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Notes

Calculation of Hydrogen-Bonding Strength in Polymer Blends by Density Functional Method

Sukmin Lee,[†] Jung Goo Lee,[†] Hosull Lee,[†] and Soonja Choe*,[‡]

Kumho Chemical Laboratory, Hwa-am dong 57-1, Yuseong ku, Taejon, 305-348 Korea, and Department of Chemical Engineering, Research Institute of Polymer Science and Engineering, Inha University, Yong-hyun dong 253, Namku, Inchon 402-751, Korea

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Introduction

Aromatic polybenzimidazole (PBI),[1] which has high thermal stability, inflammability, and outstanding mechanical performance, has been used in the aerospace applications. Polyimides,[2] which also have superior thermal stability, thermooxidative stability, high mechanical properties, and chemical resistance, have been used as new materials in electronics, high-temperature adhesives, and aerospace industries.

During the last several years, studies of the blends containing PBI and PI have been carried out to investigate the structurally dependent miscibility, phase behavior, and specific interaction for miscibility.[3−11] It was reported that the N−H and C═O groups in the blends of PBI and PI having nearly nonpolar spacers are the most important factors responsible for miscibility.

Recently, Ahn et al., investigated the hydrogen-bonding strength between PBI and various polyimides derived from BTDA (3,3′,4,4′-benzophenone tetracarboxylic dianhydride) and DSDA (diphenylsulfone tetracarboxylic dianhydride) with $DDSO_2$ (4,4′-diamine diphenylsulfone), MDA (4,4′-methylene dianiline), and ODA (4,4′-oxydianiline) (Figure 1) by means of DSC, DMTA, and FTIR.[11] They claimed that the PBI/PI blend based on BTDA shows stronger hydrogen bonding than the DSDA-based system, and this may be due to the difference in electron affinity existing in two dianhydrides.

In this work, we attempted to calculate the hydrogen-bonding strength[12] using model compounds of PBI and PIs by a quantum mechanical calculation based on the density functional theory. We simplified the model compounds as much as possible to avoid unfavorable local energy minima and enormous times for calculation.

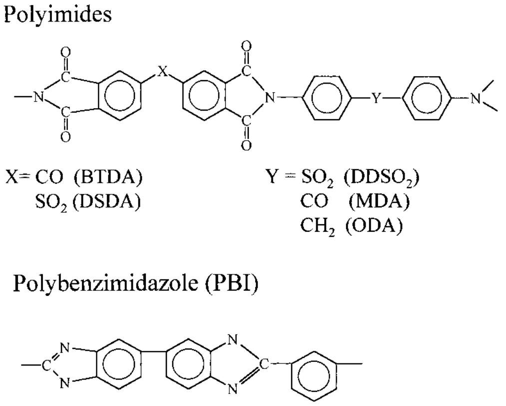

Figure 1. Chemical structures used in this study.

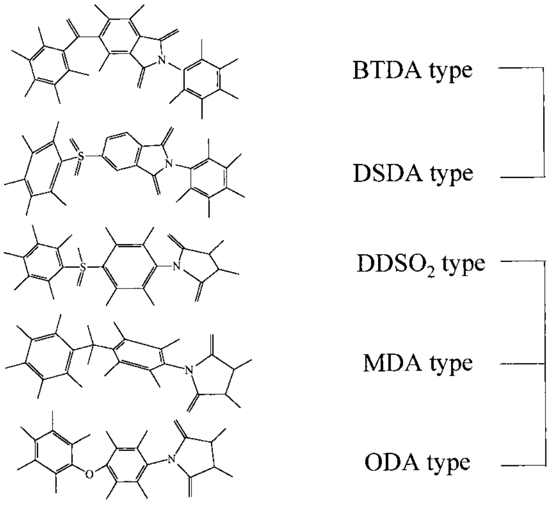

Figure 2. Model segments of polymers for calculation.

Theoretical Background

Density functional theory (DFT)[13,14] states that all ground-state properties are functions of the charge density ρ, which is given by the equation: $\rho(\mathbf{r}) = \sum|\Psi_i(\mathbf{r})|^2$ where the sum goes over all occupied molecularorbitals (MOs) Ψ_i, then the total energy E_t may be written as

$$E_t(\rho) = T(\rho) + U(\rho) + E_{xc}(\rho)$$

where $T(\rho)$ is the kinetic energy of a system of noninteracting particles of density ρ, $U(\rho)$ is the classical electrostatic energy due to Coulombic interactions, and $E_{xc}(\rho)$ is all many-body contributions to total energies, in particular the exchange and correlation energy.

The total energy can be described by

$$E_t(\rho) = \sum\langle\Psi_i|-\nabla^2/2|\Psi_i\rangle + \langle\rho(\mathbf{r}_i)[\epsilon_{xc}(\rho(\mathbf{r}_i)) + V_e(\mathbf{r}_i)/2 - V_N]\rangle + V_{NN}$$

where ρV_N is the electron−nucleus attraction, $\rho V_e/2$ is the electron−electron repulsion, V_{NN} is the nucleus−nucleus repulsion, and $\epsilon_{xc}(\rho)$ is the exchange-correlation

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* To whom correspondence should be addressed.
[†] Kumho Chemical Laboratory.
[‡] Inha University.

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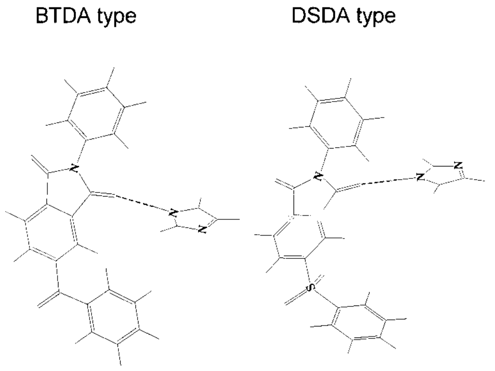

Figure 3. Optimized geometry of the coupled model compounds.

Table 1. Calculated Hydrogen-Bonding Energy and the Distance in PBI/Polyimide Blends Using Model Compounds of Different Dianhydrides and Diamines

hydrogen-bonding parameter	model compound type				
	BTDA	DSDA	$DDSO_2$	MDA	ODA
energy (kcal/mol)	4.8	4.4	4.9	5.1	5.0
distance (Å)	1.98	1.96	1.92	1.95	1.99

energy per particle energy. $T(\rho)$ is represented by $\sum\langle\Psi_i|-\nabla^2/2|\Psi_i\rangle$, $U(\rho)$ is represented by $\rho(\mathbf{r}_i)[V_e(\mathbf{r}_i)/2 - V_N] + V_{NN}$, and $E_{xc}(\rho)$ is presented by $\rho(\mathbf{r}_i)\epsilon_{xc}(\rho(\mathbf{r}_i))$. To determine the actual energy, variations in E_t must be optimized with respect to variations in ρ. The differential equation can be solved to obtain Ψ_i and ρ through the numerical analysis.

Calculation

The model compounds were constructed using polymer builder software from MSI (Molecular Simulations Inc.), and the model segments of polymers for calculation are drawn in Figure 2. The conformational search was performed to obtain thermally coarsely stable conformations followed by the energy minimization through the conjugate gradient method. To calculate optimum geometry of model compound pairs, their energies, and vibrational frequencies, the density functional method was used with the commercial package DMol by MSI on a Cray-C94A and R10000 Silicon Graphics workstation. The options of BLYP (Becke−Lee−Yang−Parr functional), DNP (double-numerical basis functions with polarization functions), no frozen core, and restricted spin for closed-shell fragments were used. Because of the quality of the exact DFT spherical atomic orbitals, the effect of the basis set superposition[15] is minimized, and a good description of even a weak bond is possible. The energy of hydrogen bonding was obtained by calculating the differences between the energies of the coupled pairs and those of the model compounds optimized separately. To consider basis set effects and correlation effects, we have carried out binding energy calculations of HF···HF and OC···HF with the previously described BLYP/DNP method, and compared with the results calculated by each of HF (Hartree−Fock), BLYP, and MP2 (Moller−Plesset) with TZ2P (triple-ζ plus polarization function) basis set. As a result, for HF···HF, we obtained 5.7, 4.1, 5.3, and 5.0 kcal/mol with BLYP/DNP, HF/TZ2P, BLYP/TZ2P, and MP2/TZ2P, respectively, while the experimental value is 4.8 ± 0.2 kcal/mol.[16] In addition, for OC···HF, those values were 4.7, 2.3, 4.2, and 4.1 kcal/mol with each of the above-mentioned methods, respectively. However, there is no experimental binding energy value for this. Overall, the BLYP/DNP method is expected to give a relatively accurate yet fast calculation for the model compounds.[16] The vibrational frequencies originating from the C═O symmetric and antisymmetric stretching of five-membered anhydrides in polyimides and the N−H stretching in PBI were calculated. The optimized geometry of a coupled model compound for PBI/PI (BTDA and DSDA types with PBI) is depicted in Figure 3.

Results and Discussion

According to the previous results of experiments, the PBI blends with polyimides derived from BTDA showed more enhanced miscibility than those derived from DSDA via thermal and FTIR spectroscopic analysis. On the other hand, diamines such as $DDSO_2$, MDA, and ODA influenced no significant differences in miscibility. Thus, we employed two series of model compounds for polyimide representing each dianhydride and diamine. Since the polymers used in this study are semirigid, we simplified the model compounds to avoid the unfavorable local minima and to obtain the most stable conformation, which is expected to be the most probable conformation.

As seen in Figure 3, the hydrogen-bonding energy and the bonding distance using the geometry optimized coupled pairs for different dianhydrides are calculated; those values for the BTDA type are 4.8 kcal/mol and 1.98 Å, respectively, whereas for DSDA they are 4.4 kcal/mol and 1.96 Å. The difference in the calculated hydrogen-bonding energy between BTDA and DSDA is 8−10%. The pairs containing model compounds derived from BTDA showed a stronger bonding energy than the model compounds of DSDA. Although a quantitative comparison is not possible at this time since the experimental data are not the absolute ones, the calculated values are relevant to the experimental observation,

For comparisons of hydrogen-bonding strength based on the different diamines, calculations of the bonding energy and the bonding distance are also employed and are listed in Table 1. The significant difference in hydrogen-bonding strength is not observed in diamines; they are within 2−4% and this is relatively smaller than that observed in dianhydrides. Direct quantitative comparison between the calculation and the experiment in binding energy is not practical due to no experimental values being available.

The vibrational frequency shifts in the C═O symmetric and antisymmetric stretching bands and the N−H stretching band for each dianhydride and diamine are also calculated. The frequency shifts by calculation for the C═O symmetric, the C═O antisymmetric, and the N−H stretching bands between BTDA and PBI are 3.8, 8.9, and 34 cm^{-1}, respectively. Those for experiments are 3−4, 7−9, and 50−53 cm^{-1}, respectively. In

Table 2. Experimental and Calculated Frequency Shifts of Functional Groups in PBI and Polyimides Using Model Compounds of Different Dianhydrides and Diamines

	frequency shifts									
	BTDA		DSDA		$DDSO_2$		MDA		ODA	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
C═O(sym) (cm^{-1})	3.8	3−4	1.2	3−4	1.2	3−4	1.6	3	2.6	3−4
C═O (antisym) (cm^{-1})	8.9	7−9	7.7	5−6	7.7	5−6	6.5	5−7	4.0	6−7
N−H (cm^{-1})	34	50−53	30	39−41	30	39−41	43	40−45	40	39−53

addition, those for DSDA and PBI are 1.2, 7.7, and 30 cm^{-1}, respectively, whereas the experimental values are 3−4, 5−6, and 39−41 cm^{-1}, respectively. Calculated values for the diamines are also employed, and the results are listed in Table 2 including the experimental ones. As seen in Table 2, the values obtained by calculation and experiments are quantitatively quite comparable, and the trends are quite similar. This implies that the difference in electron affinity existing in the two dianhydrides are the major factor influencing miscibility over the diamines, and this is consistent with the experimental results.[11]

Conclusion

Hydrogen-bonding strength in the blends of poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) (PBI) and various polyimides (PIs) derived from BTDA (3,3′,4,4′-benzophenone tetracarboxylic dianhydride) and DSDA (diphenylsulfone tetracarboxylic dianhydride) with DDSO$_2$ (4,4′-diamine diphenylsulfone), MDA (4,4′-methylene dianiline), and ODA (4,4′-oxydianiline) has been calculated using the model compounds by the density functional method. The calculated hydrogen-bonding strengths of BTDA and DSDA types were 4.8 and 4.4 kcal/mol, respectively, while those of DDSO$_2$, MDA, and ODA were 4.9, 5.1, and 5.0 kcal/mol, respectively. Calculated frequency shifts of the C═O symmetric and antisymmetric stretching bands and the N−H stretching band for BTDA type and PBI are 3.8, 8.9, and 34 cm^{-1}, respectively, whereas those for DSDA type and PBI are 1.2, 7.7, and 30 cm^{-1}, respectively. Thus, the difference in the hydrogen-bonding strength in PBI/polyimides is seen to arise from the difference in energies between BTDA and DSDA rather than between those values in diamines. Although a direct comparison between calculation and experiments in hydrogen-bonding strength is not practical since no experimental binding energy is available, the quantitative analysis of the hydrogen bonding by calculation agrees well with the previously reported experimental results using FT-IR and DSC techniques.

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