining acceptable limits for some of these parameters are in hand in advance of a further restricted intercomparison. In the meantime a report upon the project is being published jointly by the European Commission and VAMAS.

Technical Working Area 14

THE TECHNICAL BASIS FOR A UNIFIED CLASSIFICATION SYSTEM FOR ADVANCED CERAMICS

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Objectives

- To identify and assess issues inherent in the development of an internal classification system for advanced ceramics, particularly terminology and nomenclature.
- To establish a suitable classification structure and mechanisms for system implementation.

Accomplishments

- An international survey was conducted to assess industrial classification needs and practices. About 300 survey questionnaires were circulated to advanced ceramics producers and users in 14 countries. Approximately 140 responses were received; analysis of results has been completed and published in May (Report No. 5, ISSN 1016-2186).
- A classification workshop was held 21-22 June 1990 at the CEC's JRC-Ispra (Italy) to assess classification models developed thus far and to provide recommendations for the best system logic and final structure. A report on the workshop is in preparation.
- Existing classification systems on conventional materials have been reviewed; this review, in combination with the results of the international survey and the classification workshop, gave guidance on a skeletal classification system based on a model scheme, consisting of the following matrix elements:

1. Applications
2. Chemistry
3. Form
4. Processing
5. Property criteria

The matrix elements will be defined with greater specificity by a consultant, with support provided by the CEC, JFCC and ASTM/ISR. It is envisioned that the consultant's task will involve the following steps:

1 Acquire information on materials and applications from worldwide literature sources both by direct requests to manufacturers, by review of recent applications literature, and from any other relevant source.

2 Analyse the information and identify the essential groupings under the five headings given above. At this stage it is not proposed that a complete set of interlinks between the five headings for all products/applications be formulated, but the retention of some specific examples would be valuable to demonstrate how they fit into the series of headings.

3 Prepare a draft list of headings in a form suitable for submission to TWA 14 Committee, complete with several examples of how products fit.

4 Take part in industry consultations through TWA 14.

5 Modify or extend listings as suggested by the consultations, and prepare a final report to TWA 14.

6 Complete initial work by mid 1992.

Plans

Upon completion of the matrix scheme, the results will be disseminated to standards organisations in a pro-active way. Specific dissemination mechanisms will be formulated at the next TWA 14 Working Group meeting, September 16-17, 1991.

VAMAS Calendar

4th Topical Conference on Quantitative Surface Analysis
University of Washington, Eatonville, Washington, USA. 8-9 November 1991
(prior to the 38th National Symposium at Seattle, Washington)

International Symposium on Pre-Standards Research for
Advanced Materials (ISPRAM '91)
Tokyo, Japan 16-18 December 1991

VAMAS Steering Committee Meeting
Tokyo, Japan 19-20 December 1991

8th Annual TWA-4 Meeting
New Delhi, India, 28 March 1992
(immediately after the Polymer Processing Society
annual technical conference on 24-27 March 1992).

QSA-7
University of Surrey, Guildford, UK 7-11 September 1992

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