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Morphology of a PA / PTFE Blend Studied by Raman Imaging

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Summary: Raman spectroscopy has been employed for morphological studies on a polymer blend of polyamide-6,6, polytetrafluoroethylene and silicone oil used as a commercial friction bearing. New information about dimensions and distribution of polytetrafluoroethylene clusters in this composite material was revealed by Raman imaging. It was found that the applied processing conditions result in the formation of clusters, which are between 8 µm and 20 µm in diameter and distributed randomly over the whole material. The Raman results were confirmed by SEM images and SEM / EDX elemental mappings. The Raman imaging method has proved to be a good analytical tool for polymer analyses due to the speed of spectra acquisition and the easy sample preparation.

Introduction

The characterization of new high tech materials for the optimization of functional properties is a strongly growing field with many analytical techniques. Some methods are completely new, others have been well known for years or decades and meet a renaissance due to new additional features. One of this latter techniques is Raman spectroscopy. Known at least since the experiments of C.V. Raman [1] in 1928, but without many practical applications until the introduction of lasers as exciting light source [2] and Fourier Transform instruments in the 1980's [3]. One further step on the way to a widely used analytical tool was the coupling of a spectrometer with a microscope [4,5] and the introduction of the Raman imaging systems, which allow morphology studies with lateral resolutions of about 1 µm based on specific chemical information of molecular vibrations [6-11]. An application of this interesting method on the field of polymer science will be demonstrated in the context of this paper. Additionally the results are proved by other techniques, like scanning electron

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microscopy, energy dispersive X-ray spectrometry or Fourier Transform Infrared Spectroscopy.

The sample under investigation is a commercial friction bearing of the following composition: 80 % polyamide-6,6 (PA), 18 % polytetrafluoroethylene (PTFE) and 2 % silicone oil. The polyamide forms the matrix and gives stability to the bearing. PTFE, a material with a very low coefficient of friction, is used as incorporated lubricant and is not chemically linked to the PA matrix. During use a thin film of PTFE is formed at the interface between thermoplastic bearing and the metal or plastic counterphase, which diminishes friction and abrasion of material and is responsible for the long lifetime of the bearing. Silicone oil is necessary during the break-in phase, before the above mentioned thin film of PTFE is created. Due to the applied pressure the oil, which also shows no interaction neither with PA nor with PTFE, quickly migrates to the surface and behaves as boundary lubricant until the PTFE film starts working. This diminishes the abrasion during the initial phase of use, but has no influence on the long-term stability of the bearing itself.

Composite materials of this kind are used as maintenance-free friction bearing in the automobile industry, as gear wheel, or for mobile parts in electronic devices, like printers or fax machines, where external lubricants can eventually soil the paper. Up to now the distribution of the single phases has not been determined. Only empirical tests were performed to improve the materials properties.

Experimental Section

Chemical composition and structural properties of this polymeric blend material were investigated using Raman spectroscopy, scanning electron microscopy (SEM) in combination with energy dispersive X-ray (EDX) spectrometry and Fourier Transform Infrared spectroscopy (FT-IR).

The Raman instrument is a dispersive Renishaw 2000 system. A HeNe laser (632.8 nm) with a maximal output power of 17 mW is the exciting laser light source. Rayleigh scattering is removed by a set of holographic Notch filters and the signal detected by a two dimensional, Peltier cooled CCD camera. Characterization of the main components was done in the dispersive mode using a grating with 1,200 lines/mm. Spectra were recorded over the range of 3,600 to 250 Δcm^{-1}. The Raman images were acquired in the imaging mode. Dielectrical band pass filters with a resolution of about 20 cm^{-1} were in use for the selection of the specific spectral regions. The lateral information with a resolution of about 1 micrometer (determined by the microscope objective, number of used pixels on the CCD camera and Bragg's law) was obtained by selective signal read out of the two dimensional CCD camera. Image size was controlled by defocusing the laser spot to the desired size (usually between 30 and 80 μm) and limiting the read out area of the CCD camera.

Scanning electron micrographs were recorded with a Leo Gemini DSM 982 microscope equipped with a Schottky emitter at an acceleration voltage of 7 kV to get information about the morphology of the sample. The same energy was applied for the EDX mappings. Carbon, oxygen, fluorine, which is an indicator for the presence of PTFE, and silicon maps were registered. These maps revealed the distribution of the different compounds within the blend and were used to re-examine the Raman results.

Qualitative materials identification was provided by FT-IR microspectroscopy. A Spectra-Tech Advanced Analytical Microscope combined with a BOMEM MB spectrometer was used in transmission mode to characterize the main components. Attenuated Total Reflection (ATR) using a ZnSe crystal was employed to acquire a spectrum of silicone oil. Diamond knife cut sections were prepared for the investigations. The Raman spectra and images were recorded after this simple preparation. Before investigating the sample by SEM the sections were carbon coated to prevent charging. This was done with an EPA 101 instrument, which thermally vaporizes pure graphite after applying high voltage. Under vacuum conditions the carbon atoms deposit on the surface of the sample. To obtain homogeneous coverage, the sample is moved continuously during the deposition process. For the FT-IR transmission measurements thin sections of 5 μm thickness were used. The ATR spectra were obtained from the same sections as the Raman spectra.

Results and Discussion

The main components of the blend were already identified after acquiring one single Raman spectrum. An acquisition time of 10 seconds was sufficient for qualitative identification. Measurements at different positions brought varieties in relative signal intensities, as the ratio of the compounds in the focus of the laser spot changed. The main features of both PA and PTFE were visible in most spectra. Sometimes the PTFE signals got very weak or became invisible, whereas polyamide was present in every spectrum. In contrast silicone oil could not be detected using Raman spectroscopy. One reason is that this polar system, compared to PA and PTFE, is a rather weak Raman scatterer. Another one is the low concentration of only 2 % in the blend. These two reasons and the overlapping of peaks made it impossible to prove the presence in the friction bearing. Reference spectra of PA and PTFE, as well as a spectrum of the sample, are shown in figure 1.

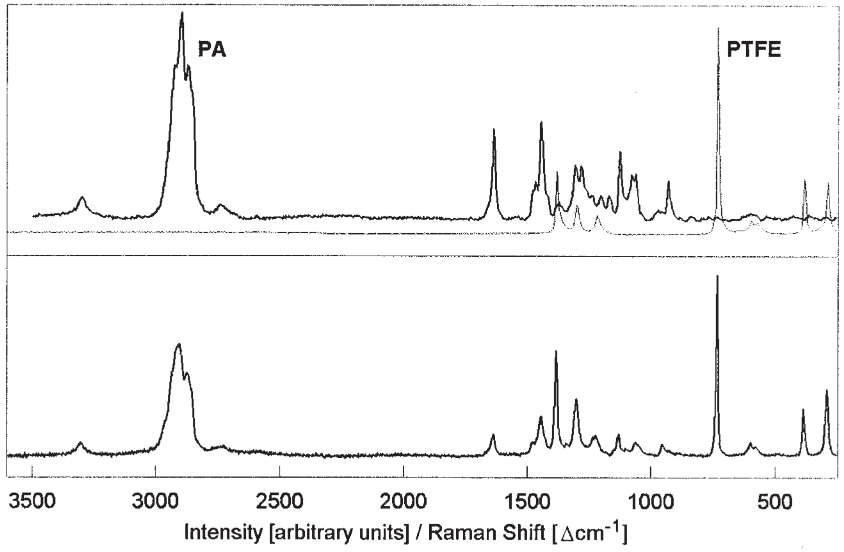

Fig. 1: Raman reference spectra of PA and PTFE in the upper part (baselines shifted for better display). A spectrum of the blend material is shown below

The qualitative characterization of all compounds was confirmed by FTIR spectroscopy. PTFE features were known from the literature [12] and from reference materials. In the spectra of the blend material they could easily be assigned due to their different intensities at the various sample positions. As observed with the Raman spectrometer, PA bands were found everywhere, whereas not always a PTFE cluster was in the center of the IR or Raman spot, which causes fluctuations in signal strengths. This observation reflects the quantitative composition of the material: a high content of

PA together with a much smaller amount of PTFE and traces of silicone oil. The very strong antisymmetric Si-O-Si stretching vibration between 1000 cm^{-1} and 1100 cm^{-1} enables the detection of the last compound. While the main components were identified by acquiring a transmission spectrum of a thin section, the signal of silicone oil was observed using a ZnSe crystal and applying ATR technique with an ATR objective. A better result with this technique can be expected, when we consider the role of silicone oil as boundary lubricant during the break-in phase. Upon pressure, here through the crystal, the oil, which is not linked to any polymer nor has a great affinity to them, migrates to the surface and hence is present there at higher concentration. The study of sample morphology was done by Raman imaging. The size of the PTFE clusters and their distribution were of particular interest. Raman images were obtained by imaging the totally symmetric A_1 mode of PTFE at 731 Δcm^{-1}, which is more likely assigned to the symmetric C-C stretching vibration than to $\nu_s(CF_2)$ [12].

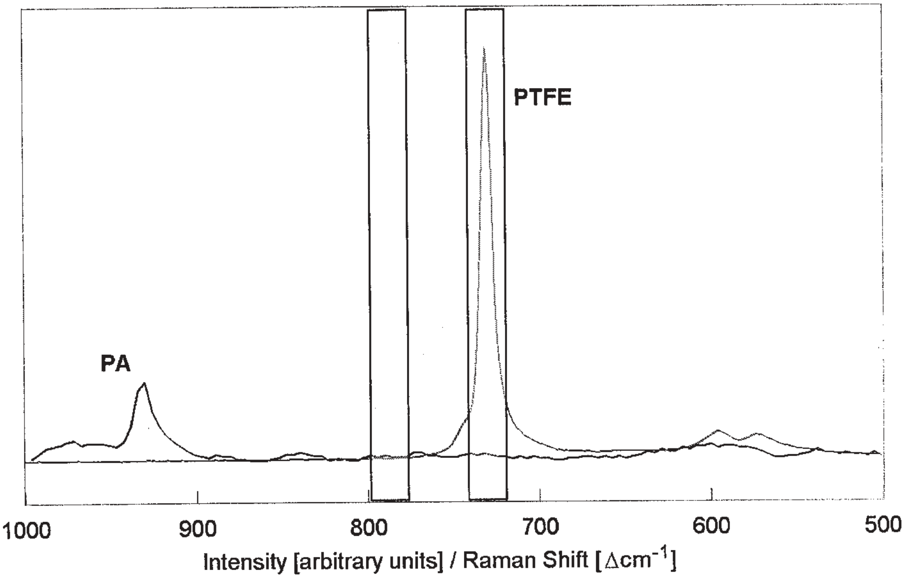

Fig. 2: Spectral regions used for Raman imaging. The area around 731 Δcm^{-1} is selective for PTFE. The second area around 790 Δcm^{-1} was used for background subtraction

For the imaging purpose the dielectrical bandpass filter of the Raman system was set exactly to the wavenumber of this vibration. The mode is very strong and not affected by any signal of polyamide. There is also no relevant contribution of another signal that could interfere, i.e. fall inside the area of 20 cm^{-1}, which is the spectral window of the filter. To take into account the background, another image was acquired at 790 Δcm^{-1}, where neither PA nor PTFE give a signal. The latter image was subtracted from the previous one under the assumption that the background is nearly the same in this area. Figure 2, which is a focus on the region between 1000 Δcm^{-1} and 500 Δcm^{-1} of the corresponding reference spectra, confirms that there is no peak interference at 731 Δcm^{-1} and no signal at 790 Δcm^{-1}. The spectral ranges employed for signal detection are marked with a shadow.

The result of one Raman image is shown in Figure 3. X and y axes scale is given in micrometer and report the lateral dimension at the sample surface. The z direction doesn't represent the materials topography but the intensity of the 731 Δcm^{-1} mode. Obviously we see two different clusters. One is situated in the center of the image with higher intensity and a second one lies behind the first, is a little bit larger and of lower intensity. As we are not sure about the depth we obtain information from, it could be that there is a small layer of PA above the second PTFE cluster or that the section goes through the cluster and only a small fragment remained.

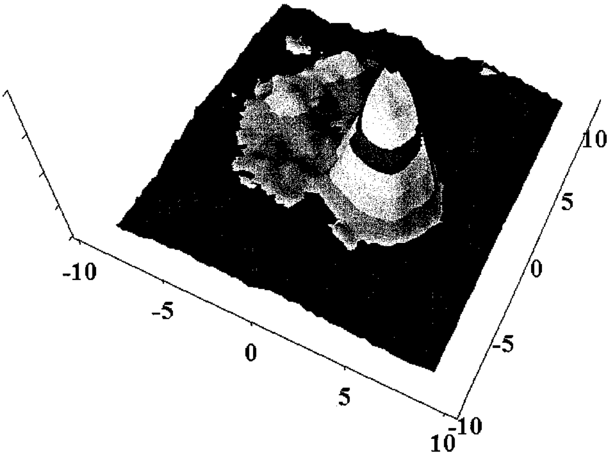

Fig. 3: Raman image of PTFE clusters in PA matrix. Image at 731 Δcm^{-1} with background subtraction (790 Δcm^{-1}). X and y axis are the lateral extent in micrometer. Z axis shows intensity of the PTFE mode.

The images of the CCD camera are summarized in Figure 4. Bright areas resemble a high number of counts. After acquiring the image at 731 Δcm^{-1} we got picture a). The background information is shown in the image called b). We observe that there is only a small amount of background in the PA matrix and a slightly higher one in the PTFE clusters. This can be due to different impurities in the feedstock. With the subtraction of these two images we eliminate not only the background but also inhomogeneities of laser intensity over the defocused laser spot. See picture c) for the result, which is a clear image with a flat nearly completely dark background and d), where a two dimensional representation of figure 3 is given.

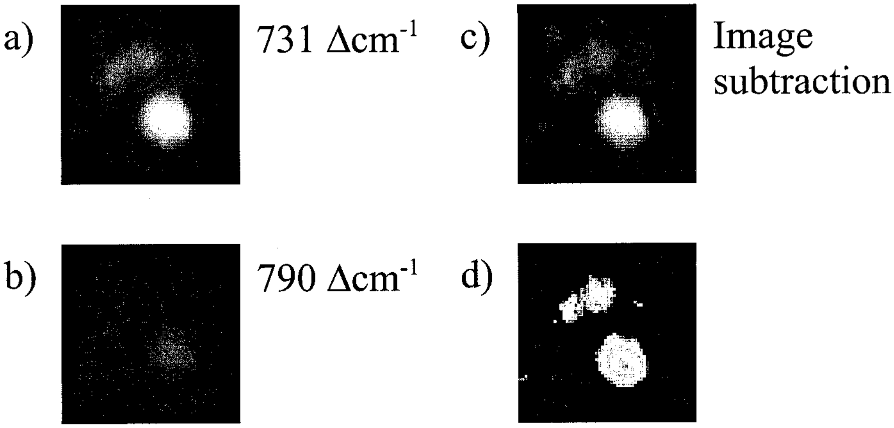

Fig.4: Image of the CCD camera after measuring at 731 Δcm^{-1} (a), at 790 Δcm^{-1} (b), after image subtraction (c) and (d) is a 2 dimensional representation of figure 3.

A number of such images was recorded under different conditions, like acquisition time or size of defocused laser spot. We always obtained PTFE clusters in the region of 8 μm to 20 μm in diameter, which are distributed randomly over the sample volume.

To confirm the results of the Raman spectroscopic investigations another section of the PA / PTFE blend was carbon coated and investigated by scanning electron microscopy. The higher lateral resolution is an advantage in examining the size of the PTFE clusters. Figure 5 shows a secondary electron picture of a section recorded with 7 kV acceleration voltage. The morphology becomes visible but no chemical information can be revealed with this technique.

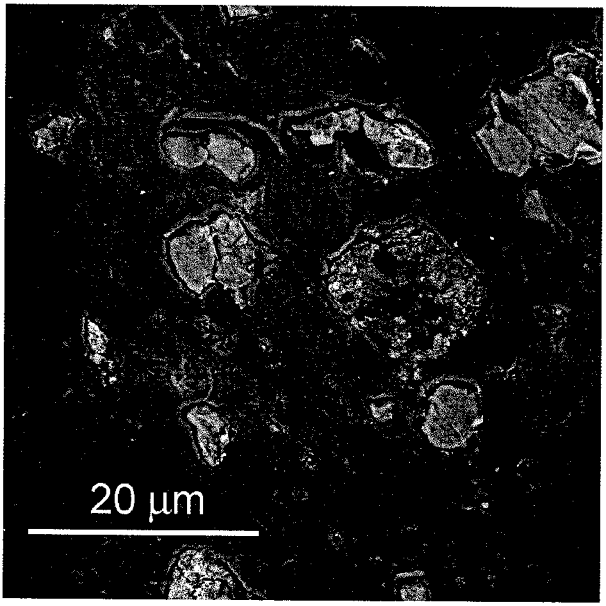

Fig. 5: SEM image of the polymer blend. Acceleration voltage 7 kV. Secondary electrons were used for image formation.

To correlate the two different phases, visible on the SEM image, with some chemical information, energy dispersive X-ray spectrometry mappings were registered. Maps of oxygen, silicon and fluorine distributions were acquired. Normally SEM and SEM / EDX suffers from the poor possibilities of differentiating between polymeric materials, if the elemental composition is the same and the only difference can be found in the ratio of the present elements. In this case the high concentration of fluorine in PTFE enables us to distinguish easily between the two main components. The regions with high fluorine content indicate the positions of PTFE clusters, whereas the rest is free of fluorine. Such a map is shown in Figure 6. As expected from the Raman images, we can detect zones of very high fluorine concentration with diameters in the already above described range of 8 µm to 20 µm. These are the PTFE clusters lying on the surface. There are also some spots, which are weaker in intensity and which are not visible in the secondary electron image of figure 5. Obviously X-rays of PTFE clusters beyond the surface reached the detector. For polymeric materials the density is normally very low and it is easy for the primary electrons to penetrate into greater depth and cause emission of photons. There is also a darker zone around some bright clusters, which means that the PTFE is partially covered by polyamide. As mentioned earlier the distribution of silicone oil could not be revealed by Raman spectroscopy, whereas the registration of an EDX mapping for silicon was easy. Figure 7 shows the distribution of silicon over the sample area. The brightness of the signal and hence the concentration of the element is not comparable to the one in figure 6. The contrast of the image was changed to enhance the display. From this image we can conclude that silicone oil is concentrated on the interface between PTFE and PA as well as in tiny holes. This can be understood by taking into account the processing conditions. An initial mixture of PTFE and silicone oil is incorporated into the PA matrix. So, the PTFE is surrounded by the oil and due to it's lower viscosity it also concentrates easily in tiny holes.

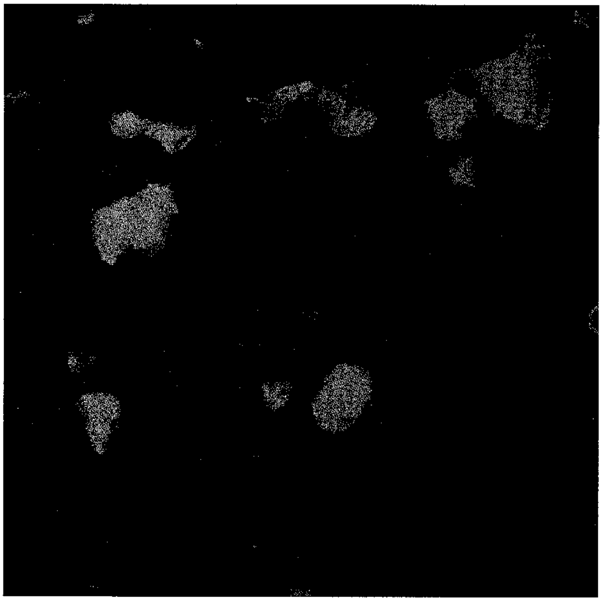

Fig. 6: SEM / EDX elemental mapping of the blend: Fluorine distribution.

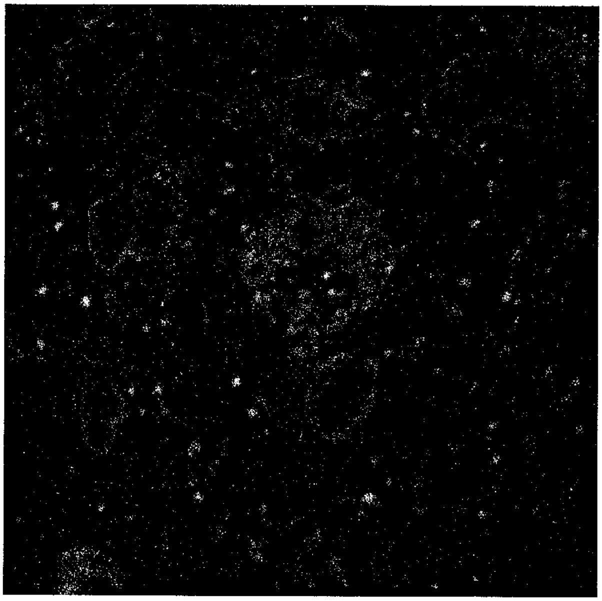

Fig. 7: SEM / EDX elemental mapping of the friction bearing. Silicon oil distribution.

Conclusion

A blend of polyamide-6,6, polytetrafluoroethylene and silicone oil, used as commercial friction bearing, was under investigation. During the materials processing, clusters of PTFE surrounded by silicone oil are formed. The size and distribution of these clusters could be described employing Raman imaging. For this purpose the mode of polytetrafluoroethylene at 731 Δcm^{-1} was used for selective imaging against the polyamide matrix. The small amount of fluorescence in the clusters and general background were removed by acquiring an image of the same area at 790 Δcm^{-1}, followed by spectral subtraction. To prove the new results, scanning electron microscopy was applied to obtain secondary electron images and energy dispersive X-ray spectrometry mappings. The latter method also gave insight into the dispersion of silicone oil, which could not be detected by Raman spectroscopy. Particle sizes and distributions determined by these methods were in good agreement with each other. In this case, a big difference in acquisition time for obtaining the same kind of information favors the use of Raman spectroscopy. It took several hours to obtain energy dispersive X-ray spectrometry mappings and only a few minutes for the Raman images. Raman spectroscopy proved to be a useful tool for investigations on the field of polymer science.

Acknowledgement

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References

[1] C.V. Raman, K.S. Krishnan, *Nature*, **1928**, *121*, 619
[2] T.R. Gilson, P.J. Hendra, *"Laser Raman Spectroscopy"*, Wiley-Interscience, London 1970, p.1-266
[3] D.B. Chase, *J.Am.Chem.Soc.*, **1986**, *108*, 7485
[4] M. Delhaye, P. Dhamelincourt, *J. Raman Spectrosc.*, **1975**, *2*, 33
[5] G.J. Rosasco, E.S. Etz, W.A. Cassatt, *Appl. Spectrosc.*, **1975**, *29*, 396
[6] D.N. Batchelder, C. Cheng, G.D. Pitt, *Adv. Mater.*, **1991**, *3*, 566
[7] L. Markword, B. Kip, *J. Appl. Polym. Sci.*, **1996**, *61*, 231
[8] A. Garton, D.N. Batchelder, C. Cheng, *Appl. Spectrosc.*, **1993**, *47*, 922
[9] R.J. Meier, B.J. Kip, *Microbeam Analysis*, **1994**, *3*, 61
[10] R.L. McCreery, *"Raman Spectroscopy for Chemical Analysis"*, Wiley-Interscience, New York 2000
[11] J.R. Ferraro, K. Nakamoto, *"Introductory Raman Spectroscopy"*, Academic Press, Inc., 1994
[12] D.I. Bower, W.F. Madams, *"The vibrational spectroscopy of polymers"*, Cambridge University Press, Cambridge 1989, p. 185-194