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Preparation of a silica gel–carbon black composite by the sol–gel process in the presence of polymer-grafted carbon black

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This paper is concerned with the preparation of a silica gel–carbon black composite by the sol–gel process, which consists of tetraethoxysilane and polymer-grafted carbon black. Polymer-grafted carbon black was synthesized by three methods: (1) cationic polymerization of *N*-vinyl-2-pyrrolidone, (2) cationic ring-opening polymerization of 2-methyl-2-oxazoline, and (3) radical polymerization of glycidyl methacrylate followed by reaction of glycidyl groups in the grafted polymer chains with 3-aminopropyltriethoxysilane. The polycondensation of tetraethoxysilane proceeded under acidic conditions in the presence of polymer-grafted carbon black to give a deep black silica gel–carbon black composite. The more the content of untreated carbon black was increased, the more the gelation time was shortened. On the contrary, gelation was retarded by grafted polymer chains on the carbon black surface in the case of polymer-grafted carbon black. The scratch hardness of the resulting silica gel–carbon black composite was almost equal regardless of the carbon black content in the presence of untreated carbon black, whereas it was liable to decrease as the content of polymer-grafted carbon black increased. The solvent adsorption properties of the silica gel–polymer-grafted carbon black composite varied with the solubility of grafted polymer chains on the carbon black surface towards the immersion solvent.

1. Introduction

During the past decade there has been great interest in the sol–gel process, i.e. the method for preparation of inorganic glass and ceramic precursors under mild conditions such as low temperature and pressure, as described by several reviews [1–5]. This method involves the hydrolysis of metal alkoxides to produce metal hydroxides, followed by polycondensation of hydroxyl groups to form a metal oxide network. Research related to the sol–gel process has been stimulated by its applicability to various fields, such as glass [6] and ceramic [7] manufacturing, optical [8] and electrical [9] devices.

One of the important extensions of the sol–gel process is the preparation of organic–inorganic hybrid materials consisting of an organic polymer and a metal oxide, such as a silica gel with molecular-level dispersion. Poly(dimethylsiloxane) [10], poly(oxytetramethylene) [11], polyamide [12], poly(oxyethylene) [13], poly(etherketone) [14], and poly (2-methyl-2-oxazoline) [15] have been successfully incorporated into an inorganic network matrix by the sol–gel process.

Carbon black is an important ultrafine inorganic particle used industrially as a reinforcing filler, a black pigment and as electroconductive material. The dispersibility of carbon black in organic solvents or polymer matrices is known to be remarkably improved by grafting of polymers onto the surface [16]. We reported that the cationic polymerization of vinyl monomers [17, 18] and the cationic ring-opening polymerization of 2-substituted-2-oxazoline [19] were initiated by carboxyl groups already on the carbon black surface. We also reported that the anionic, cationic and radical graft polymerization of various monomers were initiated by initiating groups newly

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introduced onto the carbon black surface, for example, by potassium carboxylate [20], acylium perchlorate [21], and azo [22] groups, respectively.

Organic polymer–inorganic hybrid gels containing ultrafine inorganic particles uniformly are expected to show unique characteristics and aspects, but the preparation of these materials by the sol–gel process has not been reported yet. Consequently, in this paper we wish to report sol–gel reaction in the presence of polymer-grafted carbon black to obtain a silica gel–carbon black composite in which the carbon black particles are dispersed uniformly.

2. Experimental procedure

2.1. Materials

The carbon blacks used in this experiment were colour channel black Neospectra II (Columbian Carbon Co.) and FW 200 (Degussa A. G.); both were dried *in vacuo* at 110 °C before use. The properties of these carbon blacks [Brunauer–Emmett–Teller, BET, specific surface area, particle size, pH, and the content of carboxyl (COOH), phenolic hydroxyl (OH), and quinonic oxygen (C = O) groups] are shown in Table I.

Tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APS) were used without further purification. *N*-Vinyl-2-pyrrolidone (NVPD) was dried over sodium hydroxide and distilled twice under reduced pressure. 2-Methyl-2-oxazoline (MeOZO) was dried over calcium hydride and fractionally distilled twice just before use. Glycidyl methacrylate (GMA) was dried over calcium hydride and distilled under reduced pressure.

4,4′-azobis(4-cyanopentanoic acid) (ACPA) was recrystallized from methanol, and dried *in vacuo* at room temperature. Tolylene 2,4-diisocyanate (TDI) was purified by vacuum distillation twice before use. Tetrahydrofuran (THF) was refluxed over sodium and distilled. Ethanol, hydrochloric acid and other solvents were all of reagent grade and were used as supplied.

2.2. Preparation of polymer-grafted carbon black

Poly(NVPD)- and poly(MeOZO)-grafted carbon blacks were synthesized by the cationic polymerization of NVPD [17, 18] and the cationic ring-opening polymerization of MeOZO [19], respectively, using carboxyl groups on the carbon black surface as an initiator. The cationic polymerization of NVPD was carried out under dry nitrogen in a 100 ml tear-drop flask. Into a flask, 0.50 g of carbon black, 10 ml of NVPD, and a stirrer bar were charged. The reaction mixture was stirred at 25 °C for 24 h with a magnetic stirrer. The polymerization was stopped by adding aqueous sodium carbonate solution (10 ml of 0.20 mol l^{-1}). The unreacted monomer was pumped off at 60 °C, yielding the polymer containing carbon black.

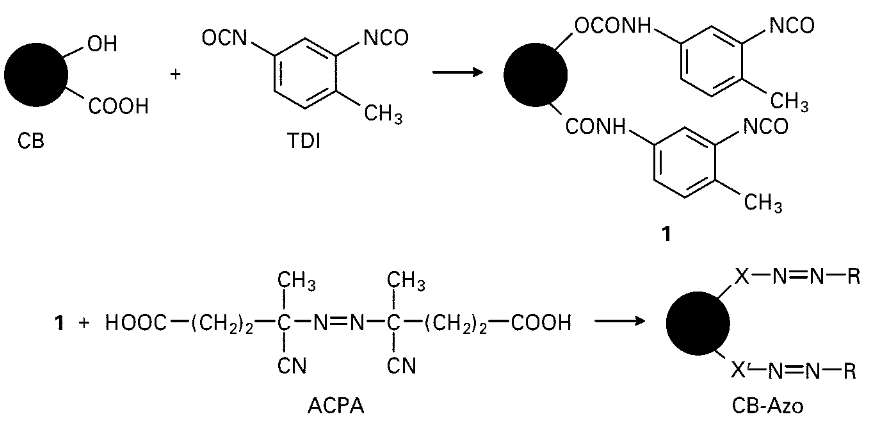
The cationic ring-opening polymerization of MeOZO was achieved in a sealed tube. Into a glass tube, 0.10 g of carbon black, 1.7 ml of MeOZO, and a stirrer bar were charged. The tube was cooled in a liquid nitrogen bath, thawed three times under nitrogen, and then sealed under vacuum. The polymerization was conducted at 110 °C for 48 h in an oil bath with stirring. After the reaction, the polymerization was brought to a stop by introducing ammoniacal methanol, and unreacted monomer was pumped off at 40 °C.

The radical graft polymerization of GMA was performed by carbon black having azo groups on the surface as an initiator. The carbon black having surface azo groups was prepared by the reaction of ACPA, which has terminal carboxyl groups, with isocyanate groups previously introduced onto the surface. The isocyanate groups were introduced onto the carbon black surface by treatment of the carbon black with TDI (Equation 1). These procedures are described in detail in [22].

Graft polymerization was carried out in a sealed tube under vacuum. Into a glass tube, 0.30 g of carbon

TABLE I Properties of carbon blacks

Carbon black	BET surface area (m^2 g^{-1})	Particle size (nm)	pH	OH (mmol g^{-1})	COOH (mmol g^{-1})	C = O (mmol g^{-1})
Neospectra II	906	13	3.0	0.24	0.40	0.92
FW 200	460	13	2.0	0.10	0.61	1.42



Equation 1.

black having surface azo groups and 10 ml of GMA were charged. The content of the tube was frozen in a liquid nitrogen bath, evacuated with a pump, and then thawed. After this operation was repeated three times, the tube was sealed under vacuum. The tube was heated at 70 °C for 1 h with shaking. After the reaction, the content of the tube was poured into an excess of methanol to precipitate poly(GMA) containing carbon black, and the precipitate was filtered.

Conversion was calculated by the following equation after the product was dried *in vacuo* at 50 °C

$$\text{Conversion (\%)} = \frac{A}{B} \times 100$$

where A is the product (grams) minus the carbon black charged (grams), and B is the monomer charged (grams).

2.3. Percentage of grafting of polymer-grafted carbon black

To separate the polymer-grafted carbon black from the reaction product containing ungrafted polymer, the product was centrifuged at 1.0×10^4 r.p.m. until carbon black was completely precipitated. The carbon black precipitated, i.e. polymer-grafted carbon black, was further extracted with a Soxhlet apparatus to remove remaining ungrafted polymer. The extracting solvents were methanol for poly(NVPD) and poly(MeOZO), and chloroform of poly(GMA). The percentage of grafting was calculated by the following equation

$$\text{Percentage of grafting (\%)} = \frac{A}{B} \times 100$$

where A was the polymer grafted (grams), and B the carbon black charged (grams). The amount of polymer grafted onto the carbon black surface was determined by weight loss through the pyrolysis of the grafted polymer chains when polymer-grafted carbon black was heated at 500 °C with the use of a thermal analyser (Rigaku, TG-DSC 8089E1).

2.4. Introduction of pendant triethoxysilyl groups to poly(GMA) chains grafted on the carbon black surface

The introduction of pendant triethoxysilyl groups to poly(GMA) chains grafted on the carbon black surface was achieved by the reaction of glycidyl groups of poly(GMA) with an excess of APS. A typical example is as follows. Into a flask equipped with a reflux condenser, 1.0 g of poly(GMA)-grafted carbon black and 20 ml of absolute THF were charged. The mixture was stirred with a magnetic stirrer under dry nitrogen in order to disperse the carbon black particles into the THF, and then 2.5 ml of APS was added into the mixture. The reaction was conducted at 40 °C for 48 h with stirring in a stream of nitrogen. After the reaction, the resulting carbon black was repeatedly washed with absolute THF and dried *in vacuo* at room temperature. The amount of pendant triethoxysilyl groups introduced to poly(GMA) chains was determined by elemental analysis.

2.5. Preparation of a silica gel–carbon black composite

Into a test tube, 1.7 ml of ethanol was charged, and then the prescribed amount of polymer-grafted carbon black was dispersed into ethanol. Some 3.0 ml of TEOS and 3.0 ml of hydrochloric acid (5% aqueous solution) were also added into the test tube. The reaction mixture was shaken in a water bath at 40 °C for gelation. After gelation, the test tube was dried in an oven until the volatile matter (ethanol and water) was completely evaporated: the temperature was held at 80 °C for 48 h, then allowed to attain 95 °C for 24 h, and maintained at 95 °C over 48 h. The temperature was subsequently raised gradually and held at 300 °C for 2 h.

2.6. Pencil scratch test of the silica gel–carbon black composite

The scratch hardness of the silica gel–carbon black composite was estimated under constant stress with pencils according to the Japanese Industrial Standard (JIS) pencil scratch test [23]. The silica gel–carbon black composite was taken out of the test tube after drying, and the surface of the composite was scratched with a pencil varying the hardness from H (soft) to 9H (hard). The limitation of scratch resistance was measured as the scratch hardness.

2.7. Solvent adsorption properties of the silica gel–carbon black composite

Into a 50 ml Erlenmeyer flask, 30 ml of solvent and a pre-weighed bit of dried silica gel–carbon black composite were charged. The flask was stoppered to prevent evaporation of the solvent and allowed to stand at 25 °C for 24 h. After taking the bit of sample out of the flask, the bit of sample was wiped dry with gauze and then weighed.

Solvent uptake was calculated by following equation

$$\text{Solvent uptake (\%)} = \frac{B - A}{A} \times 100$$

where A is the dried sample (grams), and B the solvent-adsorbed sample (grams).

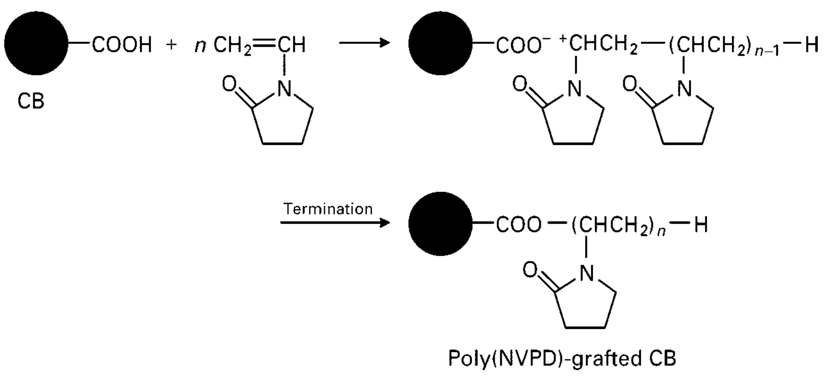
3. Results and discussion

3.1. Grafting of polymers onto carbon black surface

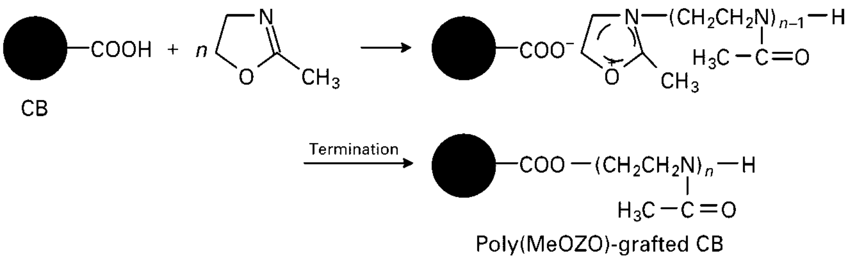
Saegusa and coworkers reported that organic polymers whose repeating units possess an N-alkyl or N,N-dialkyl substituted amide group were most suitable for the preparation of organic–inorganic hybrid materials by the sol–gel process because the polymer molecule was dispersed in the three-dimensional network of a metal oxide, such as silica gel, by the formation of hydrogen bonds between the amide carbonyl group of polymer and the silanol group of silica [24, 25]. Furthermore, the synthesis and application of polymers terminated with functional groups that can react with the metal hydroxide in the sol–gel reaction have been reported. For example, sol–gel condensation of TEOS in the presence of poly(dimethylsiloxane) with silanol terminal groups [10, 26] or triethoxysilyl–terminated poly(MeOZO) [27] can give organic polymer–silica gel hybrid materials. Therefore, in order to facilitate the dispersion of carbon black particles into the silica gel matrix, we tried to graft poly(NVPD) and poly(MeOZO) having these alkyl amide groups, and also poly(GMA) followed by reaction with APS, which resulted in poly[GMA-*co*-{2-hydroxy-3-(3-triethoxysilylpropyl)aminopropyl methacrylate}] {poly(GMA/TES)} having pendant triethoxysilyl groups, onto the carbon black surface, Equations 2–4.

Table II shows the results of the cationic graft polymerization of NVPD and MeOZO initiated by carboxyl groups on the carbon black surface. Both the carbon blacks, Neospectra II and FW 200 were found to have the ability to initiate the polymerization and part of the resultant polymer grafted onto the carbon black surface.

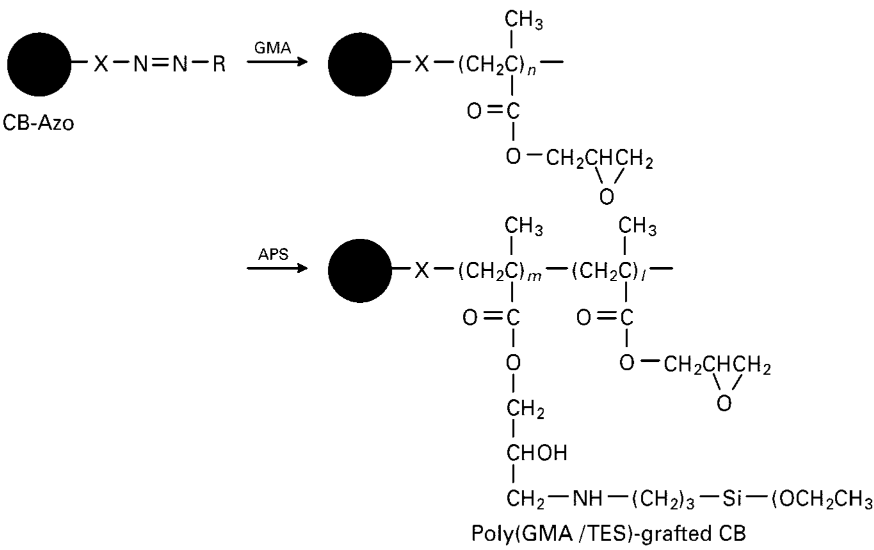
The results of the radical grafting of poly(GMA) initiated by surface azo groups attached onto the carbon black are also shown in Table II together with the amount of pendant triethoxysilyl groups introduced to poly(GMA) by reaction with APS. Poly(GMA)



Equation 2.



Equation 3.



Equation 4.

TABLE II Graft polymerization of vinyl monomers onto the carbon black surface

Carbon black	Monomer	Conversion (%)	Grafting (%)	$-Si(OEt)_3$ introduced ($mmol\,g^{-1}$)	Rr^d (%)
Neospectra II	NVPD[a]	20.9	77.6	–	–
Neospectra II	MeOZO[b]	15.2	48.2	–	–
Neospectra II	GMA[c]	7.7	67.0	1.34	47.6
FW 200	NVPD[a]	13.7	39.6	–	–
FW 200	MeOZO[b]	18.9	89.4	–	–
FW 200	GMA[c]	9.2	71.3	1.46	49.9

[a] Carbon black, 0.50 g; NVPD, 10 ml; 25 °C; 8 h.

[b] Carbon black, 0.10 g; MeOZO, 1.7 ml; 110 °C; 48 h.

[c] Carbon black, 0.30 g; GMA, 10 ml; 70 °C; 1 h.

[d] Reaction percentage of glycidyl groups of grafted poly(GMA) with APS.

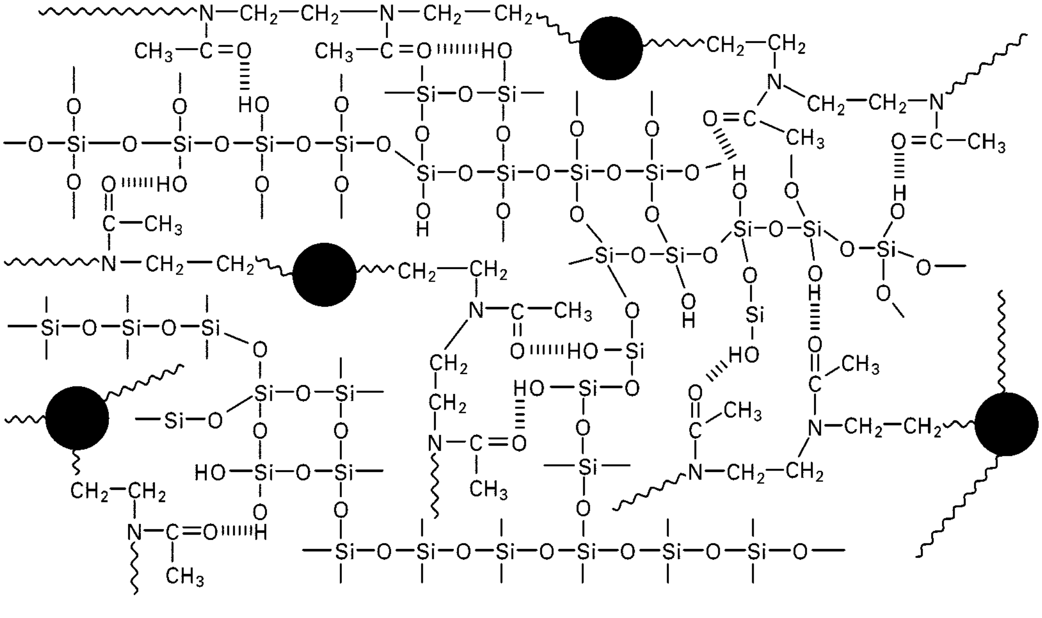


Figure 1 Sketching structure of silica gel–poly(MeOZO)-grafted carbon black composite.

also grafted effectively onto the carbon black surfaces, and the reactions of glycidyl groups in poly(GMA) chains with APS successfully progressed to give poly(GMA/TES)-grafted carbon blacks. The amount of pendant triethoxysilyl groups introduced to grafted poly(GMA) chains was determined from the nitrogen percentage increment in the nitrogen analysis after initial reaction. The percentage of glycidyl groups that reacted with APS (*R*r) was calculated from the pendant triethoxysilyl group content, and it was about 50% for both Neospectra II and FW 200, as disclosed in Table II.

3.2. Gelation time of TEOS in the presence of carbon black

Silica gel–carbon black composites were successfully prepared by the polycondensation of TEOS under acidic conditions in the presence of polymer-grafted carbon black. We examined the effect of carbon black content on the gelation time of TEOS. The results are summarized in Table III. In the cases of untreated carbon blacks, the gelation was accelerated as the content of carbon black increased. The reason for this acceleration may be that the gelation was affected by increased acidity in the reaction system caused by the increasing content of carbon black. On the contrary, the gelation time was extended as the content of poly(NVPD)- and poly(MeOZO)-grafted carbon blacks increased. This phenomenon suggests that gelation is retarded by grafted polymer chains on the carbon black surface. In the presence of poly(GMA/TES)-grafted carbon blacks, the gelation time was longer than in the absence of carbon black at low carbon black content, but it decreased gradually as the content of the carbon black increased. For this reason, we consider that gelation is strongly retarded by grafted poly(GMA/TES) chains at low poly(GMA/TES)-grafted carbon black content because poly(GMA) segments in poly(GMA/TES) are insoluble in ethanol and water in addition to the low content of pendant triethoxysilyl groups, and that gelation becomes accelerated by increasing absolute amounts of the pendant triethoxysilyl groups of grafted poly(GMA/TES) chains as the content of poly(GMA/TES)-grafted carbon black increases.

Furthermore, in the presence of untreated carbon blacks, aggregated particles of carbon black were

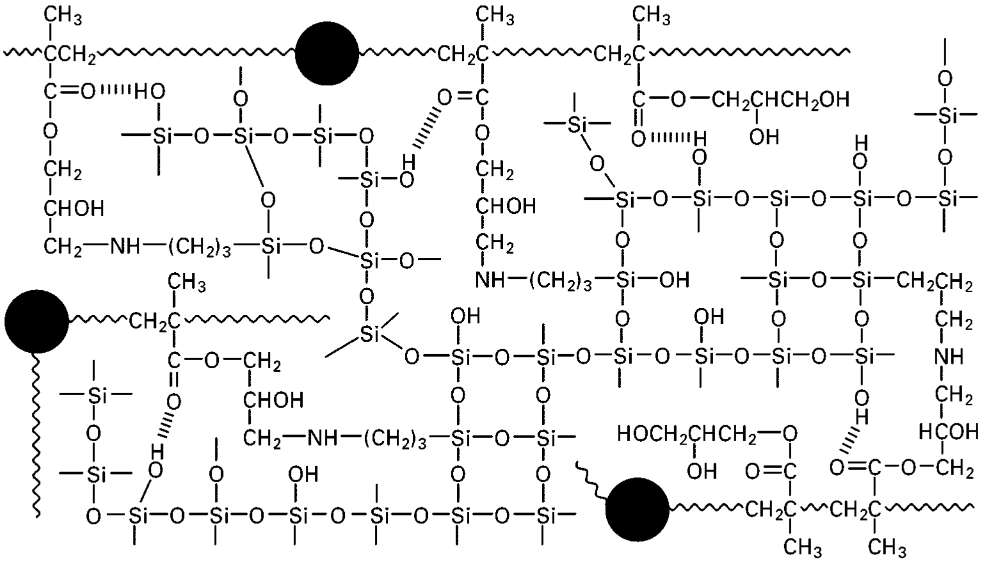


Figure 2 Sketching structure of silica gel–poly(GMA/TES)-grafted carbon black composite.

observed in the silica gel matrix, but polymer-grafted carbon blacks were uniformly incorporated into the network of silica gel to give deep black silica gel–carbon black composites. This is because the dispersibility of carbon black into the reaction mixture is improved by grafting poly(NVPD) and poly(MeOZO) onto the surface; and, in addition, it is expected that the carbonyl groups of the grafted polymer chains form hydrogen bonds with the residual silanol groups in the silica gel. A schematic representation of the silica gel–poly(MeOZO)-grafted carbon black composite is illustrated in Fig. 1.

In the case of poly(GMA/TES)-grafted carbon black, it is also expected that pendant triethoxysilyl groups can react with silanol groups of silica during sol–gel condensation to constitute a network of silica gel besides the formation of hydrogen bonds as illustrated in Fig. 2.

Figs 3 and 4 show the infrared spectra of silica gel–polymer-grafted carbon black composites together with reference to those of grafted polymer components. In each set compare the absorption of the carbonyl stretching band of the composite shifted to lower wave number with that of the polymer itself. In the case of poly(NVPD), it shifted from 1680 to 1654 cm^{-1}, and in poly(MeOZO), from 1634 to 1622 cm^{-1}. Therefore, it is clear that hydrogen bonds are formed between carbonyl groups of grafted polymer chains on the carbon black surface and silanol groups in the silica gel [24, 25].

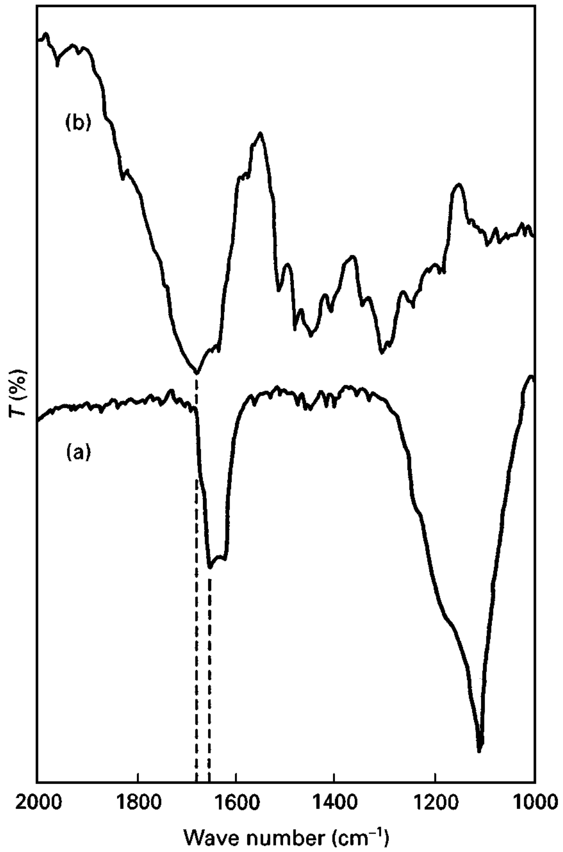


Figure 3 Infrared spectra of (a) silica gel–poly(NVPD)-grafted carbon black composite and (b) poly(NVPD).

3.3. Pencil scratch test of the silica gel–carbon black composite

We next examined the limit of scratch resistance of the surface of the silica gel–carbon black composite in the pencil scratch test. The results are shown in Table IV. In the cases of untreated carbon blacks, the scratch hardness of the composite was almost equal regardless of the carbon black content, but the composite became brittle with increasing carbon black content. On the other hand, as polymer-grafted carbon blacks were incorporated the scratch hardness of the composite was liable to decrease but was rather firm due to the effect of polymer chains in the composite.

The decrease in scratch hardness of the silica gel–poly(GMA/TES)-grafted carbon black composite was the lowest of all the silica gel–polymer-grafted

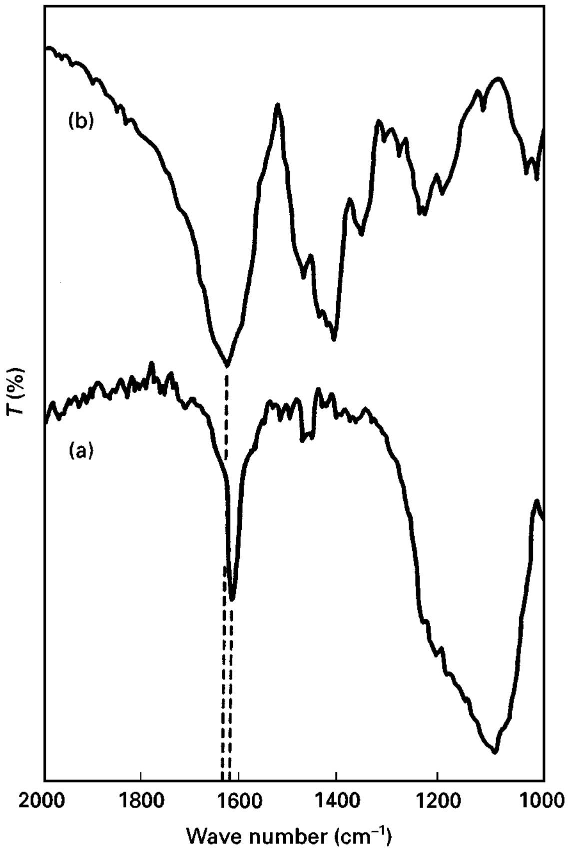


Figure 4 Infrared spectra of (a) silica gel–poly(MeOZO)-grafted carbon black composite and (b) poly(MeOZO).

carbon black composites. This reveals that poly(GMA/TES) chains grafted onto the carbon black surface are combined covalently with the silica gel network through co-polycondensation of pendant triethoxysilyl groups with silanol groups of silica during sol–gel reaction of TEOS in addition to interaction between carbonyl groups of poly(GMA/TES) and residual silica gel silanol groups through hydrogen bonding.

3.4. Solvent adsorption properties of the silica gel–carbon black composite

The dried silica gel–carbon black composites were immersed in distilled water, ethanol, THF, toluene, and *N*,*N*-dimethylformamide (DMF). The adsorption properties of the composites were estimated by the content of solvent uptake. The results are summarized in Table V. The solubility of homopolymers, which are in agreement with the polymer components grafted onto the carbon black surface, was examined in each immersion solvent and the results are shown in Table VI.

Silica gel containing no carbon black particles had an affinity for protic solvents (water and ethanol) through surface silanol groups of the network matrix. Silica gel–untreated carbon black composites showed high adsorption properties for water, ethanol and DMF. This characteristic may be due to interaction

TABLE III Gelation time of TEOS in the presence of various carbon blacks[a]

Carbon black	Gelation time (min)					
	Content of carbon black (g)					
	0	0.10	0.15	0.20	0.25	0.30
Untreated Neospectra II	230	220	220	220	190	180
Untreated FW 200	230	230	220	220	210	190
Poly(NVPD)-grafted Neospectra II	230	250	270	280	330	350
Poly(MeOZO)-grafted Neospectra II	230	250	260	280	300	330
Poly(GMA/TES)-grafted Neospectra II	230	280	280	260	260	250
Poly(NVPD)-grafted FW 200	230	210	220	230	230	250
Poly(MeOZO)-grafted FW 200	230	230	230	250	250	250
Poly(GMA/TES)-grafted FW 200	230	250	230	230	220	210

[a]TEOS, 3.0 ml; ethanol, 1.7 ml; 5% HCl aqueous solution, 3.0 ml; 40 °C.

TABLE IV Pencil scratch test of silica gel–carbon black composites

Carbon black	Scratch hardness (H)					
	Content of carbon black (g)					
	0	0.10	0.15	0.20	0.25	0.30
Untreated Neospectra II	9	9	9	9	9	8
Untreated FW 200	9	9	9	9	8	8
Poly(NVPD)-grafted Neospectra II	9	9	8	8	6	5
Poly(MeOZO)-grafted Neospectra II	9	9	9	8	7	6
Poly(GMA/TES)-grafted Neospectra II	9	9	9	8	8	7
Poly(NVPD)-grafted FW 200	9	9	8	8	6	5
Poly(MeOZO)-grafted FW 200	9	9	9	8	7	6
Poly(GMA/TES)-grafted FW 200	9	9	9	8	8	8

TABLE V Adsorption properties of silica gel–carbon black composites[a]

Carbon black	Solvent uptake (%)				
	Water	Ethanol	THF	Toluene	DMF
None	31.4	21.4	2.5	1.3	3.3
Untreated Neospectra II	45.0	34.8	9.0	1.9	40.7
Untreated FW 200	47.3	35.4	9.2	1.5	44.8
Poly(NVPD)-grafted Neospectra II	53.0	41.7	13.2	3.7	64.1
Poly(MeOZO)-grafted Neospectra II	64.7	44.9	1.2	1.8	75.7
Poly(GMA/TES)-grafted Neospectra II	14.6	7.4	23.3	8.3	33.8
Poly(NVPD)-grafted FW 200	56.8	40.5	18.0	3.2	62.8
Poly(MeOZO)-grafted FW 200	55.9	68.0	6.2	3.0	81.7
Poly(GMA/TES)-grafted FW 200	9.4	3.9	21.4	11.9	27.2

[a] Dried sample, 0.1 ≈ 0.4 g; solvent, 30 ml; 25 °C; 24 h.

TABLE VI Solubility of homopolymers[a]

Polymer	Solubility[b]				
	Water	Ethanol	THF	Toluene	DMF
Poly(NVPD)	○	○	△	×	○
Poly(MeOZO)	○	○	×	×	○
Poly(GMA/TES)	×	×	○	△	○

[a] At 25 °C; 24 h.

[b] ○, soluble; △, partly soluble; ×, insoluble.

between surface carboxyl and phenolic hydroxyl groups on the carbon black, and polar solvents. However, the silica gel–untreated carbon black composites were found to be brittle for the solvents because they cracked during immersion.

In the cases of silica gel–polymer-grafted carbon black composites, adsorption properties varied corresponding to the solubility of the grafted polymer chains on the carbon black surface towards the immersion solvent. These composites selectively adsorbed good solvents for the polymer chains grafted onto the carbon black surface as can be seen from Table VI and showed no cracking in all the solvents. Therefore, it is possible to control the solvent adsorption property of the silica gel–carbon black composite by using polymer-grafted carbon black.

Furthermore, it was found that carbon black particles were steadily incorporated into the silica gel matrix because carbon black particles ooze from the composite into the solvent was not observed in either the untreated or polymer-grafted carbon black cases.

4. Conclusions

1. Silica gel–carbon black composite was successfully prepared by sol–gel reaction of TEOS in the presence of polymer-grafted carbon black.

2. Polymer-grafted carbon black was uniformly incorporated into the silica gel matrix to give a deep black silica gel–carbon black composite.

3. The more the content of the untreated carbon black was increased, the more the gelation time was shortened; whereas gelation was retarded by grafted polymer chains on the carbon black surface in the presence of polymer-grafted carbon black.

4. Hydrogen bonding was formed between carbonyl groups in grafted polymer chains on the carbon black surface and residual silanol groups in the silica gel network.

5. Scratch hardness and solvent adsorption properties of the composites were modified by polymer-grafted carbon black.

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