FAST HEATING IN μ-THERMAL ANALYSIS

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Thermal analysis of the 10 μm surface of materials using TA Instruments' μ-TA thermal probe and pulsed force mode AFM has shown promising results. This addresses the need of additional surface characterization based on principle of Thermal Analysis, which is complementary to other surface characterization techniques, i.e., Surface-IR, TOF-SIMS, etc. The method calls for identification of surface landscape by imaging first, followed by fast heating the spots of interest. The micro thermal probe is viewed to heat a small material with a tiny heater rather than to heat small material with a large heater in conventional thermal analysis. In this paper, we demonstrate the applicability in the adhesion temperature of the topical coatings of Tyvek® HDPE sheets, fusion of the heat-processed polyethylene fibers in a bundle, the surface crystallinity of PET pellets, and two examples of phase images of toughened Nylon 66. Comparisons were made where it is possible with standard thermal analysis techniques as well as with the microscopic techniques of AFM, TEM and optical.

Introduction

Conventional thermal analysis techniques are used for identification/confirmation of organic, inorganic, biochemical, pharmaceutical and polymeric materials through their physical transitions as function of temperature. This requires of milligram of material and is to be analyzed as the bulk properties. However the property or a problem unique to the superficial skins of top 10 nm (10^{-8} m) generally relies on surface sciences of ESCA (electron spectroscopy of chemical analysis), TofSIMS (time-of-flight secondary ions mass spectroscopy), Surface-IR, AFS (atomic force spectroscopy), and microscopies of SEM (scanning electron microscopy), TEM (transmission electron microscopy) and optical microscopy. These are expensive analytical laboratories both to equip and to staff. In addition, ESCA, TofSIMS and Surface-IR may provide chemical clues to the identification puzzles, while SEM, TEM are basically visual techniques relying on staining. The unique applications of microthermal analysis, one of Mike Reading's inventions, in polymer arena have been explored and demonstrated for a few years [1–5]. It revolutionizes the traditional thermal analysis of heating a small material in relatively large furnace for the phase change of material properties, whereas the microthermal analysis heats the same small material with a tiny heater locally. It maps the surface in predetermined area on a microscopic scale of thermal conductivity image and topography image based on an AFM Z-piezoelectric scanner, scanning feedback and imaging resolution technology. It characterizes the top 10 μm of material surfaces with a sensor/heater tip. The selected interested spot of the image map is followed up with heating with fast rate up to 50 K s^{-1} through the sensor/heater tip. The tip reacts to the physical property of the selected material spot as temperature increases in penetrating into surface due to the occurrence of a glass transition and a melting transition. The draw back is the mapping of the sub-μm domains is not possible, because of the one micrometer size tip. It is shown as blurred images, and the characterization of these domains shows mixed properties. Still, it is unique enough for the homogeneous surfaces and heterogeneous surfaces of large domains. We have applied successfully in many surface problems and would like to document these unrelated characterizations revolving around this new technique.

Another useful extension of micro-thermal analysis operating mode is the pulsed force mode, a non-resonant, intermediate contact mode for application of (AFM). It is WITec product (Wissenschaftliche Instrumente und Technologie GmbH) marketed by TA instruments to be used in combination with TopoMetrix Explorer™ AFM, which is the body of μ-TA 2990. It maps the surface domains based on stiffness/adhesion by sinusoidal modulation z-piezoelectric scanner. The amplitude is adjusted so that the AFM tip jumps in/out of contact during each period to produce a complete force-distance curve at the pre-determined microscopic area.

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Instead of digitizing the curve pixel-by-pixel, the electronics extract the baseline, maximum force, maximum adhesion to form stiffness and adhesion images. Also by using with the cold/hot temperature stage, one can operate above/below the physical transition of domains, which adds another parameter. Since we are in exploration stage, the repeatability is qualitatively established.

Experimental

Instrumentation

The instrument is marketed by TA Instruments as μTA^{TM} 2990 Micro Thermal Analyzer in thermal probe and AFM probes. The scanning head is furnished a diode Class IIIa laser of wavelength of 670 nm. The thermal probe or the pulsed force mode AFM probe of μTA was set up by mounting the appropriate tip/cantilever on scanner magnets, aligning laser, adjusting mirror and photodetector. The thermal probes are a pair: one to measure the sample and the other to function as a reference probe. The sample probe *vs.* reference probe was calibrated its temperature scale with melting transition of standards, e.g., PET, and calibrated the sensor response on a semiconductor standard calibration silicon grid surface following the recommended procedures. A video camera of 100X magnification was used as the coarse image to locate the interested spot on the sample and to align laser onto the probe mirror. The thermal probe was used to obtain images based on topography and the thermal conductivity of the sample before identification of domains, features and phases using images as the road maps. The test sample was mounted onto a metal stub using a piece of graphite double-stick tape.

The pulsed force mode is a WITec (Wissenschaftliche Instrumente und Technologie GmbH) certified product using an AFM I-type silicon probe on the scanning head. The sinusoidal modulation on z-piezo of the AFM was set ~1% and frequency of 500 Hz. Setpoint was around 15–20 nA. A sinusoid is chosen at high frequency so that it would excite disturbing resonance at harmonics far above the modulation of frequency but far below the frequency of the cantilever. The amplitude is adjusted such that the I-type probe tip jumps in and out of contact during each sinusoidal cycle.

Materials

The test specimens were mounted on stubs using double stick carbon tape as it was. However, some were tested on the microtomed surfaces because they were available to us from other tests. Depending on the do-

main size, we either map or do not map before performing the fast local thermal analysis for phase transition properties.

Tyvek® is high density polyethylene flash spun into sheets marketed by DuPont company. Using HDPE parts in medical applications has seen in hips and joints replacements. Some tried gamma irradiation [6] to increase wear resistance, others [7] plasma-treated with mixed argon and oxygen to reduce aging. The topical plasma treatment of Tyvek® in this paper was intended to add adhesion to itself or to other polymeric materials. The plasma coats can be oligomeric hydrocarbons or acrylates. The heat-processed monofilament are the bundles of high density polyethylene fibers intended for medical use. The nylon blends are 20% ABS (acrylonitrile-butadiene-styrene) and 8% talc in Nylon 66, and 20% Zn Surlyn® toughened Nylon 66.

Results and discussion

Topical coats on Tyvek® sheets

The adhesion of Tyvek® to the other polymeric materials is made possible by applying topical treatments of Tyvek® surface with single or double layer of plasma, which is subsequently in situ polymerized to a ~0.5 μm layer. The thermal probe of micro-TA was used to map the fibrous structure of Tyvek® surface as shown in the Fig. 1, the thermal conductivity image of 100·100 μm area. Selecting fiber locations, e.g., 1, 2, 3 indicated on the image, from the image to be analyzed by local heating of the tip, we recorded the μ-TMA penetration as the top layer melted. In Fig. 2, the uncoated Tyvek® (in blue) shows the average onset melting of 131±5°C in 6 determinations and the melting of the two coated Tyvek®s of 129±8 (in green) and 80±3, 227±3°C (in brown). We have
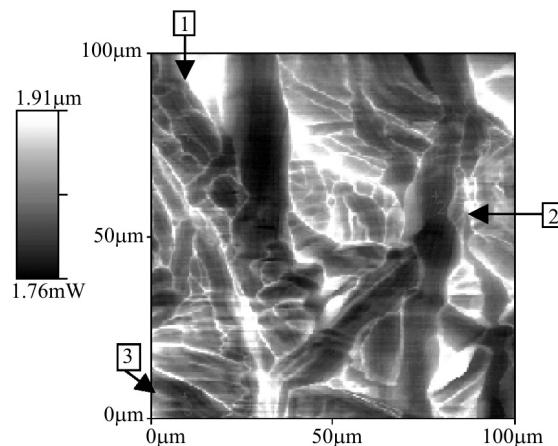
Fig. 1 Thermal conductivity image of a Tyvek®. The locations pointed out are the local heating spots

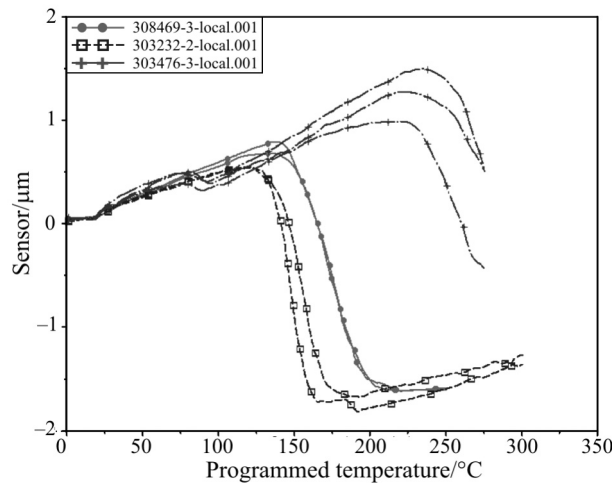**Fig. 2** Local surface heating 10 K s^{-1} of Tyvek$^{®}$ sheets

Fig. 4 Thermal conductivity image of PE bundles. The locations pointed out are the local heating spots

coated with other formulations (not shown), which do not show penetration before 300°C due to cross-link of plasma. The superficial melting profiles of the various treatments would help to determine the sealing temperatures of coated Tyvek® to other materials. The light area in Fig. 1 is the artifact of tips being contacted in all sides of polyethylene fiber voids as opposed to only in one side on the fiber top.

Heat processed polyethylene bundles

Passing a bundle of individual fibers through a heating tube produces polyethylene monofilament. The monofilament is to be used in hernia patch, which requires high burst strength. Whether the individual fiber fusing at contacts in bundles is important – lateral cohesiveness of the polyethylene fibers is to avoid germs growing. We acquired optical images as well as the thermal probe image, shown in Figs 3 and 4, however the images alone would not be absolutely sure of the lateral cohesiveness.

The subsequent localized heating at selected locations, i.e. at bundle skin, fiber center, fusing contact
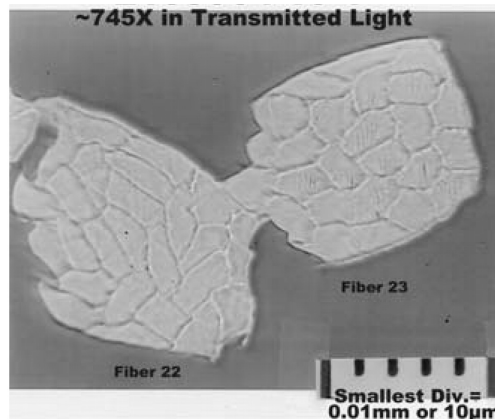

Fig. 5 Local heating traces at selected positions as indicated
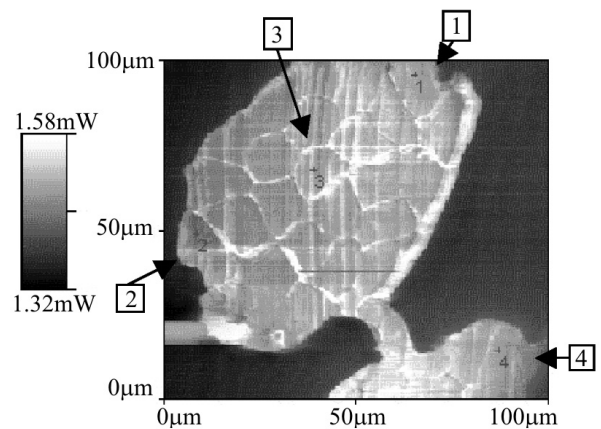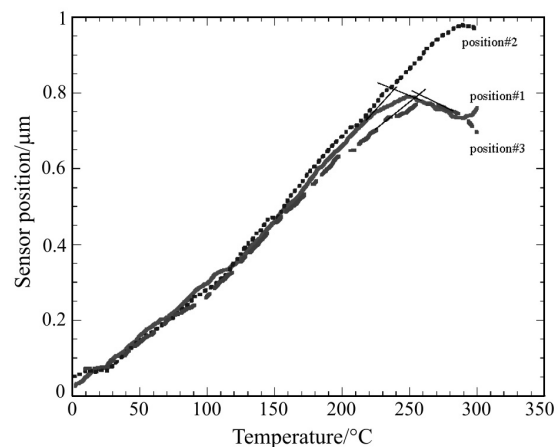
and epoxy bedding outside the bundles, we noticed neither the TMA-like melting penetration at 135°C (folded chain polyethylene) nor at 142°C (extended chain polyethylene). Instead in Fig. 5, the force and heater applied to the locations show penetration at much higher temperatures (230°–280°C). The compaction of high-density polyethylene together has been reported [8] that it did not change pore structure and remained its visco-elasticity. The industrial standard forced flow in a hydraulic press is 190°C for the run-of-the-mill polyethylene. The heat-treated extended chain polyethylene would be higher than 200°C. We believe that there are no obvious voids between the fibers in bundles based on its higher penetration temperatures.

Surface crystallinity of PET pellets

The million pounds of PET pellets were produced worldwide. To this day it still occasionally shows problem to be addressed. We observed the PET pellets processed and cut at the extruder exit sticking to
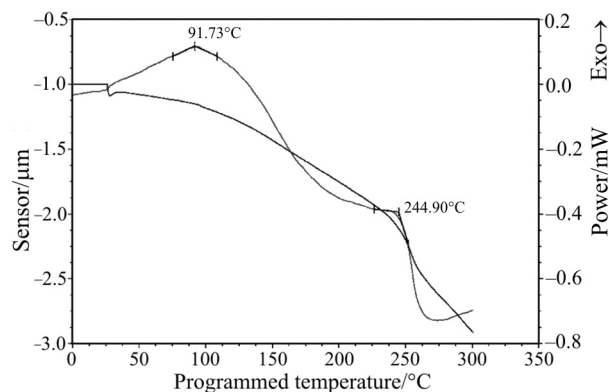

Fig. 3 Optical micrograph of PE bundles

Fig. 6 The μ-TMA scan of PET pellets on-site

Fig. 7 The μ-TMA scan of PET pellets off-site

Fig. 8 TEM image of Nylon/ABS at ambient

This encouraged us to switch to μ-TA. Using thermal probe in μ-TMA mode to heat the skin of the halved pellet, we are able to confirm that the transferred pellets have been crystallized on the skin by comparing Figs 6 and 7. The sticky PET pellets show low crystallinity by having a penetration at the glass transition temperature of PET in additional to the expected penetration at PET melting. The non-stick pellets show slight expansion in the glass transition region, but the penetration of melting region is substantial.

Phase mapping of nylon blends using pulsed force mode μ-TA

Two examples are shown here for the successful applications in phase mapping with the aid of using temperature stage. Standard methods for phase mapping of blends would be TEM and AFM. We obtained both microscopic images for comparison to the micro-thermal analysis method. In TEM the microtomed 10 μm slides were first stained with PTA, 1% aqueous phosphotungstic acid and the best for nylon staining, subject to electronic images. The (AFM) surface analytical tool uses a sharp micro-fabricated cantilever attached to a piezoelectric scanner. In tapping mode the cantilever is vibrated near its resonant frequency as the probe tip is brought into intermittent contact with the sample surface. Similar to micro-thermal analysis, a feedback loop adjusts the height of the probe above the sample to maintain a constant tip-sample interaction during image acquisition. Scanning across the sample generates three-dimensional topographical images of the surface (height Z *vs*. XY position). A Phase image is often collected simultaneously with the topography image. The contrast in the phase image is related to micro-mechanical heterogeneity of the surface, but it can also provide contrast enhancement of edge effects or finer features.
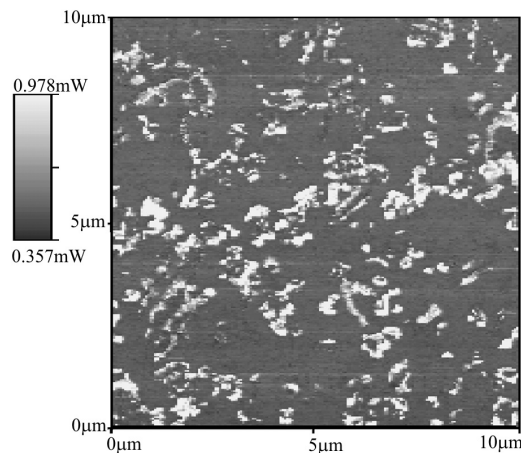
each other, while the pellets transported through a pipe to a boxcar distance away did not stick. The surface crystallinity was suspected, since DSC scans of both bulk pellets were identical. The standard TMA penetration mode using quartz probe implies that the pellets boxed on-site showed deeper penetration at temperature where the glass transition is observed.

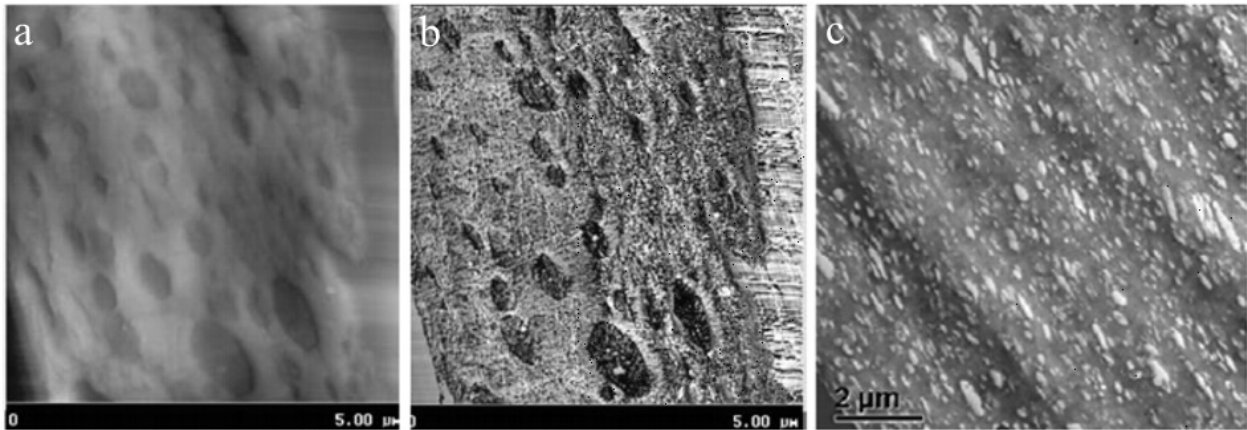**Fig. 9** The adhesion map of Nylon/ABS at 110°C

Fig. 10 a – AFM topographic image b – AFM phase image and c – TEM image of ionomer/Nylon 66

In micro-thermal analysis pulsed force mode, the polymeric domains are mapped based on their stiffness/adhesion by sinusoidal modulation z-piezo-electrics. The I-type AFM tip jumps in/out of contact during each period at predetermined force and resolution to produce complete force-distance curves at points in pre-determined material surface area. The contrast of phases is seen clearly at selected temperature above/below the transition of each component, which enhances the contrast by melting one phase.

First example is a Nylon 66 blend with ABS, acrylonitrile-butadiene-styrene. As shown in Figs 8 and 9, the transmission micrograph at ambient and pulsed force mode adhesion map at 110°C respectively, the 20% of ABS is seen the discrete phase dispersed in matrix Nylon 66. The reason of using hot stage with on this blend is to heat the blend above the glass transition of acrylonitrile-styrene (SAN) blocky phase, so that the adhesion of the phase of SAN would be high, while nylon matrix stays stiff (the melting temperature is 265°C). The adhesion would be high at ambient temperature. The short rod-like material is the added talc. We've used standard DSC to confirm the transitions of all these components. The butadiene's glass transition is very low below –60°C. Nylon 66's T_g is 40–60°C depending humidity, SAN at 100–105°C.

The second example is the 20% Zn Surlyn® (ionomer) toughened Nylon 66. The ionomer and nylon show melting points by DSC at 95 and 265°C, respectively. The domain images are identical to that obtained in stained TEM and tapping AFM images. The microscopic images show the 20% ionomer dispersed in the Nylon 66 matrix. The softer phase of the ionomer is seen in AFM topographic image as the recessed cycles in 25–77 nm deep and 0.6–1 μm for the larger domains in Fig. 10a and phase image in Fig. 10b. The ionomer is seen in TEM as similar dispersed cycles in Fig. 10c.
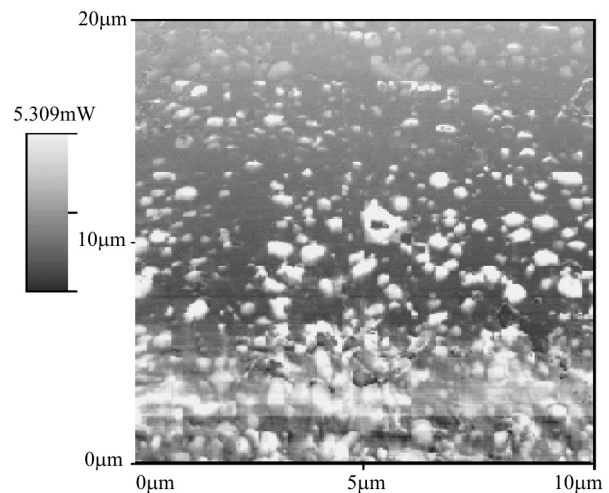

Fig. 11 The adhesion image of ionomer/Nylon 66 at 105°C

The ionomer toughened Nylon 66 on 105°C hot stage shows the same image as that from AFM and TEM given in Fig. 11. The 105°C was selected to be at the temperature above the melting of Zn ionomer of 95°C.

Conclusions

We have explored the characterization power of μ-TA in two modes of μ-TA because of its unique temperature capability that does not come with surface and microscopic techniques. Thermal probe is useful in large domain or no domain characterization of physical transitions. The melting guide of plasma treated of Tyvek® sheets is useful to predict the adhesion temperature. The pressure and heat compaction of HDPE fiber bundles do not show typical of HDPE, but a higher melting tight fused monofilament. The surface crystallinity of PET pellets is suspected before demonstrated using micro-TA thermal probe. With the aid of temperature stage we are able to distinguish do-

mains below/above a transition. The PFM adhesion image of μ-TA operation at selected temperature agrees with TEM and AFM's stained images.

Acknowledgements

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