

## TABLE OF CONTENTS

	Page
<b>ABSTRACT (CHINESE) .....</b>	<b>i</b>
<b>ABSTRACT .....</b>	<b>ii</b>
<b>ACKNOWLEDGEMENT .....</b>	<b>iii</b>
<b>TABLE OF CONTENTS .....</b>	<b>iv</b>
<b>LIST OF TABLES .....</b>	<b>vii</b>
<b>LIST OF FIGURES.....</b>	<b>viii</b>
<b>CHAPTER 1. INTRODUCTION .....</b>	<b>1</b>
1.1 <b>Background.....</b>	<b>1</b>
1.2 <b>Aim and Objectives.....</b>	<b>3</b>
1.3 <b>Brief Structure of the Research .....</b>	<b>4</b>
 <b>CHAPTER 2. LITERATURE REVIEW .....</b>	<b>7</b>
2.1 <b>Synthesis and Applications of Organic/Inorganic .....</b>	<b>7</b>
Nanocomposites	
2.2 <b>General Background of Sol-Gel Chemistry.....</b>	<b>10</b>
2.3 <b>Synthesis and Properties of Metal-containing Polyimides.....</b>	<b>15</b>
2.4 <b>Motivation .....</b>	<b>16</b>
2.5 <b>References.....</b>	<b>17</b>
 <b>CHAPTER 3. FUNDAMENTAL THEORY .....</b>	<b>20</b>
3.1 <b>Five Regions of Viscoelastic Behavior .....</b>	<b>20</b>
3.1.1 <b>The Glassy Region .....</b>	<b>20</b>
3.1.2 <b>The Glass Transition Region .....</b>	<b>21</b>
3.1.3 <b>The Rubbery Plateau Region .....</b>	<b>22</b>
3.1.4 <b>The Rubery Flow Region.....</b>	<b>23</b>
3.1.5 <b>The Liquid Flow Region .....</b>	<b>23</b>
3.2 <b>Definitions of the Terms “Transition”, “Relaxation”,.....</b>	<b>24</b>
“Dispersion”	
3.3 <b>Dynamic Mechanical Behavior through the Five Regions .....</b>	<b>24</b>
3.4 <b>Two-Phase Systems .....</b>	<b>27</b>
3.5 <b>Adhesion Theories .....</b>	<b>28</b>

<b>3.5.1</b>	<b>Mechanical Interlocking .....</b>	<b>28</b>
<b>3.5.2</b>	<b>Theories Based on Surface Energetic, Wetting and Adsorption .....</b>	<b>29</b>
<b>3.5.3</b>	<b>Diffusion Theory.....</b>	<b>29</b>
<b>3.5.4</b>	<b>Acid-Base Theory .....</b>	<b>29</b>
<b>3.5.5</b>	<b>Chemical Bonding .....</b>	<b>30</b>
<b>3.5.6</b>	<b>Weak Boundary Layer Mechanism .....</b>	<b>31</b>
<b>3.6</b>	<b>Adhesion Measurement .....</b>	<b>32</b>
<b>3.7</b>	<b>References .....</b>	<b>36</b>

## **CHAPTER 4. EXPERIMENT METHODOLOGY .....** **37**

<b>4.1</b>	<b>Materials .....</b>	<b>37</b>
<b>4.1.1</b>	<b>Diamines.....</b>	<b>37</b>
<b>4.1.2</b>	<b>Dianhydrides .....</b>	<b>37</b>
<b>4.1.3</b>	<b>Solvents .....</b>	<b>37</b>
<b>4.1.4</b>	<b>Additives .....</b>	<b>37</b>
<b>4.2</b>	<b>Synthesis Procedures.....</b>	<b>38</b>
<b>4.3</b>	<b>Metallization Process .....</b>	<b>40</b>
<b>4.4</b>	<b>Measurements .....</b>	<b>41</b>
<b>4.4.1</b>	<b>FT-IR and UV Analyses .....</b>	<b>41</b>
<b>4.4.2</b>	<b>X-ray Analysis .....</b>	<b>41</b>
<b>4.4.3</b>	<b>X-ray Photoelectron Spectroscopy (XPS) Analysis .....</b>	<b>42</b>
<b>4.4.4</b>	<b>Transmission Electron Microscope (TEM) Analysis .....</b>	<b>42</b>
<b>4.4.5</b>	<b>Atomic Force Microscope (AFM) Analysis.....</b>	<b>42</b>
<b>4.4.6</b>	<b>Scanning Electron Microscope (SEM) Analysis.....</b>	<b>42</b>
<b>4.4.7</b>	<b>Mechanical Properties Analysis.....</b>	<b>42</b>
<b>4.4.8</b>	<b>Thermal Expansion Analysis .....</b>	<b>43</b>
<b>4.4.9</b>	<b>Thermal Stability Analysis .....</b>	<b>43</b>
<b>4.4.10</b>	<b>Electrical Properties Analyses.....</b>	<b>43</b>
<b>4.4.11</b>	<b>Surface Energy Analysis.....</b>	<b>43</b>
<b>4.4.12</b>	<b>Measurements of Peel Strength .....</b>	<b>43</b>

## **CHAPTER 5. SYNTHESIS AND CHARACTERISTICS STUDY OF PI/TiO<sub>2</sub> NANO HYBRID FILMS .....** **45**

<b>5.1</b>	<b>Titanium Precursor .....</b>	<b>45</b>
<b>5.2</b>	<b>FT-IR Analysis .....</b>	<b>46</b>
<b>5.3</b>	<b>UV-vis Transmittance Analysis .....</b>	<b>47</b>
<b>5.4</b>	<b>XRD Analysis .....</b>	<b>49</b>
<b>5.5</b>	<b>XPS Analysis .....</b>	<b>50</b>

<b>5.6</b>	<b>TEM Analysis .....</b>	<b>53</b>
<b>5.7</b>	<b>Thermal Decomposition Analysis .....</b>	<b>55</b>
<b>5.8</b>	<b>Conclusion.....</b>	<b>56</b>
<b>5.9</b>	<b>References .....</b>	<b>57</b>
<b>CHAPTER 6. PHYSICAL AND MECHANICAL PROPERTIES OF PI/TiO<sub>2</sub> NANO HYBRID FILMS.....</b> <b>59</b>		
<b>6.1</b>	<b>PI/TiO<sub>2</sub> Hybrid Films Appearance .....</b>	<b>59</b>
<b>6.2</b>	<b>Coefficients of Thermal Expansion (CTE) Analysis .....</b>	<b>61</b>
<b>6.3</b>	<b>Dynamic Mechanical Analysis (DMA) .....</b>	<b>63</b>
<b>6.4</b>	<b>The Mechanical Properties of PI/TiO<sub>2</sub> Hybrid Films .....</b>	<b>69</b>
<b>6.5</b>	<b>The Thermal Stability of PI/TiO<sub>2</sub> Hybrid Films .....</b>	<b>69</b>
<b>6.6</b>	<b>The Electrical Properties PI/TiO<sub>2</sub> Hybrid Films.....</b>	<b>72</b>
<b>6.7</b>	<b>Conclusion.....</b>	<b>74</b>
<b>6.8</b>	<b>References .....</b>	<b>75</b>
<b>CHAPTER 7. INTERFACIAL ADHESION BETWEEN THE PI/TiO<sub>2</sub> NANO HYBRID FILMS AND COPPER SYSTEM.....</b> <b>77</b>		
<b>7.1</b>	<b>AFM Analysis .....</b>	<b>77</b>
<b>7.2</b>	<b>Surface Energy Analysis .....</b>	<b>79</b>
<b>7.3</b>	<b>Peel Strength Analysis .....</b>	<b>80</b>
<b>7.4</b>	<b>XPS and SEM Analysis .....</b>	<b>82</b>
<b>7.5</b>	<b>EDS Analysis.....</b>	<b>88</b>
<b>7.6</b>	<b>Conclusion.....</b>	<b>92</b>
<b>7.7</b>	<b>References .....</b>	<b>92</b>
<b>CHAPTER 8. CONCLUSION AND RECOMMENDATIONS .....</b> <b>95</b>		
<b>8.1</b>	<b>Conclusion.....</b>	<b>95</b>
<b>8.2</b>	<b>Recommendations for Future Research .....</b>	<b>98</b>
<b>LIST OF PUBLICATIONS .....</b> <b>99</b>		
<b>RESUME .....</b> <b>100</b>		

## LIST OF TABLES

	<b>Page</b>
<b>2.1</b> Electronegativity ( $\chi$ ), coordination number ( $N$ ), and degree of unsaturation ( $N-Z$ ) for some metals .....	<b>13</b>
<b>2.2</b> The types of metal additives in polyimide system .....	<b>16</b>
<b>5.1</b> The surface content of Ti atoms for PI/TiO <sub>2</sub> hybrid films measured by XPS... .....	<b>53</b>
<b>6.1</b> Chemical structures of PI and PI/TiO <sub>2</sub> hybrid films appearance .....	<b>60</b>
<b>6.2</b> Coefficients of thermal expansion (CTE) of PI/TiO <sub>2</sub> hybrid films .....	<b>61</b>
<b>6.3</b> The glass transition temperatures ( $T_g$ ) of PI/TiO <sub>2</sub> hybrid films .....	<b>68</b>
<b>6.4</b> The mechanical properties of PI/TiO <sub>2</sub> hybrid films .....	<b>70</b>
<b>6.5</b> The thermal decomposition temperatures ( $T_d$ ) of PI/TiO <sub>2</sub> hybrid films .....	<b>70</b>
<b>6.6</b> The dielectric constants ( $D_k$ ) and dielectric dissipation factors ( $D_f$ ) of PI/TiO <sub>2</sub> hybrid films .....	<b>73</b>
<b>6.7</b> The surface and volume resistivities of PI/TiO <sub>2</sub> hybrid films .....	<b>74</b>
<b>7.1</b> Surface roughness ( $R_a$ ) of PI/TiO <sub>2</sub> hybrid films after plasma treatment.....	<b>78</b>
<b>7.2</b> Surface energies of various PI/TiO <sub>2</sub> hybrid films with different plasma treatments .....	<b>79</b>
<b>7.3</b> The component percentages and atomic ratios of PI/TiO <sub>2</sub> - 9wt% hybrid films after various plasma treatments.....	<b>83</b>

## LIST OF FIGURES

	<b>Page</b>
1.1 Applications of polyimides .....	3
2.1 The sol-gel reaction of a metal alkoxide .....	11
3.1 Five regions of viscoelastic behavior for a linear, amorphous polymer. Also illustrated are effects of crystallinity (dashed line) and cross-linking (dotted line).....	21
3.2 Effect of molecular weight on length of plateau .....	22
3.3 Simplified definition of $E'$ and $E''$ . When a viscoelastic ball is dropped onto a perfectly elastic floor, it bounces back to a height $E'$ , a measure of the energy stored elastically during the collision between the ball and the floor. The quantity $E''$ represents the energy lost as heat during the collision .....	25
3.4 Schematic of dynamic mechanical behavior .....	27
3.5 Dynamic mechanical behavior of polystyrene-block-polybutadiene-block-polystyrene, a function of the styrene-butadiene mole ratio.....	28
3.6 (a) Schematic diagram of the proposed structure of anodic oxide film on aluminum. (b) Interface failure surface of polyethylene on anodized aluminum.....	29
3.7 (a) Modified 90 degree peel test (b) standard 90 degree peel experiment ....	34
3.8 Scanning electron micrographs of the peeled surface of (a) PAA PI on $\text{SiO}_2$ 580 J/m <sup>2</sup> (b) PAE PI on $\text{SiO}_2$ 800 J/m <sup>2</sup> (c) PAA on $\text{Al}_2\text{O}_3$ 620 J/m <sup>2</sup> (d) PAE PI on $\text{Al}_2\text{O}_3$ 750 J/m <sup>2</sup> (e) PAA PI on $\text{MgO}$ 170 J/m <sup>2</sup> and (f) PAE PI on $\text{MgO}$ 530 J/m <sup>2</sup> .....	35
4.1 Flow chart of the procedures to prepare the PI/TiO <sub>2</sub> hybrid films .....	39
4.2 The metallization processes of PI/TiO <sub>2</sub> hybrid films .....	41
4.3 Schematic diagram of peel test.....	44
5.1 Poly(amic acid) (PAA) from BAO/ODPA .....	45

<b>5.2</b>	The reaction between acetylacetone and titanium alkoxide.....	<b>46</b>
<b>5.3</b>	FT-IR absorption spectra of the PI/TiO <sub>2</sub> hybrid films.....	<b>47</b>
<b>5.4</b>	UV-visible spectra of the PI/TiO <sub>2</sub> hybrid films.....	<b>48</b>
<b>5.5</b>	XRD patterns of pure PI, PI/TiO <sub>2</sub> hybrid films and standard of TiO <sub>2</sub> (anatae).	
	.....	<b>49</b>
<b>5.6</b>	XPS survey spectrum of the PI/TiO <sub>2</sub> -40 wt% hybrid film .....	<b>50</b>
<b>5.7</b>	The composition-depth profiles for the titanium component in the PI/TiO <sub>2</sub> -30 wt% hybrid film .....	<b>51</b>
<b>5.8</b>	XPS spectra of Ti 2p in hybrid films.....	<b>52</b>
<b>5.9</b>	TEM photographs of the PI/TiO <sub>2</sub> -5 wt% hybrid film in different magnification.....	<b>54</b>
<b>5.10</b>	TEM photographs of the PI/TiO <sub>2</sub> -30 wt% hybrid film in different magnification.....	<b>54</b>
<b>5.11</b>	Selected-area electron diffraction (SAED) patterns (a) PI/TiO <sub>2</sub> -5 wt% (b) PI/TiO <sub>2</sub> -30 wt% .....	<b>55</b>
<b>5.12</b>	Thermogravimetric profiles of the PI/TiO <sub>2</sub> hybrid films .....	<b>56</b>
<b>6.1</b>	TEM photrapgy of BTDA/ODA-TiO <sub>2</sub> 9wt% hybrid film.....	<b>60</b>
<b>6.2</b>	Thermal expansion of PMDA/ODA-TiO <sub>2</sub> hybrid films.....	<b>62</b>
<b>6.3</b>	Thermal expansion of BPDA/ODA-TiO <sub>2</sub> hybrid films.....	<b>62</b>
<b>6.4</b>	Thermal expansion of BTDA/ODA-TiO <sub>2</sub> hybrid films .....	<b>63</b>
<b>6.5</b>	(a) the storage modulus, (b) the loss modulus and (c) the tan δ curves of PMDA/ODA-TiO <sub>2</sub> hybrid films at different temperatures.....	<b>64</b>
<b>6.6</b>	(a) the storage modulus, (b) the loss modulus and (c) the tan δ curves of BPDA/ODA-TiO <sub>2</sub> hybrid films at different temperatures .....	<b>65</b>
<b>6.7</b>	(a) the storage modulus, (b) the loss modulus and (c) the tan δ curves of BTDA/ODA-TiO <sub>2</sub> hybrid films at different temperatures .....	<b>66</b>
<b>6.8</b>	The thermogravimetric profiles of the PMDA/ODA-TiO <sub>2</sub> hybrid films .....	<b>71</b>

<b>6.9</b>	The thermogravimetric profiles of the BPDA/ODA-TiO <sub>2</sub> hybrid films .....	<b>71</b>
<b>6.10</b>	The thermogravimetric profiles of the BTDA/ODA-TiO <sub>2</sub> hybrid films .....	<b>72</b>
<b>6.11</b>	Variation of dielectric constants of the PI/TiO <sub>2</sub> hybrid films as a function of TiO <sub>2</sub> content .....	<b>73</b>
<b>7.1</b>	AFM images of PI/TiO <sub>2</sub> -1wt% hybrid film after various plasma treatments (a) no plasma (b) Ar plasma (c) Ar/N <sub>2</sub> plasma (d) Ar/O <sub>2</sub> plasma.....	<b>78</b>
<b>7.2</b>	The surface roughness and surface energy of PI/TiO <sub>2</sub> -1wt% hybrid film after various plasma treatments .....	<b>80</b>
<b>7.3</b>	The peel strengths between the PI/TiO <sub>2</sub> hybrid films and Cu .....	<b>81</b>
<b>7.4</b>	XPS spectra of PI/TiO <sub>2</sub> -9 wt% hybrid films surface treated with various plasma treatments after peel test .....	<b>83</b>
<b>7.5</b>	XPS spectra of both polymer side and Cu side with Ar/N <sub>2</sub> plasma treatment (a) pure PI (b) PI/TiO <sub>2</sub> -1 wt% (c) PI/TiO <sub>2</sub> -3 wt% (d) PI/TiO <sub>2</sub> -9 wt% .....	<b>85</b>
<b>7.6</b>	SEM images of peeled-off surface of hybrid film with Ar/N <sub>2</sub> plasma treatment (a) pure PI (b) PI/TiO <sub>2</sub> -1 wt% (c) PI/TiO <sub>2</sub> -3 wt% (d) PI/TiO <sub>2</sub> -9 wt% .....	<b>86</b>
<b>7.7</b>	XPS spectra of both polymer side and Cu side with Ar/O <sub>2</sub> plasma treatment (a) pure PI (b) PI/TiO <sub>2</sub> -1 wt% (c) PI/TiO <sub>2</sub> -3 wt% (d) PI/TiO <sub>2</sub> -9 wt% .....	<b>89</b>
<b>7.8</b>	SEM images of peeled-off surface of hybrid film with Ar/O <sub>2</sub> plasma treatment (a) pure PI (b) PI/TiO <sub>2</sub> -1 wt% (c) PI/TiO <sub>2</sub> -3 wt% (d) PI/TiO <sub>2</sub> -9 wt% .....	<b>90</b>
<b>7.9</b>	PI/TiO <sub>2</sub> -3 wt% hybrid film with Ar/N <sub>2</sub> plasma treatment (a) SEM image (b) SEM image (c) EDAX mapping .....	<b>91</b>
<b>7.10</b>	PI/TiO <sub>2</sub> -1 wt% hybrid film with Ar/O <sub>2</sub> plasma treatment (a) SEM image (b) SEM image (c) EDAX mapping .....	<b>92</b>