Supporting Information

1. About the PGMs

Up to now, there are a lot of articles can be found on the net about the fabricating and analyzing of the polymer gradient/graded materials or the bilayer materials. But topics of these articles are mainly about the fabricating method, mechanical or the biological properties (as cell growth substrates). Besides, fabrications of these PGMs need heavily on the devices and expensive.

Taking advantage of the relative poor compatibility and the curing rates discrepancy between epoxy (EP) and polyurethane (PU) resins, we fabricated a composition gradient-distributing interpenetrating polymer networks (IPN), simply and inexpensively. And our research is mainly focused on the damping analysis. So far as we know, there are no papers have been published before about this kind of damping materials.

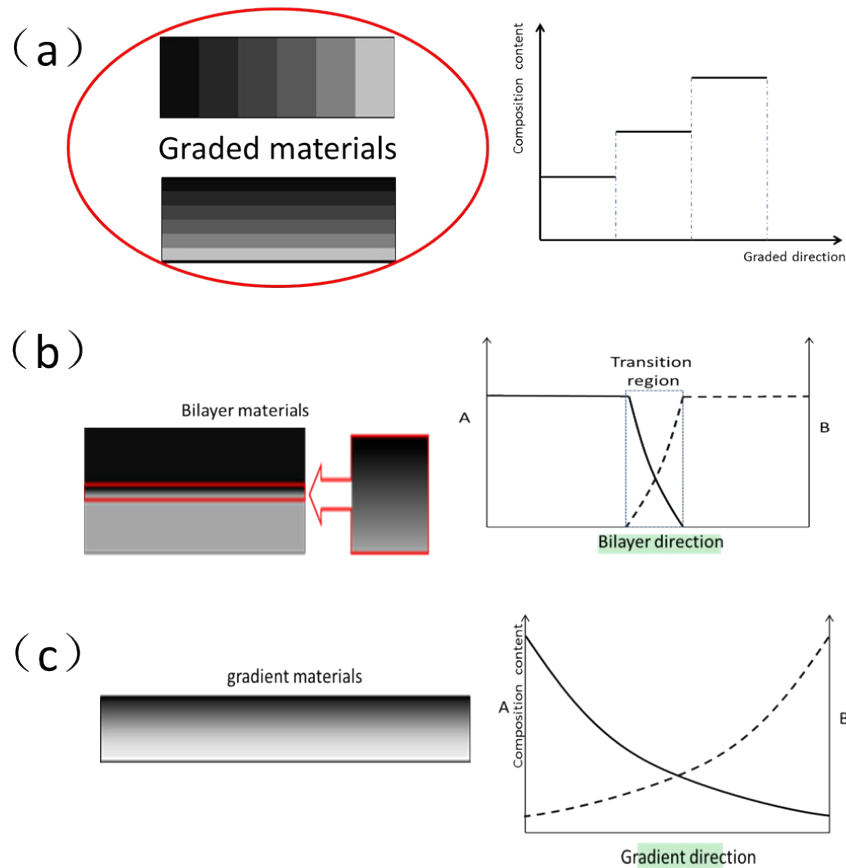A detailed comparison is listed below.

Fig.1 Schematic illustrations of the graded/bilayer/gradient materials. (a) the graded materials; (b) the bilayer material; (c) the gradient material

Graded materials consist of a layered structure where the layer composition changes stepwise along one axis. The graded material consists of multiple discrete sections. Properties are stepwise different from the adjacent sections. In the bilayer materials, there is usually a thin transition region. The compositions are constant before the region and compositions usually experience a sharp change in the transition zone. But in the gradient materials, the compositions change gradually with no sharp interfaces.

2. Ways to fabricate the PGM

Ways to fabricate the polymer gradient materials (PGMs) published in the articles are usually those as listed below.

(a). The electrophoresis method. This method is realized using the migration of the polymer ions under the electric field in the polymer solutions. The polymers are then cured by the evaporations of the solvent or the polymerizations of the polymers.

(b). Gradient distributing of the fillers are realized by the gravity or the centrifugal force. This method is mainly concentrate on the distributing of the fillers, other than the gradient distributing of the component resins.

(c). Temperature difference of the mold can also be utilized to generate the gradient structure of the polymers. This fabricating method is based on the different curing rate of the compositions under different environment (temperatures). The frontal polymerization is a typical example of this method.

(d). Photopolymerization. The Irradiation polymerization using a shield is a common technique for the fabricating of the gradient IPN materials. The gradient structure is realized by artificially controlling the exposure time.

(e). Utilizing of the microfluidic setups. Microfluidic technique is a useful way for the synthesis of materials with defined compositions. This method possesses the ability to control the accurate content of the resins

in a gradient material. But the devices are not purchasable on the market and are not easy to make by the material scientists as well.

(f). Layer-by-layer method. By subsequently casting blend solutions of different polymers with variable compositions onto a substrate, PGMs are obtained after evaporation of the solvents and the diffusion of the polymers. This method needs the operators to have an accurate controlling of the solvents evaporations and resins migration rate. This is complicated for the operators. Usually, it is more suitable for the generation of the multi-layer structures.

(g). Dissolution/diffusion methods. The main polymers are usually swelling in a solvent (containing the second kind of monomers). The second kind of monomers is then cured by the in-situ polymerization or the solvent evaporations before the balance of the diffusion.

(h). Utilizing of the surface/interface tension difference. This method has been published in some articles. The surface/interface tension difference and the poor compatibility of the resins are the driving force for the self-gradient phenomenon of the materials.

To sum up, all the means mentioned above for the fabrication of the PGMs need heavily on the devices and are expensive, such as the microfluidic techniques. Besides, those methods are complicated to operate and time-consuming.

As far as know, several kinds of the PGMs generated applying the

difference of the surface/interface tensions are about the PDMS/PMMA system, other than the EP/PU IPN composite. This kind of the EP/PU gradient IPN composite is realized applying to the surface/interface tension difference, the absorption to the mold and the curing rate discrepancies of the components. This method for the fabricating of the gradient materials is simple, cheap and easy to operate. None of this kind of gradient material has been published before.

Besides, papers published before of the PGMs are about their mechanical properties or the transmissions of the light. They are usually used as the cell growth substrates, the semipermeable membrane and the optical fibers. Differ from the PGMs mentioned above; the gradient EP-PU IPN material is used as the damping materials. The concerns of the paper are about the self-gradient mechanism, damping ability under different temperatures or frequencies and the fatigue durability.

What's more, the gradient materials can be used as a replacement of the constrained damping structures (the gradient material can be directly generated on the substrates. The soft sides of the gradient structure will act as the cores while the hard sides are exposed outside, acting as the constrained layers). This is another novelty of this article. But damping performances of the structures are a complicated issue (including the thickness ratios, shape etc.). This is not included in this manuscript.

3. Adjustment of the AFM instrument

Modulus images were taken in the air with Peak Force QNM mode on a MultiMode8 Scanning Probe Microscopy (Veeco Instruments) at room temperature after the absolute calibration method according to literatures.[a) G. Gao, M. Zhang, P. Lu, G. Guo, D. Wang, T. Sun, Angew. Chem. Int. Ed., 2015, 54, 2245-2250; b) M. E. Dokukin, I. Sokolov, Langmuir 2012, 28, 16060-16071; c) J. Adamcik, C. Lara, I. Usov, J. S. Jeong, F. S. Rugeri, G. Dietler, H. A. Lashuel, L. W. Hamley, R. Mezzenga, Nanoscale 2012, 4, 4426-4429;]

Each modulus image was carried out at a resolution of 512 × 512 pixels using a J scanner. The spring constant was measured by thermal tune method, and it changed with different tips. Since the radius of the cantilever tips is important for the result and might change during the mapping, it was measured before and after every sample by testing the tip check standard sample. SPIP soft was used to calculate the actual tip radius. The trigger threshold of the cantilever deflection was set to 4.0 nm and thus the trigger force was about 15 nN. Same position of each specimen was tested twice and no reduce in DMT modulus can be found. Therefore, plastically deforming the sample surface can be avoided in the 15 nN trigger force. The Young's modulus of samples can be calculated from the Derjaguin, Muller, Toropov (DMT) modulus according to equation 1, which directly reflects the hardness of samples on surface:

$$E_s = \frac{1 - v_s^2}{\dfrac{1}{E} - \dfrac{1 - v_{tip}^2}{E_{tip}}}$$

Here Es and vs represent the Young's modulus and the Poisson's ratio of sampled, E*represents the DMT modulus, vtip and Etip represent the Poisson's ratio and the Young's modulus of the tip.

4. FTIR absorption of the homogeneous

Mixture (EP/PU=40/60) that cured under 80℃ will cure within half an hour, the time that it takes to gel must be less. Different from the continuous gradient IPN, Mixture that cured within a short time would be homogeneous. Properties such as the elasticity modulus, elemental distribution, etc. should be all the same in everywhere of the samples. For a detailed insight of the mixture (cured under 80℃), infrared absorption was done using a Thermo Nicolet FTIR spectrometer (Nexus) using KBr pellets. Locations that chose from the cured resin were the same as the gradient IPN.
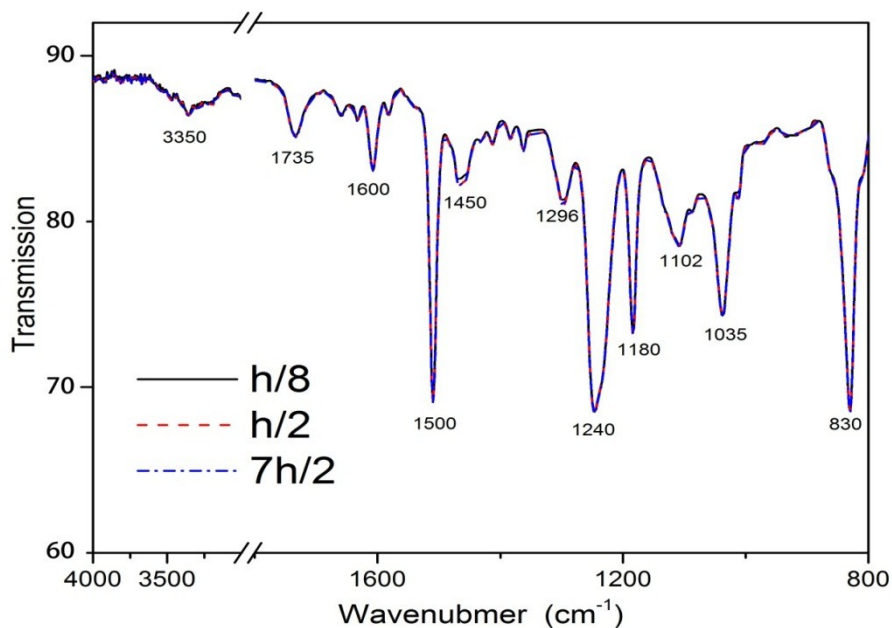
Fig. 2 FTIR spectra of the locations chosen from the homogeneous IPN

Comparing these three infrared absorption spectrums acquired from different locations in the material, nearly no difference can be found. This proved that the mixture cured under 80℃ has a homogeneous structure. Association peaks from 3100 cm^{-1} to 3500 cm^{-1} plus with the band at 1650 cm^{-1} confirm the existence of secondary amide root. Peaks at 1657 cm^{-1} as well as 1240 cm^{-1} are ascribed to the acylamino groups. The peak at 1735 cm^{-1} is the characteristic absorption of the ester group (in elastomer). Band at 1180 cm^{-1} corresponds to the carbon-oxygen single bond's asymmetrical stretching vibration of the ester group. Bands around 1296 cm^{-1}, 1102 cm^{-1} and 1035 cm^{-1} offer the exiting evidence of the ether bonds. Bands around 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1} are attributed to the vibrations of C=C stretching deformation of quinoid and benzene ring respectively. Band of triazine ring is located at

1709 cm^{-1}, figure above shows that there were no absorption peak at this point, which proves that there are no trimerization of isocyanate root.

5. Element distribution test

To investigate the resin distributions in the homogenous IPN and the gradient one (all are in the same components dosage, PU/EP=40/60), samples (thickness is 2.17um) were sectioned into 100 layers under -50℃ from top surface to the bottom using a CM1950 kryotome (Lecia) with a thickness of 21.5um per layer. The 5th, 32nd, 77th and 97th layers were randomly selected from the slices and test through an elementary analyzer (Vario EL cube). For the nitrogen atom exists only in the PU phase, thus detection of the component distributions can be simplified by assaying the nitrogen content.

The results are shown in Table 4. "h" in table means the homogeneous IPN and "g" represents the gradient one. From result we can see that the

N element is monotone increasing in the gradient IPN from top surface to bottom while element in the homogeneous fluctuates around 1.180%. Then we can safely say that PU is gradiently distributed in the composite cured under the stepwised curing process. Composite cured under high temperature has a homogeous structure.

Table 1. Element distribution in the homogeneous IPN and gradient IPN

	Layer NO.	Mass(mg)	N%	C%	H%
5th	h	5.1650	1.170	64.775	7.598
	g	5.1326	0.800	63.970	7.389
32th	h	5.1550	1.180	64.890	7.618
	g	5.2382	1.070	64.310	7.544
77th	h	5.2420	1.170	64.870	7.598
	g	5.4624	1.340	64.490	7.719
97th	h	5.1100	1.190	65.150	7.618
	g	5.2536	1.480	70.720	6.586

6. UV-Vis absorption of the gradient IPN

At the very beginning, mixture of the liquid resins is colorless; but when finally cured, the casting bodies are russet. And the tonality grows darken from the bottom far away to the surface. The g-IPN presents a gradient absorption to visible light as Figure 2 illustrates; thus ultraviolet absorption can be used for detection of the gradient structure. After specimen was fractured (along the direction of thickness) at a high speed and well-polished, regions were symmetrically selected from the fracture surface. The chosen regions are h/8, h/2 and 7h/8 respective from the bottom to the top. Figure 2 is the UV-Vis absorption spectrum of the g-IPN.
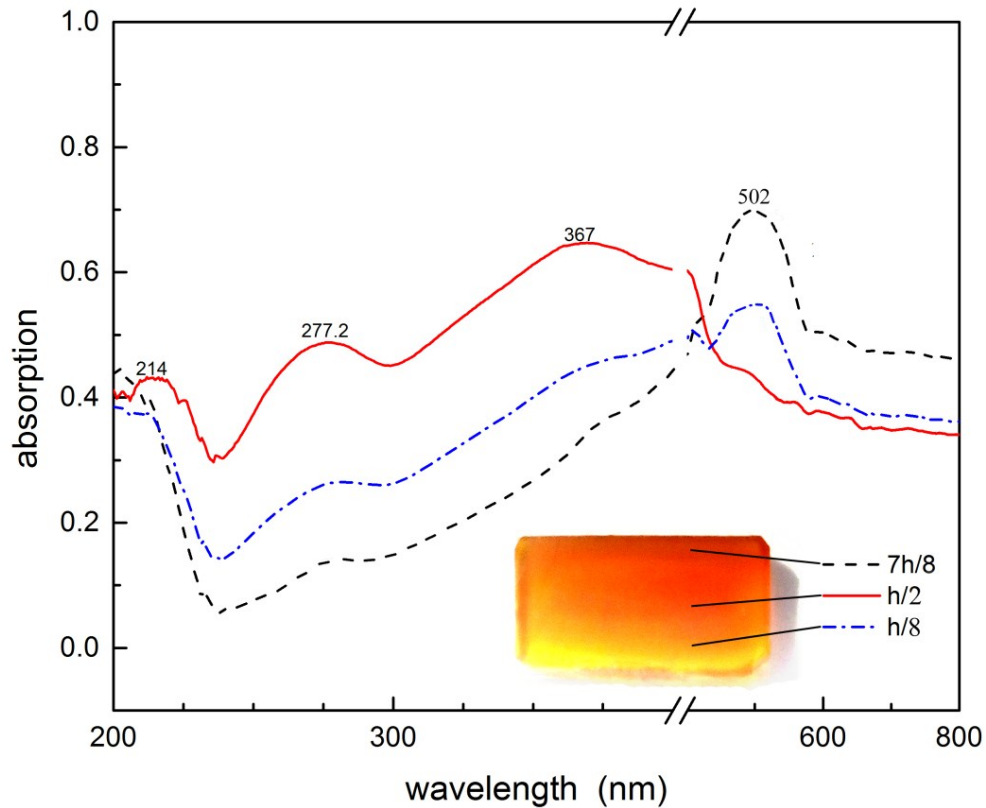
Fig. 3 UV-Vis absorption of the chosen regions of the g-IPN. Regions are symmetrically selected from 7h/8, h/2 and h/8 from the fracture surface.

Absorption of the electromagnetic wave can be explained respectively in the ultraviolet region ($\lambda \leqslant 400nm$) and the visible light region($400nm \leqslant \lambda \leqslant 800nm$). Absorption peaks in the ultraviolet region are almost the same except for intensity. λ max near the bottom is 367nm, this is the characteristic absorption band of the long chain ether bond in PU phase. Absorption at 214nm is the original absorption of acylamino group. Linking with the auxochrome of the imino group (-NH-) and alkoxy group (-OR), absorption band of the acylamino red-shifted to 277nm. Conclusion can be drawn from the spectrum that PU phase (corresponding to the absorptions of ether bond and acylamino group) is

gradient reducing from the bottom to the top surface. Peak at 203nm are the absorption E_2 bond of benzene ring. Layer nears the surface has the biggest absorption, which indicates the maximum content of epoxy near the top surface.

Light which ranges from 450nm to 570nm shows blue and green color. This g-IPN has a gradient absorption to blue and green colors from the top surface to the bottom, thus the gradient IPN composite has a gradual loss of russet color from the top surface far away to the bottom.

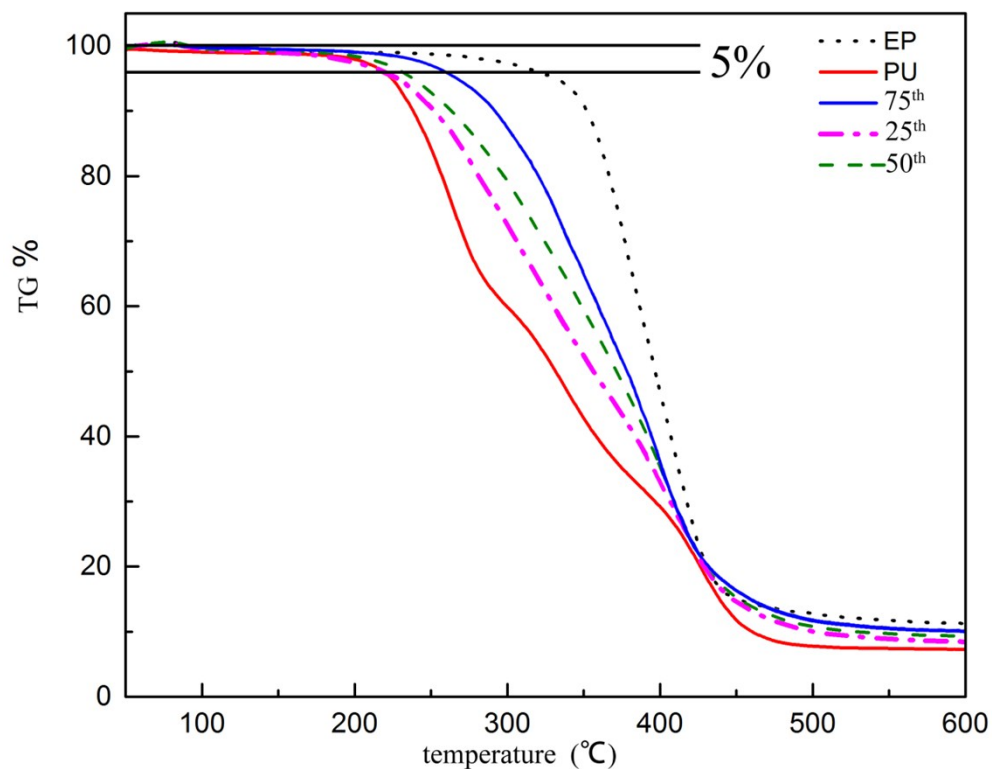## 7. Thermogravimetic analysis of the gradient IPN composite

Fig. 4 TG curves of the pure resins and the slices of the gradient IPN

TG curves of the pure EP, PU and the slices (the 25th, 50th and 75th layers) of the gradient IPN. EP is cured by DMP-30 (8% weight of EP), PU is cured according to the recommended dosage (A:B=5:4 by weight), the gradient samples are selected from the slices that left for the element analysis.

Thermal stability of the gradient IPN was measured by thermogravimetric analysis (NETZSCH STA449c/3/G) under nitrogen flow rate of 30 mL/min with a heating rate of 10 ℃/min from 50 to 700℃.

From the thermo-gravimetric curves above we can see that pure EP has the highest thermal decomposition temperature (about 330℃), and the terminated temperature of the thermal decomposition is about 470℃.

During this temperature interval (140℃), pure EP loss its 83% weight. On the contrary, the thermal decomposition temperature of pure PU is about 210℃ (about 120℃ lower than EP). Thermal decomposition of PU can be separated into 3 steps: 210～280℃, 300～380℃ and 400～450℃. The first step starts from the decomposition of the C-O bond of the carbamate, generating the isocyanate roots and polyhydric alcohols. Volatilization of the isocyanate causes the weight loss of the first step. At this time, the generated isocyanate will have dimerization and terpolymerization itself. The second stage starts from the decomposition of the dipolymers or tripolymers and produces amines, alkenes and carbon dioxide. Volatilization of decompositions caused the second weigh loss. Dissociation of the first two stages loses about 55% of its weight, which is just the percentage that the isocyanate resin takes. The final decomposition is the pyrolysis of the polyhydric alcohols. Pyrolysis products are water and carbon dioxide. The final residuum is about 7% of the original mass.

Slice of the 25th layer locates near the bottom, it contains much more PU phase comparing to the other two layers. So this layer has the lowest thermal decomposition temperature (Td =223℃) and the lightest residual weight, but this section has the broadest temperature interval. The 75th layer come is nest to the top surface and has the maximum content of EP, so Td of this layer is 260℃, relatively, the residual mass is about 11%.

The 50th layer is taken from the middle part in the gradient IPN, comparing to the 25th and 75th layers, this section has an intermediate Td (240℃) and residual mass (10%). Meanwhile, curves of the gradient IPN is different from the pure PU, this may be caused by the synergistic effect of the IPN structure.

8. SEM-EDX analysis of the gradient IPN (EP/PU=7:3)

Element	Wt%	At%
CK	76.00	81.94
NK	02.69	02.49
OK	17.53	14.19
ClK	03.78	01.38
Matrix	Correction	ZAF

Element	Wt%	At%
CK	77.70	83.39
NK	03.92	03.60
OK	14.30	11.52
ClK	04.09	01.49
Matrix	Correction	ZAF

Element	Wt%	At%
CK	75.90	81.62
NK	02.79	02.57
OK	18.18	14.67
ClK	03.13	01.14
Matrix	Correction	ZAF

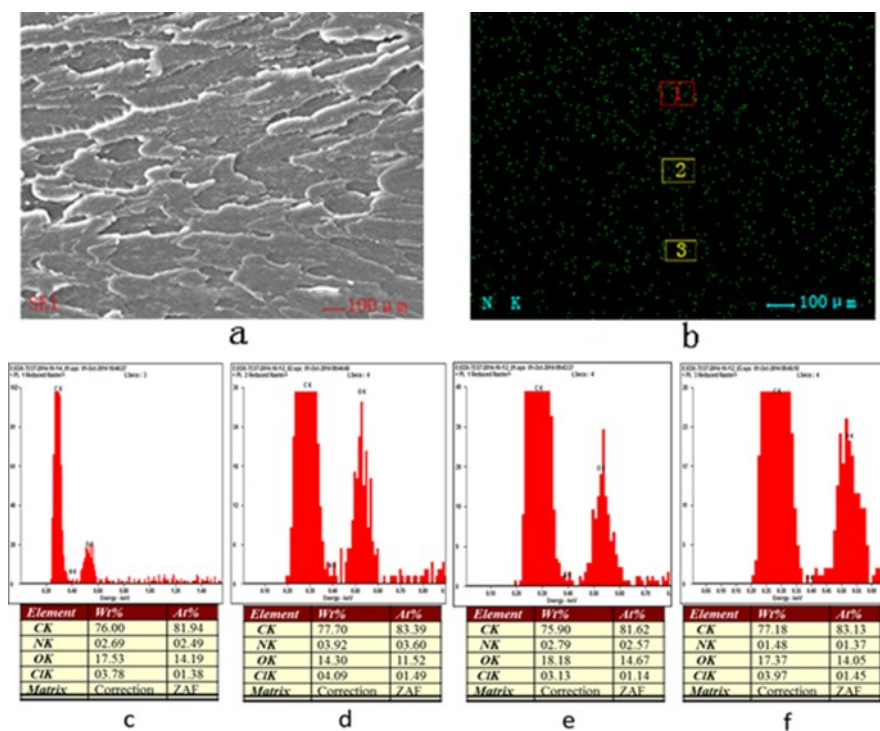| Element	Wt%	At%
CK	77.18	83.13
NK	01.48	01.37
OK	17.37	14.05
ClK	03.97	01.45
Matrix	Correction	ZAF

c   d   e   f

Fig. 5 The SEM-EDX analysis of the 70/30 (EP/PU) gradient material. (a). fracture surface of the gradient material; (b). N element distribution of Fig. 5(a) and the chosen region for the content analysis; (c) the whole N atom content in Fig. 5(a), the data is 2.69% by weight; (d). N content in the region 1, content is 3.92%; (e). N content in region 2, relative data is 2.57%; (f). N content in region 3, data here is 1.37% by weight.

Special explanation should be made here is that the SEM-EDX analysis (EP/PU=70/30) result is higher than the CHNS/O analysis

(EP/PU=60/40). Three reasons can be used to clarify this abnormal result.

Firstly, the measuring mechanism of the SEM-EDX (the X-ray) and the CHNO/S (combustion) test are different. Secondly, the instruments are produced by two different factories and being operated by different operators. Thirdly, the SEM-EDX analysis is more suitable for atoms that heavier than nitrogen. The nitrogen is too light that it is only appropriate for the semiquantitative analysis for this instrument.

I list some of the test results that I think they might be useful to prove the gradient structure. Even some of the pictures come from different group (component ratio) of the gradient materials. But they are all fabricated using the same mechanism.