The Comparison of Relaxation Events with Spectroscopic Properties of Polymer Composites with Fibrillar Dopings on the Basis of Low Density Polyethylene and Polypropylene

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SUMMARY: In this study, the mechanical and electrical degradation properties of the composites of polypropylene (PP)+PP fibers, low-density polyethylene(LDPE)+PP fiber, and PP+fiber glass have been investigated and the validity of *Zhourkov's thermofluctuation theory* has been shown.

Introduction

For contemporary polymer industry, the problem of obtaining composites whose characteristics can be changed draws much attention recently. As an example of these composites, the polymer-polymer composites are very important because many significant problems examined in pure polymers have not been ascertained completely in these composites and a lot of questions are left unanswered. For example, in polymer composites, "neutral" scattering and the scattering proportional to wavelength that occur with the effects of various factors of polymer on the boundaries of supramolecular formations and determine the subsequent physical characteristics and technological parameters of the samples used in the experiments and industrial materials were not investigated. On the other hand, the changes of the optical densities of only two peaks of the samples in the IR spectra were examined, but the vibrations of the groups in the amorphous and crystalline regions were not examined for composites. It is possible to find answers to many questions by comparing the results obtained both from the measurements of the dynamical-mechanical properties and the application of spectroscopic methods in the same samples. This study lies in the direction of the clarification of the above-mentioned problems.

The Preparation of Samples and the Experimental Methods

In the experiments, the composites of PP+PP fibbers and LDPE+PP fibers and PP+fiber glass have been used.

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The composites with PP fibers dopings whose percentages vary from 10 to 60 and fiber glass at the percentages (0.1, 0.5, 1, 5, 10, 15, 20, 25, 30) were prepared with the method of hot-pressing (the temperature of the press is around 440 and 460 K, the pressing time is about 15 or 20 min.). For all the composites, the initial activation energies of mechanical rupture (U_0) and electrical punching(W_0), and the parameters(γ,χ) depending on the structure were explored. The logτ vs. σ, logτ vs. 1/T, ε vs. τ, and σ vs. ε curves were drawn and relaxation processes were examined by these curves. On the other hand, the structural changes in the same specimens were observed in the IR spectra and microphotographs and also the changes of the areas remaining under the relaxation curves and of structure-sensitive parameters (γ,χ) were compared with those obtained from microscopy and IR spectrometer.

In these experiments, the lever mechanism presented in was used$^{1)}$. Here, the change of the lever arm in accordance with the cross section of the sample maintains σ at a constant level during the measurement. The structure of the sample was examined by the polarisation microscope (Olympos) and the IR spectrum (Watson 1000 FTIR). The thicknesses of the samples being in the layer state are between 40 and 200 μm. In order to change the structures of the composites, the samples were cooled by two different methods (i.e., at a low rate from 440-460 K to room temperature, cooled by itself; and at a high rate, the rate of cooling equalling 2000K/min. In the latter case the sample is plunged in an ice-water mixture as soon as it is taken from the press).

Experimental Results and their Interpretations

The dynamical-mechanical and electrical degradation properties were examined for all the composites. All properties were measured in the same samples in order for the above mentioned properties to be compared with the properties of the structure obtained by the IR spectrometer and microscope. The typical graphs of the dependencies of log$\tau_{\sigma(E)}$ on σ and E, and of U on σ, for these composites, are given in Figures 1(a, b), 2(a, b), and 3. As seen from these figures, both mechanical and electrical degradation of the composites comply with Zhourkov's thermofluctuation theory$^{1)}$, (that is, $\tau_\sigma = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right)$ or $\tau_E = \tau_0 \exp\left(\frac{W_0 - \chi E}{kT}\right)$ where τ_σ and τ_E are the mechanical and electrical durabilities respectively, at given σ and E stresses, $\tau_0 \cong 10^{-12}$ - 10^{-13} sec. is a universal constant equalling

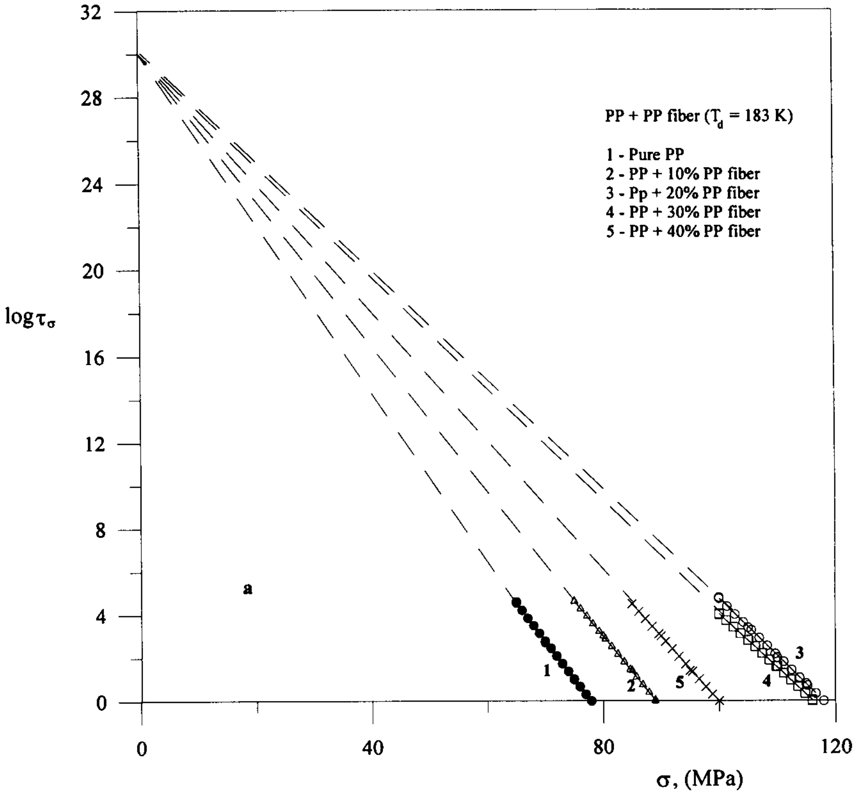

Figure 1a. The dependences of $\log\tau$ on σ for PP+PP fibers composites

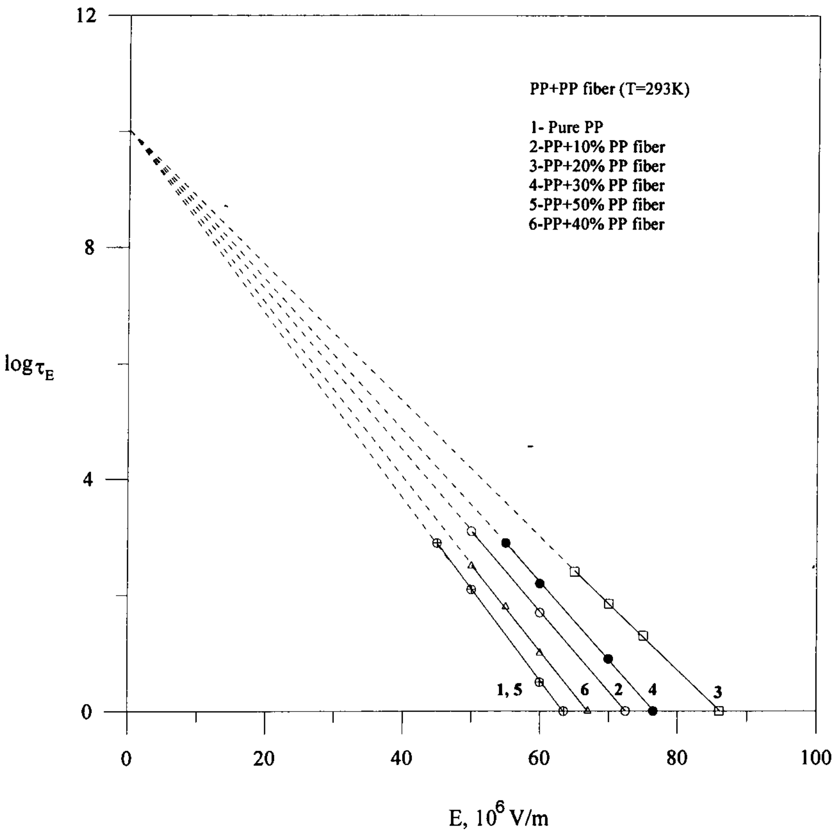

Figure 1b. The dependences of log τ on E for PP+PP fibers composites at room temperature

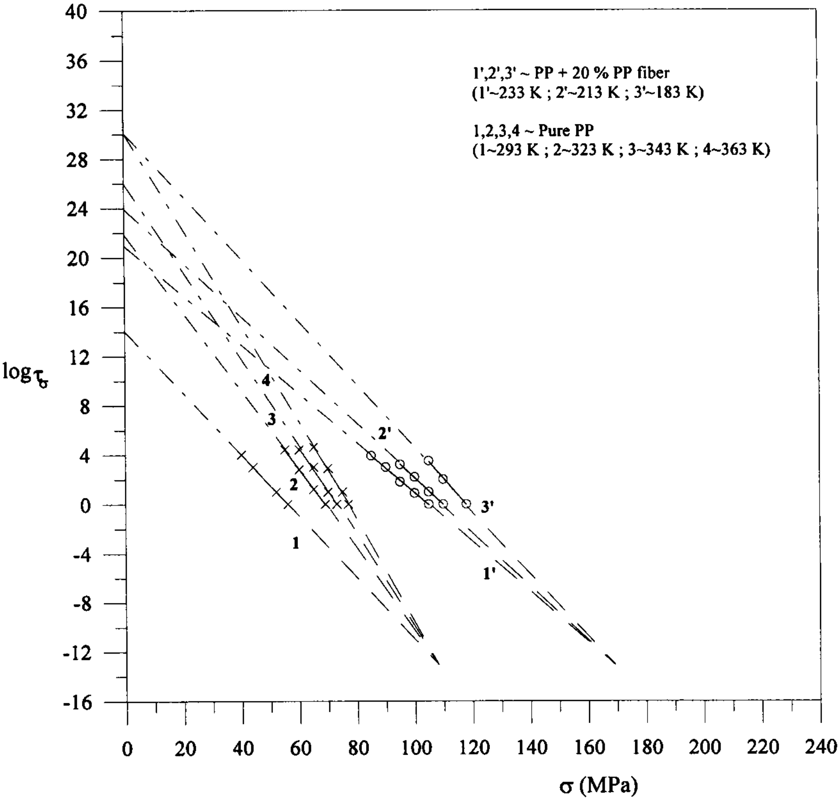

Figure 2a. The dependence of $\log\tau_\sigma$ on temperature for PP+PP fibers composites

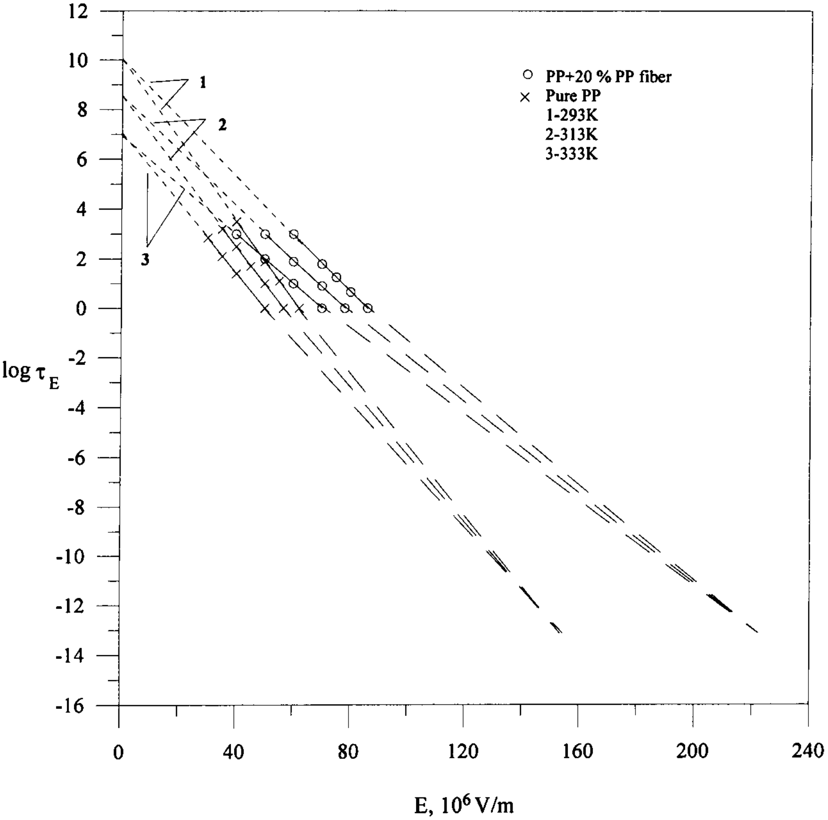

Figure 2b. The dependence of $\log\tau_E$ on temperature for PP+PP fibers composites

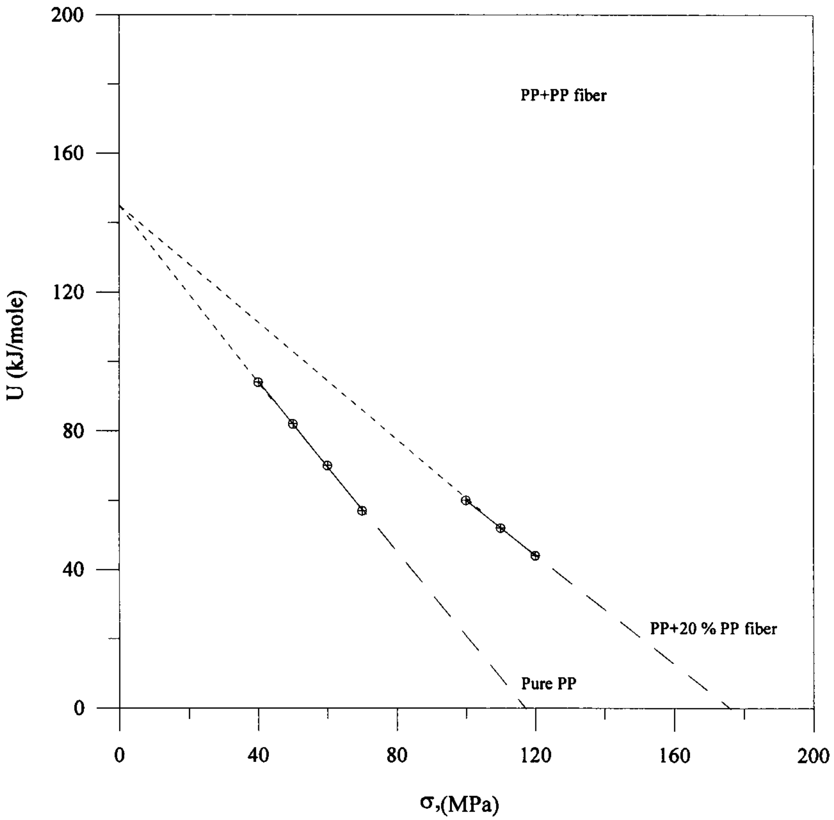
200
160
120
80
40
0
U (kJ/mole)
PP+PP fiber
PP+20 % PP fiber
Pure PP
0
40
80
120
160
200
σ,(MPa)

Figure 3

period of the peculiar vibrations of atoms around their equilibrium positions, U_0 and W_0 are the first energy barriers of the mechanical and electrical degradation processes, i.e., the activation energy of the degradation process, k is the Boltzmann constant, γ and χ are the structure-sensitive parameters). The exponential proportionality shown in fig.1a. was taken at T_d= 183 K and each line corresponds to a certain percentage of PP fibers. The dependences of $\log\tau_{\sigma(E)}$ on σ and E were measured at different temperatures (Fig. 2(a-b)). The dependence of $\log\tau_{\sigma(E)}$ on 1/T was depicted and U and W were calculated by these graphics. From the U vs. σ and W vs. E curves, U_0, W_0, γ, and χ were calculated. The obtained results were displayed in Tables 1,2, 3, 4, 5, 6. From these tables and Figures, that τ_0, U_0 and W_0 are the same for all the states proves the validity of thermofluctuation theory (the degradation mechanism). The only varying parameters are structure-sensitive parameters γ and χ. Especially, that the structures of the polymer composites vary with the effects of various external factors changes the dynamical-mechanical and other properties of the composites. The graphs of σ depending on the amounts of PP fibers and fiber glass were shown in Figures 4a and b. As seen from these figures, σ and E (the punching stress) pass through maximum values, depending on the amount of doping, whereas γ and χ pass through minimum values that is, extremal characteristics are observed in these composites, as we and other researchers did. For example, all the characteristics get better (increases up to 50%) at the percentages (20, 30) of PP fiber in PP. However, they pass through optimum for fiber glass whose ratio becomes between 0,2 and 0,5. The value of the tensile strength in the direction of the fiber (observed in the fibrillar structure) varies more than that in the perpendicular direction and the case when the fiber is added after having been broken (increases up to 50%). From these measurements, two results emerge: The changes of the structures of composites in accordance with the changes of γ and χ; The extremal values of the changes in the properties of the composites.

Structural changes have been observed in the IR spectra and microphotographs, the results are compared with the dynamical-mechanical and electrical degradation properties, and examined with the theory that some authors had developed previously[2, 3)]. In particular, that the optical densities of the peaks belonging to C=C and C-O groups pass through their minimum values for the maximum values of σ and E and appropriate fibrillar structure, and well-stacked globular structures were observed(Fig.5).

These results are explained by the principle of the existince of the supramolecular formations in polymers and of their mutual effective effects with dopings at the optimum surface-volume

Table 1. Dynamical-mechanical properties for PP+PP fiber composites

Samples	σ, MPa (T=183K, τ=1sec.)	τ_0, sec.	U_0, kJ/mole	γ, kJ/mole $(MPa)^{-1}$	τ, sec. (σ=70 MPa T=183K)
Pure PP	77	10^{-13}	152.82	1.29	$8\ 10^{2}$
PP+10%PPfiber	89	10^{-13}	152.82	1.15	$2.5\ 10^{6}$
PP+20%PPfiber	118	10^{-13}	152.82	0.879	$1.5\ 10^{12}$
PP+30%PPfiber	116	10^{-13}	152.82	0.920	$8.5\ 10^{11}$
PP+40%PPfiber	100	10^{-13}	152.82	1.04	$3.2\ 10^{8}$
PP+50%PPfiber	90	10^{-13}	152.82	1.13	$2.8\ 10^{6}$

Table 2. Dynamical-mechanical properties for LDPE+PP fiber composites

Samples	σ, MPa (T=183K, τ=1sec.)	τ_0, sec.	U_0, kJ/mole	γ, kJ/mole $(MPa)^{-1}$	τ, sec. (σ=70 MPa T=183K)
Pure LDPE	73	10^{-13}	0.177	1.800	10
LDPE+10%PPfiber	80	10^{-13}	0.177	1.615	$9\ 10^{3}$
LDPE+20%PPfiber	96	10^{-13}	0.177	1.423	$1.2\ 10^{8}$
LDPE+30%PPfiber	87	10^{-13}	0.177	1.495	10^{6}
LDPE+40%PPfiber	83	10^{-13}	0.177	1.540	$3\ 10^{4}$

Table 3. Electric strength for LDPE+PP fiber composites

Samples	E, 10^{6} V/m (T=293K, τ=1sec.)	τ_0, sec.	W_0, kJ/mole	χ, 10^{-6} kJ/mole $(V/m)^{-1}$	τ, sec. (E=55 10^{6} V/m T=293K)
Pure LDPE	60	10^{-13}	121.1	0.40	$3.6\ 10^{1}$
LDPE+10%PPfiber	72	10^{-13}	121.1	0.34	$1\ 10^{3}$
LDPE+20%PPfiber	80	10^{-13}	121.1	0.30	$7.2\ 10^{4}$
LDPE+30%PPfiber	76	10^{-13}	121.1	0.32	$3\ 10^{3}$
LDPE+40%PPfiber	68	10^{-13}	121.1	0.36	$5\ 10^{2}$
LDPE+50%PPfiber	63	10^{-13}	121.1	0.38	$2\ 10^{2}$

Table 4. Electric strength for PP+PP fiber composites

Samples	E, 10^{6} V/m (T=293K, τ=1sec.)	τ_0, sec.	W_0, kJ/mole	χ, 10^{-6} kJ/mole $(V/m)^{-1}$	τ, sec. (E=55 10^{6} V/m T=293K)
Pure PP	62	10^{-13}	129.58	0.9 10^{-6}	3 10^{1}
PP+10%PPfiber	72	10^{-13}	129.58	0.77 10^{-6}	3.5 10^{2}
PP+20%PPfiber	86	10^{-13}	129.58	0.65 10^{-6}	3.5 10^{3}
PP+30%PPfiber	77	10^{-13}	129.58	0.73 10^{-6}	1 10^{3}
PP+40%PPfiber	67	10^{-13}	129.58	0.82 10^{-6}	8 10^{1}
PP+50%PPfiber	61	10^{-13}	129.58	0.92 10^{-6}	1.5 10^{1}

Table 5. Dynamical-mechanical properties for PP+ fiber glass composites

Samples	σ, MPa (T=183K, τ=1sec)	τ_0, sec	U_0, kJ/mole	γ, kJ/mole $(MPa)^{-1}$	τ, sec (σ=70 MPa, T=183K)
Pure PP	77	10^{-13}	152.57	1.39	8 10^{2}
PP+0.1% fiber glass	84	10^{-13}	152.57	1.25	1 10^{5}
PP+0.3% fiber glass	90	10^{-13}	152.57	1.19	5 10^{6}
PP+0.5% fiber glass	95	10^{-13}	152.57	1.14	1 10^{9}
PP+0.7% fiber glass	90	10^{-13}	152.57	1.19	5 10^{6}
PP+1% fiber glass	84	10^{-13}	152.57	1.25	1 10^{5}
PP+5% fiber glass	72	10^{-13}	152.57	1.50	10

Table 6. Electric strength for PP+fiber glass composites

Samples	E, 10^{6} V/m (T=293K, τ=1sec)	τ_0, sec	W_0, kJ/mole	χ, kJ/mole $(V/m)^{-1}$	τ, sec (E=40 10^{6} V/m, T=293K)
Pure PP	62	10^{-13}	129.58	0.9 10^{-6}	3.5 10^{3}
PP+0.1% fiber glass	66	10^{-13}	129.58	0.82 10^{-6}	9 10^{3}
PP+0.3% fiber glass	72	10^{-13}	129.58	0.77 10^{-6}	3 10^{4}
PP+0.5% fiber glass	83	10^{-13}	129.58	-0.7 10^{-6}	2 10^{5}
PP+0.7% fiber glass	75	10^{-13}	129.58	0.75 10^{-6}	7 10^{4}
PP+1% fiber glass	56	10^{-13}	129.58	0.99 10^{-6}	3.5 10^{2}
PP+5% fiber glass	49	10^{-13}	129.58	1.07 10^{-6}	9 10^{4}

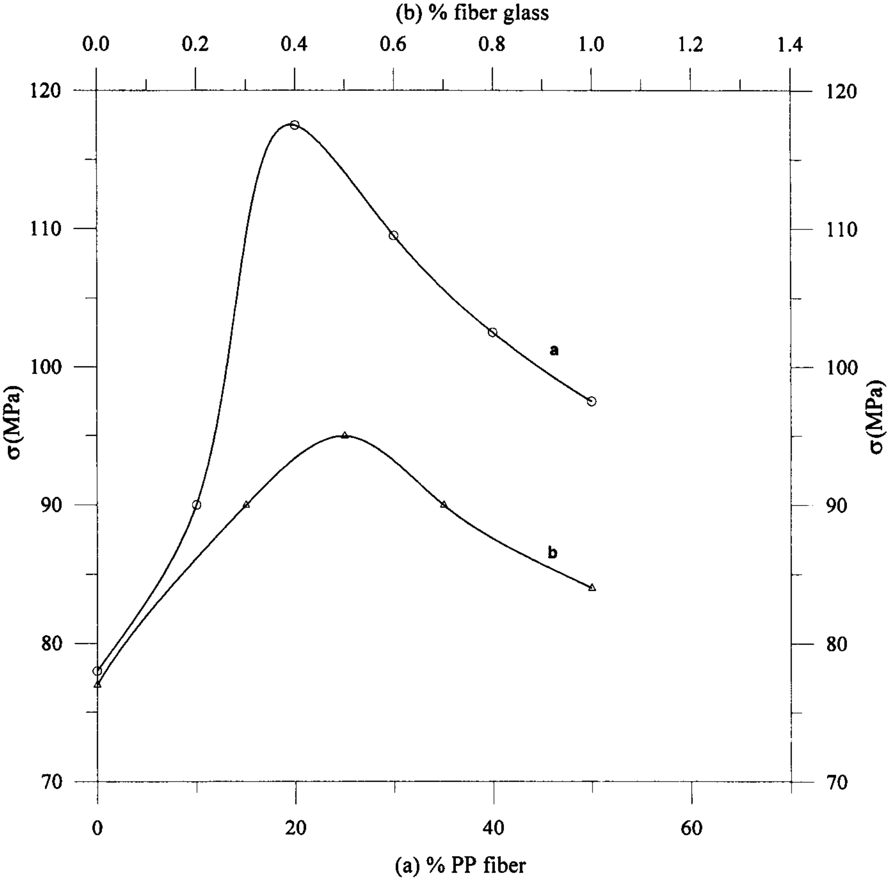

Figure 4. At T_d =183K and τ =1sec., the dependences of σ on the amount of dopings:

a) for PP+PP fibers composites,

b) for PP+fiber glass composites

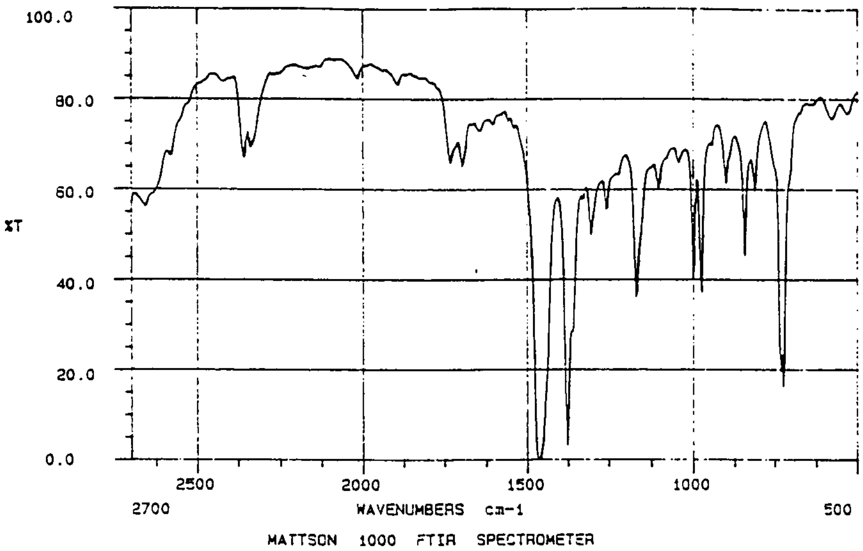
100.0
80.0
60.0
40.0
20.0
0.0
%T
2500
2000
1500
1000
2700
WAVENUMBERS cm-1
500
MATTSON 1000 FTIR SPECTROMETER

Figure 5

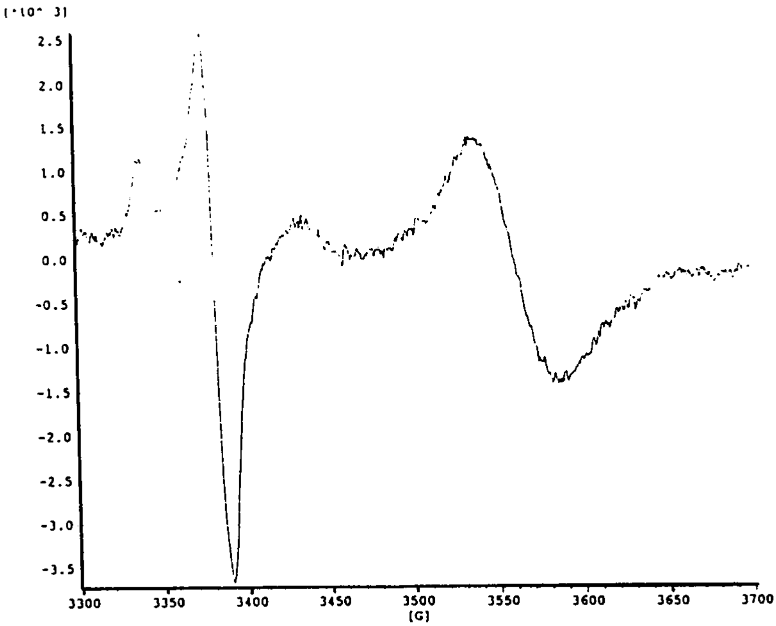
[*10^ 3]
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
3300
3350
3400
3450
3500
3550
3600
3650
3700
[G]

Figure 6a

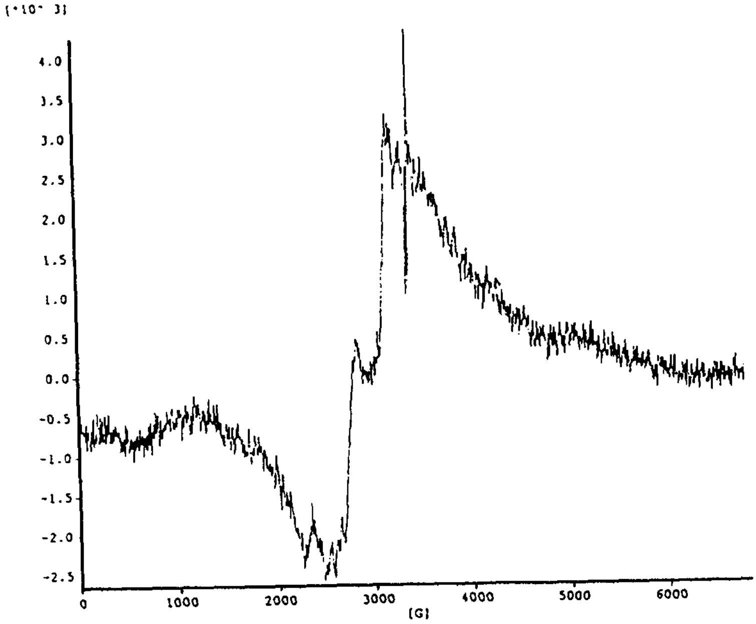
[*10^ 3]
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
0
1000
2000
3000
4000
5000
6000
[G]

Figure 6b

ratio (S/V) that we had previously presented[4)]. As seen from the results, PP fibers dopings construct polymer-polymer composites and plays a filler role, and also change molecular and supramolecular formations (SMF). As seen from fig.5, the IR spectra of both components are observed separately. This event is understood by the exact observation of the peak peculiar for PE in the wave number range from 715 to 731 cm^{-1}. The other peaks cover one another and their intensities increases very slightly. However, it is thought that the very small amounts of dopings are subjected to the chemical effects at the boundaries of supramolecular formations. Fiber glass, as we had previously observed, plays the role of anorganic dopings and affects chemically until it forms a monolayer at the boundaries of SMFs (0,2-0,5 %) and furthermore it forms a 2nd phase at the amounts greater than those, and also hinders the growth and arrangement of SMFs.

It can be said from the experimental results below that fibrillar and glass dopings are subjected to the chemical effects at the boundaries of SMFs as well. Indeed, for the PP fibers dopings, a spin resonance spectrum is observed in the magnetic field appropriate to the g-factor with free radicals (figure 6a). On the other hand, the spin resonance signals appropriate both to free- radicals and to the peroxide radicals are observed for the PE (or PP) specimens taken from the different parts of extruder(figure 6b). Consequently, when PP fiber doping are added to PP or PE, in addition to the other processes, the chemical effects with free-radicals are possible.

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