Elastic Interlayer Toughening of Potassium Titanate Whiskers–Nylon66 Composites and Their Fractal Research

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ABSTRACT: Potassium titanate whiskers–nylon66 composites were effectively toughened with an elastic interlayer of epoxy resin. The optimal fraction of epoxy resin was 1.5 wt % of whiskers, which corresponded to an interlayer thickness of 3% of the radius of whiskers. SEM images showed that interfacial adhesion was improved with elastic interlay. The impact strength of the composite increased 132% compared with neat nylon66, whereas the bending and tensile strengths increased 55 and 48%, respectively. Digital image method was adopted to carry out fractal research of fracture surfaces of the composites. Fractal dimensional calculations were based on perimeter–area relation. It was found that with the sizes of measured slit islands increasing, calculated fractal dimensions increased first and became stable after area threshold reached about 500 η^2 (η was a yardstick). The toughness of composites increased with fractal dimensions, which was explained from the point of fracture mechanism. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 368–374, 2001

Key words: fractal; potassium titanate whiskers; elastic interlayer; toughening; nylon

INTRODUCTION

Potassium titanate whiskers (PTW) are the only whiskers that have achieved breakthrough in commercial use. PTW is tiny with length sizable to diameters of most glass fibers, which brings about a micro-reinforcing effect in PTW composites. Recently, the applications of PTW as a reinforcer of engineering plastics, similar to nylons, have attracted extensive attention.[1,2] In most reports concerning PTW–nylon composites prepared through double-screw extruding, tensile and bending strengths of the composites increased, whereas impact strength did not, or even decreased.[3–5] In the middle of the 1970s, the concept of toughness of fiber-reinforced plastics being improved with an elastic interlayer between matrix and fibers was raised and has obtained much success since then.[6–9] Together with this, various theoretical explanations of the effects of elastic interlayer have appeared.[10–13]

Possible effects of elastic interlayer in different systems can be concluded as follows: accelerating multiple crazing and shear yielding of the matrix, reducing stress concentrations in the matrix caused by thermal contraction and mechanical loading, reducing interfacial shear stress and increasing critical transfer length of fibers, bumping interfacial impact and preventing fibers from breaking, enhancing adsorption of deformation energy, improving interfacial adhesion, increasing compatibility of fibers and matrix, and favor-

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ing more ordered crystalline structures of the matrix.

However, there have been no similar reports concerning PTW composites. In this article, elastic interlayer toughening is applied to PTW–nylon66 composites. The effects of elastic interlayer are explained through fractal research of fracture surfaces on the basis of perimeter–area relation. It is believed that the sizes of measured slit islands can influence calculated fractal dimensions considerably,[14] and there is no general direction on selecting slit islands. Therefore, the reasonable standard on selecting slit islands in PTW–nylon66 composites is investigated.

EXPERIMENTAL

Materials and Instruments

PTW, with an average length of 15.64 m and average diameter of 1.38 m (microscopic method), was supplied by Shengyang Jinjian Co. in China. The silane coupling agent, A-187, was supplied by Shuguang Chemicals in Nanjing, China. The elastic interlayer modifier was a merchant epoxy resin with laboratory modification. Nylon66, 1000-2, was supplied by Hoechst and Celanese. Optical microscopy, Cambridge Instruments Gallen III, was assembled by Jiangnan Optical Instrument Co., China. The digital camera used was a Panasonic WV CP410/G CCTV, manufactured by Matsushita Communication Industrial Co. Ltd. (Japan).

Whiskers Treatment

Silane coupling agent A-187 of 1 wt % of whiskers was dissolved in 10 × 90% ethanol aqueous solution, and the pH of the solution was adjusted to 4 with acetic acid. Modified epoxy resins of 0–3 wt % of PTW were then dissolved into the solution. After standing for 30 min, the solution was sprayed slowly into a high-speed mixer to blend with PTW for 10 min. Treated whiskers were dried at 120°C for 24 h.

Mechanical Properties

Treated PTWs were double-screw extruded with nylon66 at a ratio of 30 : 70 wt %. Obtained composites were pelleted and injection molded into standard test pieces after being dried at 60°C for 24 h. Notched impact, bending, and tensile strengths were tested according to Chinese National Standard GB1043-79, GB1042-79, and GB1040-79, respectively. Impact strengths were averaged among 10 specimens, whereas bending and tensile strengths were averaged among five.

Image Capture

Notched impact fracture surfaces were laid on the stage of optical microscope. To avoid image distortion brought by the shadows of projecting parts, an 8-cm-across ring illuminant was fixed 2 cm above the fracture surfaces. Digital images with amplification of 100 and size of 500 × 500 pixels were captured and stored in a personal computer. This optimal amplification was obtained experimentally, under which the fractal structures caused by interlayer could be fully observed while avoiding disturbance from pulled-out whiskers. Each composite took 15 individual images.

Image Pretreatment

Image software was used to transform fracture surface images [illustrated in Fig. 1(a)] into gray level ones with intensities ranging from 0 to 255 [Fig. 1(b)]. Gray level images were then converted into binary images containing equal areas of black and white [Fig. 1(c)], and white areas were regarded as slit islands. This avoided arbitrarily sectioning fracture surfaces in traditional slit island analysis.[15] Slit islands cut by image boundary were abandoned by blackening [Fig. 1(d)]. Pretreated individual images of the same composite were merged to measure subsequently.

Fractal Dimensional Calculation

A computer program was programmed to measure the perimeter L and area A of each slit island. The yardstick, which was pixel edge, was calibrated to be 5.814 μm. The plot of log L–log S was linearly fitted, and twice the slop was the fractal dimension of contour lines of slit islands D'. $D' - 1$, fractal dimensional increment, was equal to $D - 2$, where D was the fractal dimension of fracture surface.[15]

RESULTS AND DISCUSSION

Mechanical Properties

Table I shows the influences of elastic interlayer on mechanical properties. Although it is reported

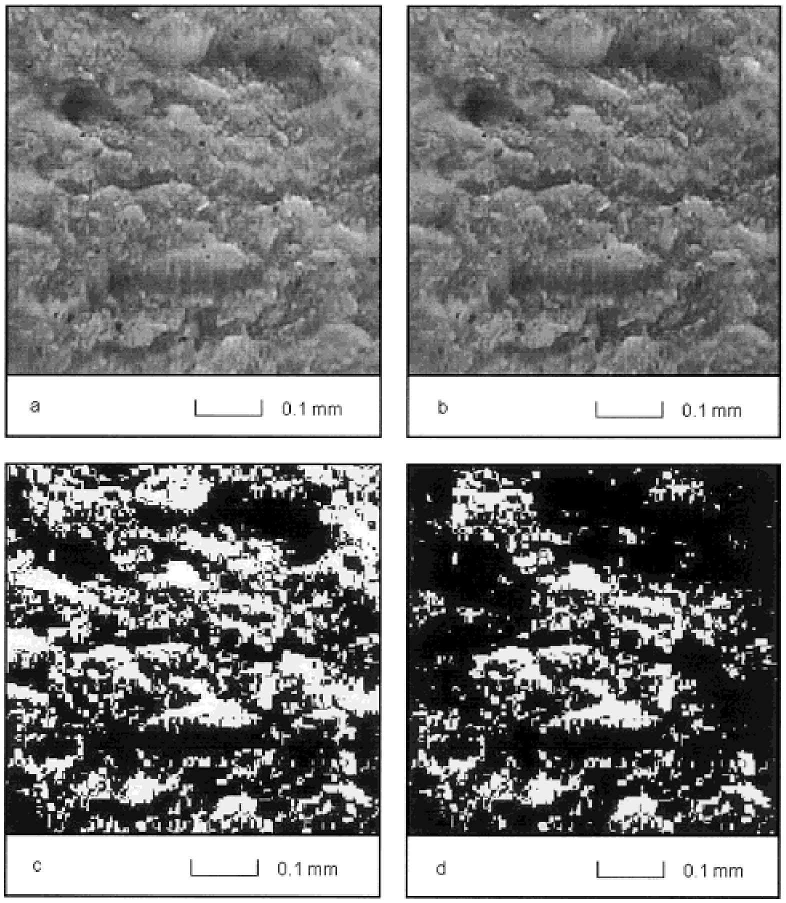

Figure 1 Illustration of fracture surface images at different pretreatment stages. (a) Original image of fracture surface; (b) gray level image; (c) binary image; (d) after neglecting slit islands with incomplete contour lines.

that elastic interlayer toughening can decrease tensile strength,[6,16] the notched impact, bending, and tensile strengths of PTW–nylon66 composites all increased as an elastic interlayer of epoxy resin was introduced. This might be attributed to the fact that epoxy resin not only serves as an impact bumper but also improves the interfacial adhesion. Such improvement is illustrated with SEM images in Figure 2.

Although the fraction of interlayer is 1.5 wt % of PTW, notched impact, bending, and tensile strengths of the composite increase 132, 55, and 48%, respectively, compared with neat nylon66. According to the density of interlayer material (ρ

Table I Effects of Interlayer on Mechanical Properties of 30 wt % PTW-Nylon66 Composites

		Epoxy Resin Content (wt %)			
	Neat Nylon	0	1.0	1.5	3.0
e		0.0069	0.0139	0.0208	0.0416
e/r (%)		0.996	2.007	3.004	6.007
Impact Strength (kJ/m^2)	4.56	6.92	9.59	10.59	9.53
Bending Strength (MPa)	106.14	132.84	162.45	164.67	158.00
Tensile Strength (MPa)	58.45	63.47	78.79	86.37	82.55

e, thickness of interlayer; r, radius of PTW.

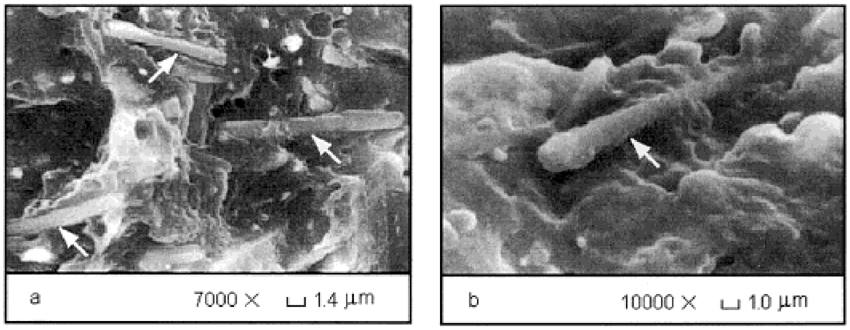

Figure 2 SEM images of impact fracture surfaces of PTWE–nylon66 composites with and without elastic interlayer. (a) PTW (arrows) treated with silane coupling agent A-187 only; (b) PTW (arrow) treated with silane coupling agent A-187 and 1.5 wt % of epoxy resin.

$= 1.091$ g cm^{-3}) and the specific area of PTW, mass fraction of interlayer is expressed as interlayer thickness e, and a ratio between e and PTW radius r. The optimal e/r is about 3%, which falls into the range of results in similar research of glass fiber composites.[7–9]

Influence of Slit Island Areas on Calculated Fractal Dimensions

Figure 3 is a typical log L–log S plot of PTW–nylon66 composites; good linearity of scattered points suggests the fractal character of the corresponding fracture surface. An area threshold is set, and only the log L–log S of slit islands larger than the threshold is fitted to calculate fractal dimension. Figure 4 shows the effects of area threshold on calculated fractal dimensions. As threshold increases, fractal dimensions increase first and become stable after the threshold reaches about 500 η^2.

Theoretically, all slit islands on a fractal surface possess the same characteristic self-similarity. Because each image-analytical instrument bears a limit of resolution, when a slit island appears on the image-analytical instrument, some small levels are lost. The smaller a slit island, the greater the proportion of its lost levels. Thus, islands small to some extent bear no self-similarity to large ones. It can be concluded that in this research, the upper limit of self-similar region of slit islands covering about 500 η^2 is η, and the fractal dimensions of smaller islands cannot be measured accurately.

Table II shows the statistics of slit island areas on one merged image. It is clear that most slit islands are smaller than 500 η^2. Because of the disappearance of characteristic self-similarities of small slit islands, if all slit islands are measured,

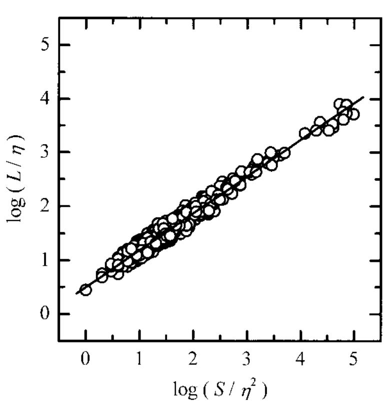

Figure 3 Typical perimeter–area slit islands on fracture surfaces of PTW–nylon66 composites.

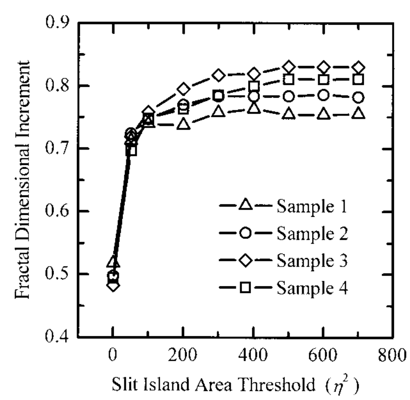

Figure 4 Influence of slit island area threshold on calculated fractal dimensional increments of fracture surfaces of PTW–nylon66 composites. In samples 1–4, PTW was treated with 0, 1.0, 1.5, and 3.0 wt % of epoxy resin, respectively.

Table II Statistics of Slit Island Areas on Fracture Surfaces of PTW-Nylon66 Composites

Area (η^2)	Number	Percentage (%)
⩾10	796	17.58
⩾50	218	4.82
⩾100	121	2.67
⩾300	50	1.10
⩾500	38	0.84
⩾700	32	0.71
⩾1000	28	0.62
Total	4527	100

the calculated fractal dimension will be lowered remarkably. Besides, there will be little difference among fractal dimensions of different fracture surfaces, as can be seen from Figure 4.

There are few discussions about how to select slit islands in slit island research. Kaye[16] suggested that the yardstick should be < 0.3 times the projected length of slit island perimeter. Gómez-Rodríguez et al.[17] set a restriction by only considering slit islands $> 30\ \eta,^2$ the standard of which was adopted by Williams and Beebe[18] to obtain results with less precision.

Slit islands on different surfaces have different complexities and up-limits of self-similar region, which determines the reasonable area threshold. In other words, the selection of slit islands should depend on the fractal dimension of the fracture surface. In Figure 4, the standards given by Kaye and Gómez-Rodríguez et al. are obviously impractical.

Increasing area threshold will sharply decrease the number of suited slit islands. The merged images of 15 individual islands in the present work contain only 30–50 islands larger than 500 η^2. If the measurements are carried out on individual images, as in many reported slit island researches, statistical errors will be introduced because of the insufficiency of suited islands.

Fractal Dimension and Toughness

It was found in many investigations that as the fractal dimension of fracture surface increases, impact strength goes up as to ductile material and down as to brittle material. This can be used as a criterion of fracture mechanism of materials. Figure 5 is such a relation of elastic interlayer-toughened PTW–nylon66 composites; the fractal dimensions are calculated with an island area threshold of 500 η^2, and the only difference among these composites is the thickness of the elastic interlayer. The positive linearity indicates that the composites are ductile. The influence of interlayer fraction on fractal dimensions of fracture surfaces can also be seen in Figure 4.

During the fracture of composites, microcracks have greater propagating velocities in the matrix than in the elastic interlayer. When entering into the elastic interlayer, microcracks will be deflected with sudden changes of propagating velocities. Such deflections cannot only absorb fracture energy but also buffer interfacial impact stresses and prevent whiskers from breaking, so that the toughness of the composites is improved. Because whiskers are densely dispersed in matrix, deflections of microcracks in the interlayer will determine the fractal structures on fracture surfaces. The scales of such fractal structures, in which the fractal measurements should be carried out, are related to the size of whiskers. The yardstick in this research is determined on the basis of the above consideration. Elastic interlayer can terminate microcracks as well. If the interlayer is too thick, microcracks tend to be terminated before being fully deflected. Therefore, both energy adsorption and fractal dimension are decreased.

Figure 6 shows the optical microscopic images of the fracture surface of neat nylon66 and PTW–nylon66 composites. The fracture surface of neat nylon is typically brittle with large and flat blocks on it, which suggests that cracks can propagate a long way in initial directions. Although the composite bears no elastic interlayer, large blocks can still be discerned on the fracture surface. The elastic interlayers cause deflections of microcracks and add to tortuosity and complexity of the fracture surfaces, which result in greater fractal dimensions.

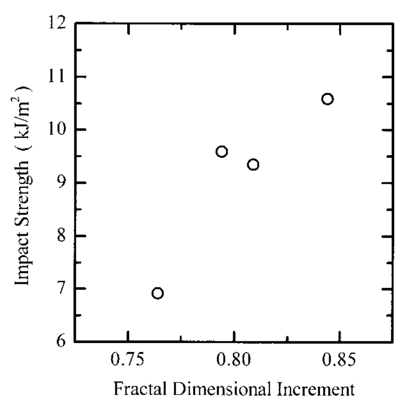

Figure 5 Relation between fractal dimensional increment of fracture surfaces and impact strength of PTW–nylon66 composites.

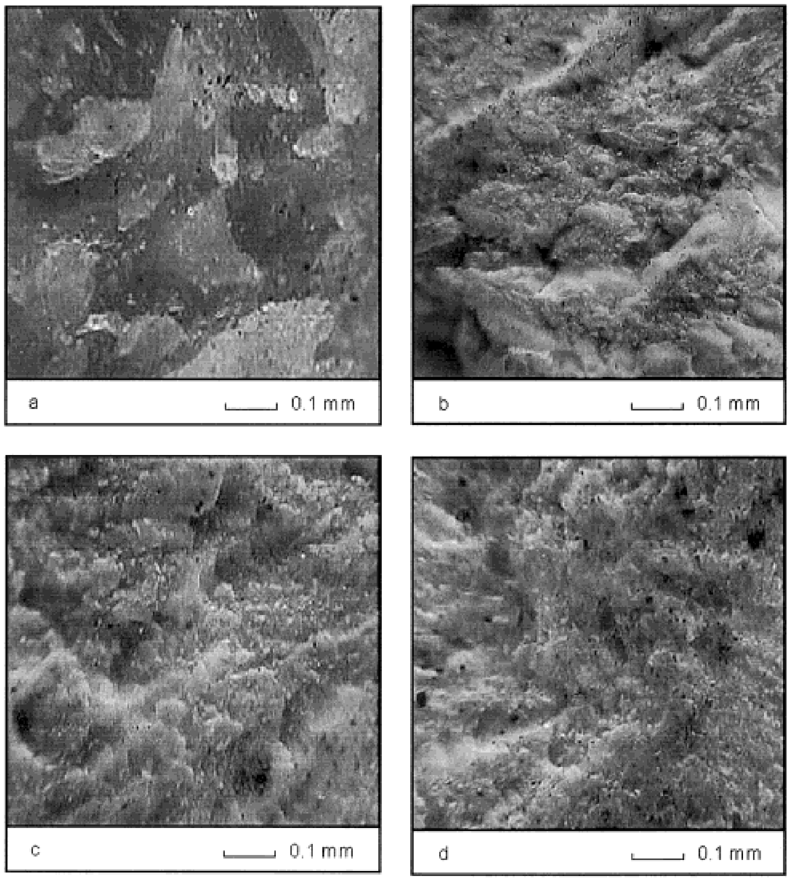

Figure 6 Microscopic images of impact fracture surfaces of neat nylon66 and 30 wt % of different amounts of epoxy resin-treated PTW–nylon66 composites. (a) Neat nylon66; (b–d) fractions of epoxy resin of 0, 1.0, and 1.5 wt % of whiskers, respectively.

CONCLUSION

PTW–nylon66 composites can be effectively toughened with an elastic interlayer of epoxy resin. Up to 132, 55, and 48% of increases of impact, bending, and tensile strengths, respectively, are observed when the fraction of interlayer material is 1.5 wt % of PTW, which corresponds to an interlayer thickness of 0.02 m, or 3% of the radius of PTW. To correctly calculate fractal dimensions of fracture surfaces using the slit island method, the measured slit islands must be carefully selected. As to PTW–nylon66 composites, stable fractal dimensions can be obtained when measured slit islands are larger than about 500 η^2. If area threshold is too small, calculated fractal dimensions will be greatly lowered, and fractal dimensions of different fracture surfaces will differ little to each other. Elastic interlayer can aggravate deflections of microcracks, which bring about more rugged fracture surfaces with higher fractal dimensions and cause more energy dissipation. The impact strength of elastic interlayer-toughened PTW–nylon66 composites increases with fractal dimensions of fracture surfaces, which suggest a ductile fracture mechanism.

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REFERENCES

1. Ou, Y. C.; Yang, F.; Chen, J. J Appl Polym Sci 1997, 64, 2317.
2. Feng, X.; Lü, J. Z.; Lu, X. H.; Bao, N. Z.; Cheng, D. L. Fu He Cai Liao Xue Bao (Chinese) 1999, 4, 1.
3. Wei, X. L.; Zhao, K. F.; Lü, J. T.; Xie, H. C.; Zhu, Q. A. in Proceeding of Chinese 1994 Autumn Material Symposia; Vol. 125, Beijing, 1994.

4. Lü, J. T.; Wei, X. L.; Zhao, K. F.; Li, Y.; Ni, K.; Gu, C. M.; Suo, L. X. Gong Cheng Su Liao Ying Yong (Chinese) 1995, 6, 5.
5. Tjong, S. C.; Meng, Y. Z. Polymer 1998, 39, 5461.
6. Plueddeman, E. P. in Proceeding of Reinforced Plastics Division; Society of the Plastics Industry Inc.: New York, February 1974.
7. Peiffer, D. G.; Nielsen, L. E. J Appl Polym Sci 1979, 23, 2253.
8. Gerard, J. F. Polym Eng Sci 1988, 28, 568.
9. Podgaiz, R. H.; Williams, R. J. J. Comp Sci Tech 1997, 57, 1071.
10. Broutman, L. J. Polym Eng Sci 1974, 14, 581.
11. Arridge, R. G. C. Polym Eng Sci 1975, 15, 757.
12. Carman, G. P.; Averill, R. C. J Comp Mater 1993, 27, 589.
13. Fu, S. Y.; Lauke, B. J Mater Sci 1997, 32, 1985.
14. Lung, C. W.; Mu, Z. Q. Phys Rev 1988, 38, 11781.
15. Mandelbrot, B. B.; Passoja, D. E.; Paulay, A. J. Nature 1984, 308, 721.
16. Kaye, B. H. In The Fractal Approach to Heterogenous Chemistry; Avnir, D., Ed., Wiley: New York, 1989.
17. Gómez-Rodríguez, J. M.; Baró, A. M.; Vázquez, L.; Salvarezza, R. C.; Vara, J. M.; Arvia, A. J. J Phys Chem 1992, 96, 347.
18. Williams, J. M.; Beebe, T. P., Jr. J Phys Chem 1993, 97, 6255.