

ACID-BASE INTERACTIONS BETWEEN POLYMERS AND FILLERS

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ABSTRACT

Inverse gas chromatography (IGC) and Fourier-transform infrared (FT-IR) techniques were applied to determining the relative acid-base strength of polymers and coupling agents. The acid-base characteristics of fillers such as CaCO_3 could be altered by treatment with different coupling agents. It was shown that some mechanical properties of filled polymers were obviously associated with acid-base interactions between polymers and fillers.

INTRODUCTION

In polymer-filler systems, coupling agents are usually used to alter the surface characteristics of fillers. In order to guide the syntheses and selections of coupling agents, many theories have been proposed. Among them chemical bonding theory^[1], entangling theory^[2], and wetting theory^[3] are generally believed to be reasonable. In the present work, the functions of some coupling agents were studied in the light of the acid-base interactions between polymers and fillers proposed by Fowkes and his co-workers^[4-6]. For this purpose three different silane coupling agents were employed to modify CaCO_3 fillers, and diverse analytical methods were applied to determining the relative acid-base strength of polyethylene (PE), poly(vinyl chloride) (PVC), chlorinated poly(vinyl chloride) (CPVC), coupling agents and the modified CaCO_3 fillers. Ultimate tensile strength of filled polymers and adhesion strength of polymers to glass were also tested.

EXPERIMENTAL

Materials

All polymers used were industrial products and were used without further purification. Coupling agents N-42 and N-43 were prepared by our laboratory, and their chemical structures are - $\text{NHCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{Cl}_2\text{CHSi}(\text{OC}_2\text{H}_5)_3$ respectively. KH-550 was furnished by Gaixian Chemical Plant, and its chemical structure is $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$.

Inverse Gas Chromatography (IGC) Analysis

A SP-2305 dual-column gas chromatography with thermal conductivity detector was used for retention time measurements. The flow rate of the hydrogen carrier gas measured by a soap-bubble flowmeter was 30 ml/min. Oven temperature was controlled to $60 \pm 0.5^\circ\text{C}$. The polymers were coated onto 80-100 mesh, AW-DMCS-treated Chromosorb W, to give a loading of 5%. Xylene was the solvent for PE, THF for PVC and CPVC. Coupling agents were coated onto the

same support as mentioned before giving a loading of 6%.

FT-IR Analysis

FT-IR spectra of the sample solutions were recorded on a Nicolet 170SX instrument. Solutions containing PVC or CPVC sample were prepared as follows: a solution of polymer in dry CH_2Cl_2 (3% w/w) was prepared first, and then the same amount of ethyl acetate (EtAc) as the polymer was added into the solution. Other sample solutions were prepared by mixing EtAc or CHCl_3 with CH_2Cl_2 , THF, N-42, N-43 and KH-550 respectively. The volume ratio was 1:1.

Colour change test

1 ml solution of adsorbing indicator in benzene was added into a tube containing about 20 mg fillers. The colour change of the fillers was visually observed after shaking.

Adhesion of Polymers to Glass

Three pieces of glass treated with water-ethanol solution of coupling agents were dried at 120°C for 6 hours. At different positions of the treated glass, about 0.5 ml polymer solution was dropped. THF was the solvent for PVC and CPVC, CHCl_3 for poly(methyl methacrylate) (PMMA). The concentration was 3% (w/v). After the solvent was evaporated, the polymer films were peeled off, and the adhesion strength between the same kind of polymers film treated with different coupling agents were compared.

RESULTS AND DISCUSSIONS

IGC analysis

The concept of acid-base interaction parameter Ω was put forward by Schreiber^[7] in 1982. It was defined as

$$\Omega = (v_g^\circ)_{\text{acid}} / (v_g^\circ)_{\text{base}} \quad (1)$$

where $(v_g^\circ)_{\text{acid}}$ and $(v_g^\circ)_{\text{base}}$ are specific retention volume of the acid probe and of the base probe respectively. Obviously, for increasingly acidic or basic stationary phases the Ω should shift toward zero and to high positive values respectively.

In the present work, CHCl_3 was selected as acid probe, and THF as base probe. The stationary phases were PE, PVC, CPVC, N-42, N-43 and KH-550, respectively. The retention time of the probe t_R and the dead time of air t_a were measured. According to chromatography theory^[8] and reference [7],

$$\Omega = \frac{(v_g^\circ)_{\text{acid}}}{(v_g^\circ)_{\text{base}}} = \frac{(t_R)_{\text{acid}} - t_0}{(t_R)_{\text{base}} - t_0} = \frac{(t'_R)_{\text{acid}}}{(t'_R)_{\text{base}}}, \quad (2)$$

where t'_R is adjusted retention time. The data of $(t'_R)_{\text{acid}}$, $(t'_R)_{\text{base}}$ and Ω are summarized in Table 1. Since the support used is neutral, the results indicate that PE and N-42 are nearly neutral, KH-550 is basic, N-43, CPVC and PVC are acidic.

FT-IR Analysis

The carbonyl oxygens of EtAc are basic (electron donor) sites which can form acid-base bonds with the electron-accepting sites of acidic molecules such as chloroform. The stretching frequency of such bonded carbonyl oxygens is decreased by an amount $(\Delta\nu_{\text{C=O}}^{\text{ab}})$ proportional to the enthalpy of bonding (ΔH^{ab}) ^[6]. Similarly, if basic solute containing lone pair electrons is dissolved in CHCl_3 , according to Sheppard's theory^[9], the stretching adsorption bands of C—H should shift to lower frequency. Therefore, from the wave numbers of the shifts, the relative acid-base strength

of polymers and coupling agents can be determined. Table 2 lists $\Delta\nu_{C=O}$ values for EtAc in different chemical environments. It shows that PVC and CPVC are acidic polymers and their acid strength is about that of CHCl_3 . Table 3 lists $\Delta\nu_{C-H}$ values for CHCl_3 . Obviously, the base strength of coupling agents is $\text{KH-550} > \text{N-42} > \text{N-43}$, where the base strength of KH-550 is close to that of THF.

Table 1 Data of $(t_R)_{acid}$, $(t_R)_{base}$ and Ω

Stationary phase	$(t_R)_{acid}$ (sec.)	$(t_R)_{base}$ (sec.)	Ω
KH-550	102.1	37.7	2.71
N-42	26.9	38.0	0.71
N-43	92.3	303.9	0.30
CPVC	3.5	8.6	0.41
PVC	2.5	5.4	0.46
PE	20.2	21.9	0.92
none	2.1	2.4	0.87

Table 2 Stretching frequency shifts $\Delta\nu_{C=O}$ for EtAc owing to the presence of solute

Solute	$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
None	1742	—
CH_2Cl_2	1739	-3
$\text{PVC} + \text{CH}_2\text{Cl}_2$	1734	-8
$\text{CPVC} + \text{CH}_2\text{Cl}_2$	1733	-9
CHCl_3	1733	-9

Table 3 Stretching frequency shifts $\Delta\nu_{C-H}$ for CHCl_3 owing to the presence of solute

Solute	ν_{C-H} (cm^{-1})	$\Delta\nu_{C-H}$ (cm^{-1})
None	3020	—
N-43	3015	-5
N-42	3012	-8
KH550	3008	-12
THF	3006	-14

Colour Change Test

It was reported that if neutral red is adsorbed by acidic fillers, the colour of the fillers will change from white to red; if by basic fillers, no particular colour change appears. Whereas if bromothymol blue is adsorbed by acidic fillers, no colour change appears; if by basic fillers, the colour of the fillers will become blue^[10]. Thus with the aid of colour change of the two indicators, we can see qualitatively whether the acid-base characteristics of CaCO_3 can be altered by treatment with different coupling agents or not.

Results of the colour change test listed in Table 4 indicate that CaCO_3 and N-42 treated CaCO_3 are neutral, but when CaCO_3 is treated with KH-550 or N-43, the acid-base characteristics of it can be altered. KH-550 makes it basic, N-43 makes it acidic.

Ultimate Tensile Strength

On the assumption that the acid-base interaction parameters of modified CaCO_3 fillers are equal to those of the corresponding coupling agents, it can be shown from Figure 1 that in PVC or CPVC system, where associative forces can exist at polymer-filler contacts, treatments of CaCO_3

Table 4 Results of the colour change test

Sample	Adsorbing indicators	
	Neutral red	Bromothymol blue
CaCO ₃	Slight red	Slight blue
KH-550 treated CaCO ₃	—	Blue
N-42 treated CaCO ₃	Slight red	Slight blue
N-43 treated CaCO ₃	red	—

with coupling agents produce remarkable effects, and the shift to basic properties in CaCO₃ produces enhancement in ultimate tensile strength. But in PE system, where only dispersion force interactions are involved, the response to filler surface modifications is very mild.

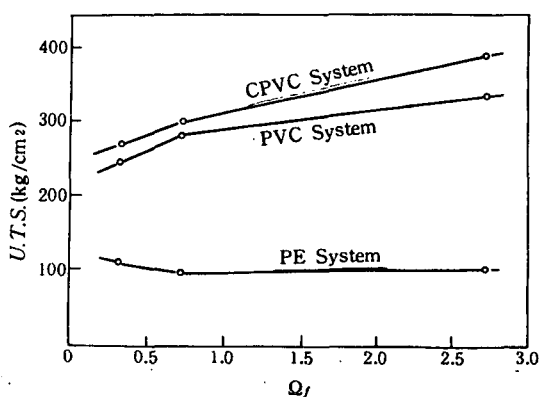


Fig. 1 Effect of filler's acid-base interaction parameter Ω_f on the ultimate tensile strength of PE/CaCO₃, PVC/CaCO₃ and CPVC/CaCO₃

Adhesion of Polymers to Glass

It was found that acidic polymers such as PVC or CPVC adhere very strongly to KH-550 treated glass, but basic polymers such as PMMA do not. However, on N-43 treated glass, PMMA adheres strongly, and PVC or CPVC does not. Up to now, it had been difficult to measure the interactions between polymers and fillers directly, but from this experiment, we can deduce that in filled polymer systems, the acid-base interactions are important.

CONCLUSIONS

1. IGC and FT-IR techniques can be applied to determining the relative acid-base strength of polymers and coupling agents. It is shown that the base strength of KH-550 is close to that of THF; the acid strength of PVC or CPVC is close to that of CHCl₃; N-42 and PE are neutral; N-43 is a stronger acid than PVC and CPVC.

2. The acid-base characteristics of fillers such as CaCO₃ can be altered by treatment with different silane coupling agents. It is reasonable to explain the functions of such coupling agents from the point of acid-base interactions.

3. For filled PVC and CPVC composites, ultimate tensile strength depends on acid-base characteristics of fillers. Some mechanical properties of those composites may be controlled by means of controlling the acid-base characteristics of fillers with coupling agents.

Keywords: Acid-Base Interaction; Polymer-Filler System; Coupling Agents; Composites

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REFERENCES

- [1] Plueddemann, E.P., *Polymer Preprints*, **1983**, 24(1), 196.
- [2] Monte, S.J., "Titanate Coupling Agents in Filler Reinforced Thermoplastics", presented at 33rd Annual Technical Conference, **1978**.
- [3] Plueddemann, E.P., *Interfaces in Polymer Matrix Composites*, New York, Academic Press **1974**.
- [4] Fowkes, F.M., in "Adhesion and Adsorption of Polymers", Lee, L.H., Plenum, New York, **1980**, 43.
- [5] Fowkes, F.M., *Org. Coat. Plast. Chem.*, **1979**, 40, 13.
- [6] Fowkes, F.M., *J. Polym. Sci. Polym. Chem. Ed.*, **1984**, 22(3), 547.
- [7] Schreiber, H.P., *J. Appl. Polym. Sci.*, **1982**, 27, 2269.
- [8] 中国科学院化学研究所色谱组, 气相色谱手册, 科学出版社, **1977**. (Institute of Chemistry of Academia Sinica, "Handbook of Gas Chromatography", Science Press **1977**).
- [9] Sheppard, N., in "Hydrogen Bonding", Hadzi, D., Pergamon Press London, **1957**, 85.
- [10] 田部 浩三著, 赵君生译, 固体酸碱及其催化性质, 化学工业出版社, **1979**. (Tanabe Kôzô, "Solid Acids and Bases and Their Catalyzing Properties", Translated by Zhao Junsheng, Chemical Industry Press **1979**).