

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

## Interfacial Effects on the Magnetic Susceptibility of PMMA Composites

A. Tawansi<sup>a</sup>; H. M. Zidan<sup>a</sup>

<sup>a</sup> Dept. of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt

**To cite this Article** Tawansi, A. and Zidan, H. M.(1991) 'Interfacial Effects on the Magnetic Susceptibility of PMMA Composites', *International Journal of Polymeric Materials*, 15: 1, 45 – 56

**To link to this Article:** DOI: 10.1080/00914039108031520

**URL:** <http://dx.doi.org/10.1080/00914039108031520>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Interfacial Effects On The Magnetic Susceptibility Of PMMA Composites

A. TAWANSI and H. M. ZIDAN

*Dept. of Physics, Faculty of Science, Mansoura University, Mansoura 35516, Egypt*

*(Received July 17, 1990)*

Polymethylmethacrylate composites filled with various fractions of Fe, Co,  $Y_3Fe_5O_{12}$ ,  $Er_3Fe_5O_{12}$  and  $YbFe_5O_{12}$  were prepared by casting method. The prepared samples were thermally analysed by differential scanning calorimetry. The magnetic susceptibility was measured in the temperature range of 80–470 K. The behaviour of the room temperature susceptibility (RTS), as a function of the filler content, did not obey the magnetic dilution model (MDM). A reasonable agreement was found between the RTS and a previously suggested theoretical model. The variance between the experimental results and those of MDM was attributed to a long range ferromagnetic interaction between the moment of the filler particle and the spin moment of non classical polymeric segments in the interfacial regions. The nonclassical segments may be arised from benzylradical (due to benzene solvent) or from the one dimensional PMMA alternant.

**KEY WORDS** PMMA composites, magnetic susceptibility, interfacial effects, polymeric keeper for garnets.

## 1. INTRODUCTION

Apart from some works,<sup>1–4</sup> the magnetic properties of polymeric composites filled with transition metals have been largely neglected. Investigation of such composites makes the problem of magnetic order more suitable for consideration as amorphous magnetism.<sup>3</sup> The magnetic properties of a material can provide important details of its electronic structure. The temperature dependence of the magnetic susceptibility ( $\chi$ ), of samples loaded with various contents of metallic powder, are of interest in reference to the role of the induced defects (in the polymer chains) in the electronic structure of composites. It is worthy to explore the influence of such induced defects on the magnetic properties of composites. Therefore, in the present work we have investigated the temperature dependence of  $\chi$  for five systems of PMMA composites filled with various contents of: Fe, Co,  $Y_3Fe_5O_{12}$ ,  $Er_3Fe_5O_{12}$  and  $YbFe_5O_{12}$ .

## II. EXPERIMENTAL

The studied PMMA composites were prepared by casting method as follows.<sup>5</sup> PMMA material was dissolved in benzene. The filler powder (of particle

size  $\approx 40 \mu\text{m}$ ) was added and the mixture was cast to a glass dish and kept in a dry atmosphere at  $30^\circ\text{C}$  for two weeks. Composite films (200–600  $\mu\text{m}$  thick) were obtained. The magnetic susceptibility was measured using a Faraday pendulum technique<sup>6</sup> with accuracy of 3%. Differential scanning calorimetry (DSC) was carried out using a thermoanalyser (GDTD 16-Setaram) with a temperature range of  $-193$  to  $1200^\circ\text{C}$ , heating rate of  $9^\circ\text{C min}^{-1}$ , and sensitivity  $2.5 \mu\text{V}$ .

### III. RESULTS AND DISCUSSION

#### III.A. Thermal analysis

Figure 1 depicts the differential scanning calorimetry (DSC) plots for PMMA free from and filled with 5, 40, 60 and 80 wt% Fe. It is clear that all of the mentioned plots exhibit approximately the same characterizing transition temperatures. This implies that the present additives do not change the main structure of PMMA. The observed transitions can be assigned as follows.

The  $T_{gg}$  endotherms (at 340–352 k) may be arised from the rotation of the ester sidegroup about the C–C bond which links it to the main-chain.<sup>7</sup> The corresponding experimental activation energy<sup>8</sup> is 17 k cal./mole. According to the work of Koppelman,<sup>9</sup> there is an interaction between the main-chain submolecule motion and the ester group rotation, so this transition of the sample.

The  $T_g$  endotherms (at 400–416 k) can be assigned to the glass-rubber transition due to the microbrownian motion of main chain segments, submolecules containing about 50–100 C-bonds. The glass transition temperature is strongly dependent on the thermal history of the sample.

At  $T_1$  endotherms (544–547 k) the viscoelastic fluid becomes viscous. This transition involves large scale mobility of large parts of the polymer chains. Probably there is a structural change at  $T_1$ , but it has not been verified yet.

The endothermic transitions (576–583 k) may refer to dissociation of the polymeric material. Table I lists the values of the transition temperatures denoted in Figure 1.

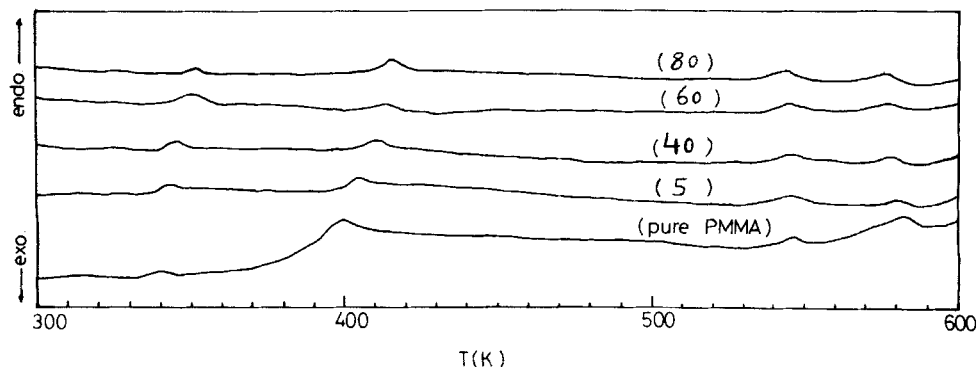


FIGURE 1 DSC plots of pure PMMA and PMMA composites loaded with various volume fractions of Fe.

TABLE I

Values of the transition temperatures shown in Figure 1

Fe Wt%	$T_{gg}$ (K)	$T_g$	$T_i$	$T_d$
pure	340	400	547	583
5	343	405	546	580
40	346	411	545	578
60	351	414	547	577
80	352	416	545	576

### III.B. Magnetic susceptibility

*B.i. PMMA composites filled with Fe* Figures (2, 3) show the temperature ( $T$ ) dependence of the magnetic susceptibility ( $\chi$ ) for PMMA composites loaded with various contents of Fe in the temperature ranges of 90–300 and 300–470 K respectively. It is clear that  $\chi$  increases slightly with  $T$  in the glassy range. For  $T > T_g$  a broad bending is observed in the  $\chi(T)$  behaviour. The plots of susceptibility  $\chi$  (measured at 300 K) as a function of Fe content, (up to  $y = 10$  wt%) are shown in Figure 4. The experimental data were fitted to a previously suggested model<sup>10</sup> in which the susceptibility can be expressed as a step function

$$\chi(Y) = \frac{\chi_0}{2} (1 + \tanh((Y - Y_0)/\Delta Y)) \quad (1)$$

where  $\Delta Y$  measures the sharpness of the step,  $Y_0$  signals the closing of the energy gap,

$$\chi_0 = \mu_B^2 N(E_F)$$

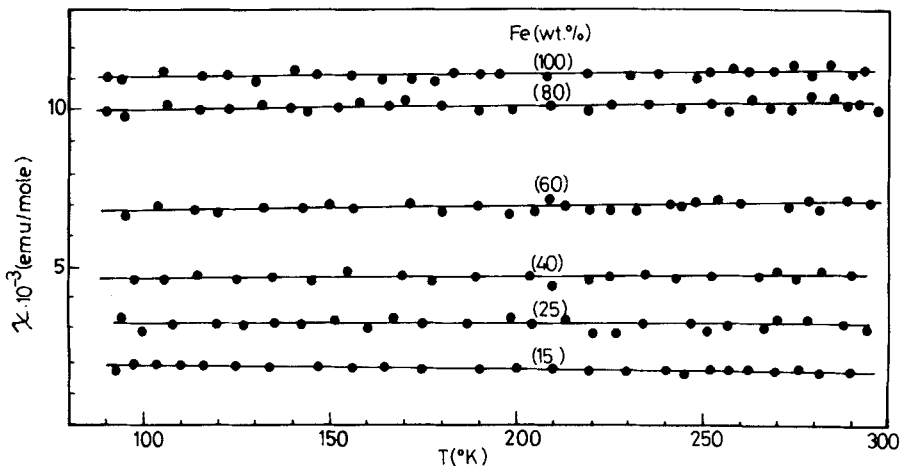


FIGURE 2 The temperature dependence of  $\chi$  for PMMA composites loaded with Fe in the low temperature range.

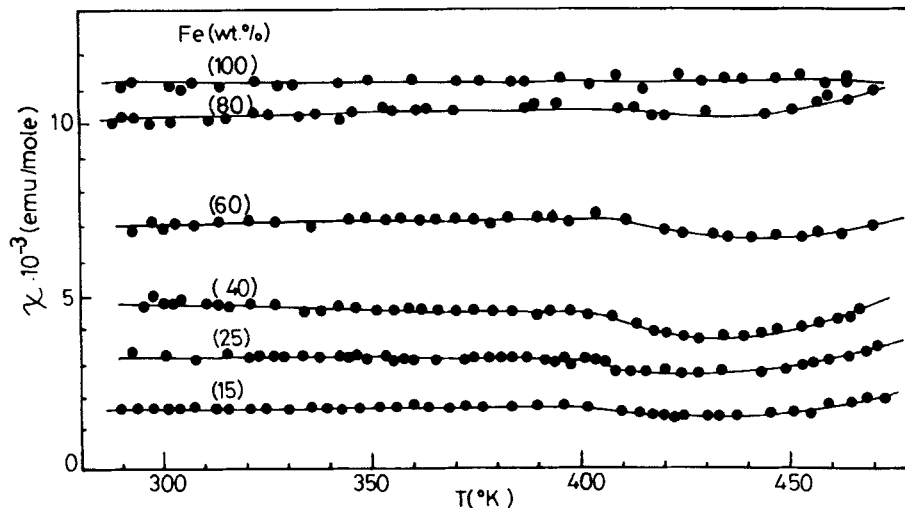


FIGURE 3 As in Figure 2, but for the high temperature range.

is the Pauli susceptibility in the metallic state,  $\mu_B$  is the Bohr magneton and  $N(E_F)$  is the density of states at the Fermi energy  $E_F$ . Thus, in terms of the known linear morphology of PMMA,<sup>11</sup> the demonstration of the nonuniform doping suggests a concentration gradient across the main chain diameter with the center essentially undoped.<sup>10</sup> The present experimental results imply that in the limit of uniform doping  $\chi(Y)$  remains small for  $Y < Y_0$  and then rises rapidly for  $Y \sim Y_0$ .<sup>12</sup>

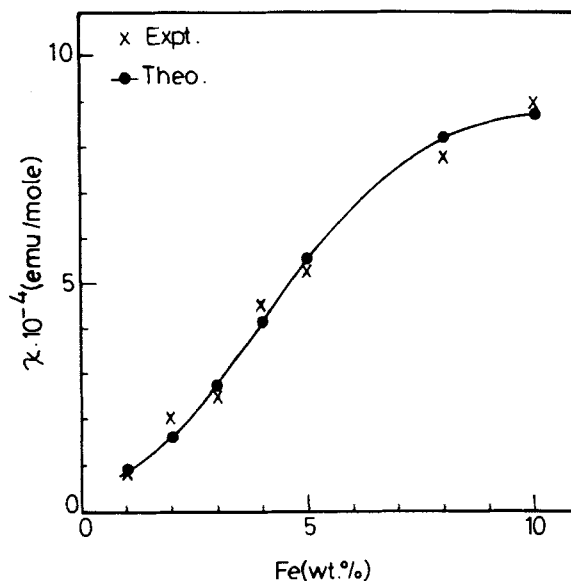


FIGURE 4 The effect of the low Fe-content on  $\chi$  for PMMA composites. (The theoretical parameters are  $\Delta y = 0.03$ ,  $y_0 = 0.042$  and  $\chi_0 = 8.92 \times 10^{-4}$  emu/mole).

The effect of higher metallic contents of  $\chi$  are shown in Figure 5. It is interesting to notice that the experimental values of  $\chi$ , for  $Y > 10$  wt%, exhibit a reasonable fitting to Eq. (1) with different values of the model parameters.

In Figure 6 the experimental plots of  $\chi$  are compared with the plots of the calculated susceptibility according to the magnetic dilution model. It is clear that the experimental values of  $\chi$  exceed the calculated ones, which suggests a ferromagnetic interaction between the metallic particles and the polymeric matrix. For a more quantitative explanation the effective magnetic moments ( $\mu_e$  and  $\mu_d$ ) were calculated using the experimental and magnetic dilution values of  $\chi$  respectively, and applying the following known formula

$$\mu = 2.84\sqrt{\chi T} \quad (2)$$

Both of  $\mu_e$  and  $\mu_d$  are plotted as functions of  $Y$  in Figure 7. The difference ( $\mu_s$ ) between  $\mu_e$  and  $\mu_d$  is plotted as a function of  $Y$  in Figure 8. It is clear from this figure that there is a threshold at  $y = 17$  after which there are nonzero values for  $\mu_s$ . Moreover  $\mu_s$  exhibits a peak value at  $Y = 73$  wt%.

It is important to identify the origin of the magnetoactivity of the polymeric matrix. Taking in consideration that the pure PMMA is a diamagnetic material, one may think that the magnetoactivity of the loaded PMMA arises from the polymeric shell in the close vicinity of the metallic particle.<sup>13</sup> It is thought that this shell consists of an alternant non-classical polymeric fragments. An alternant homonuclear system may be represented by two sub-systems of starred and

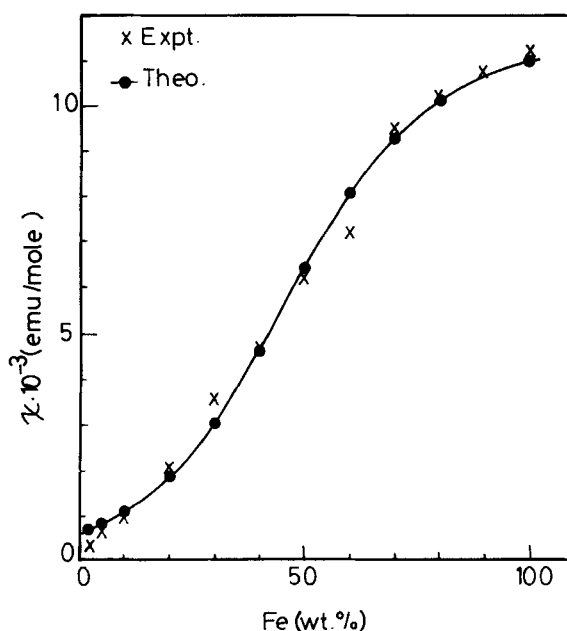


FIGURE 5 The dependence of  $\chi$  on Fe-content for PMMA composites. (The theoretical parameters are  $\Delta y = 0.32$ ,  $y_0 = 0.46$  and  $\chi_0 = 11.38 \times 10^{-3}$  emu/mole).

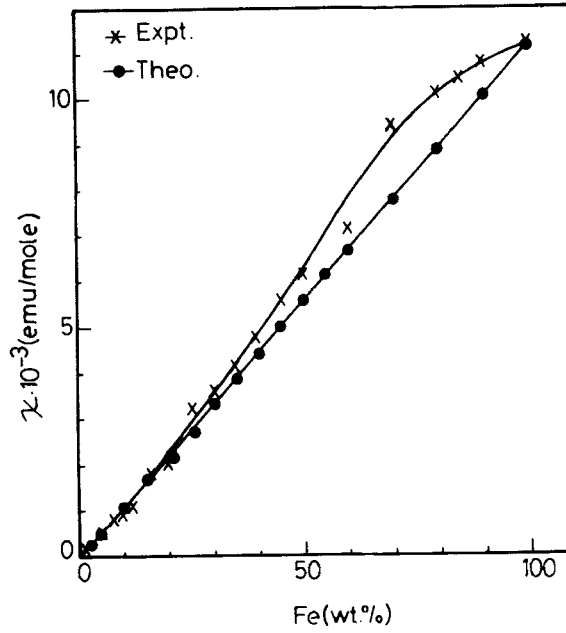


FIGURE 6 The effect of Fe-content on the experimental and magnetic dilution values of  $\chi$ .

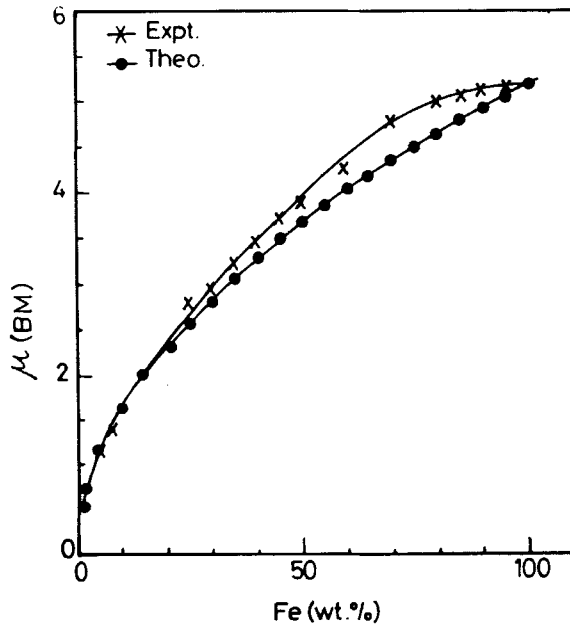


FIGURE 7 The effect of the Fe-content on the effective magnetic moment (calculated from the experimental and magnetic dilution values of  $\chi$ ).

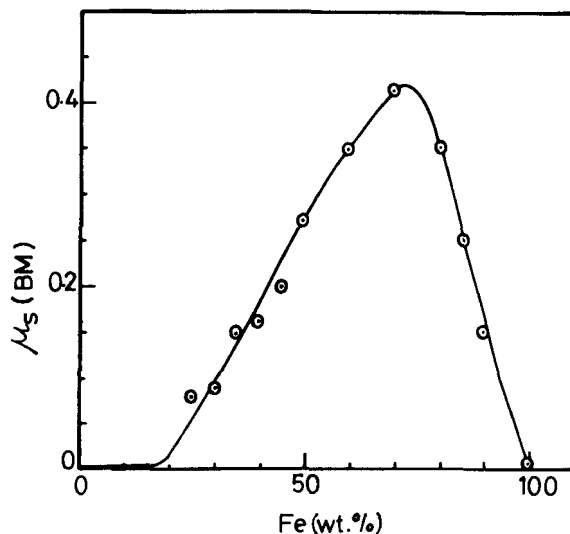


FIGURE 8 The dependence of  $\mu_s$  on Fe-content for PMMA composites.

non-starred atoms, respectively, so that every starred atom is connected to non-starred atom and vice versa.<sup>14</sup> Although polyradicals, these polymers have a considerable delocalization energy which may determine their relative stability. The energy characteristics of the polymers are strongly determined by the electron spin distribution of the degenerate nonbonding molecular orbitals, the full spin configuration,  $S > 0$ , is favoured. The spin densities depend on the electron correlation and alternate; this corresponds to a ferrimagnetic state of the polymer at 0°K.<sup>15</sup>

An alternant hydrocarbon with  $R$  starred and  $S$  nonstarred carbon atoms is a nonclassical system. It has at least  $|R - S|$  degenerate non-bonding molecular orbitals (NBMO). As an example may serve the benzylradical, where  $R - S = 4 - 3 = 1$ , see Figure 9a. It is remarkable that benzene is used as a solvent for the investigated composites in the present work. Thus benzene acts as a source of benzyl-radical in the shells closed to the metallic particles. Moreover, according to Figure 9b, PMMA itself may act as a one dimensional alternant nonclassical polymer in the mentioned shell.

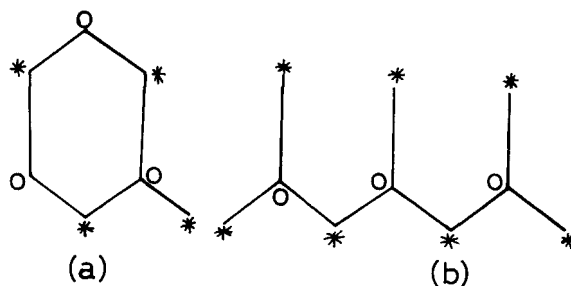


FIGURE 9 Alternant non-classical systems: a) the benzyl radical b) one dimensional polymer.<sup>15</sup>



*B.ii. PMMA composites filled with garnets* The present section is devoted to offer an evidence that PMMA can be used as a good keeper for rare earth iron garnets (REIG). For this purpose the following fillers were selected:  $Y_3Fe_5O_{12}$ ,  $Er_3Fe_5O_{12}$  and  $YbFe_5O_{12}$ . These materials are interesting because of their technological wide applications.<sup>16</sup>

Magnetic susceptibility measurements, over the temperature range 90–480°K, are made on PMMA composites loaded with various REIG contents, and the results are shown in Figures 10–15. It is clear from these figures that temperature dependence of  $\chi$  for composites loaded with 60 wt% REIG exhibits a similar trend to that of pure REIG. Slight decrease of  $\chi$  as a function of  $T$  was observed for composites loaded with 4 and 20 wt% REIG, except for the case of ErIG at  $T < 185$  K. The effective magnetic moment  $\mu_e$  was calculated at 300 K for each sample using Eq. (2) and the results are listed, together with the corresponding theoretical values  $\mu_d$  according to the dilution model, in Table (II). The results in this table imply that PMMA can be considered as a good keeper for REIG for the magnetic susceptibility. The observed difference between  $\mu_e$  and  $\mu_d$  is reasonably attributed to the magnetoactivity of the polymeric shell in the close vicinity of the garnet particles, discussed in section (B.i.).

It could be concluded that the polymeric thin shell, formed in the close vicinity of the filler particles, plays an important role in the magnetic properties of the

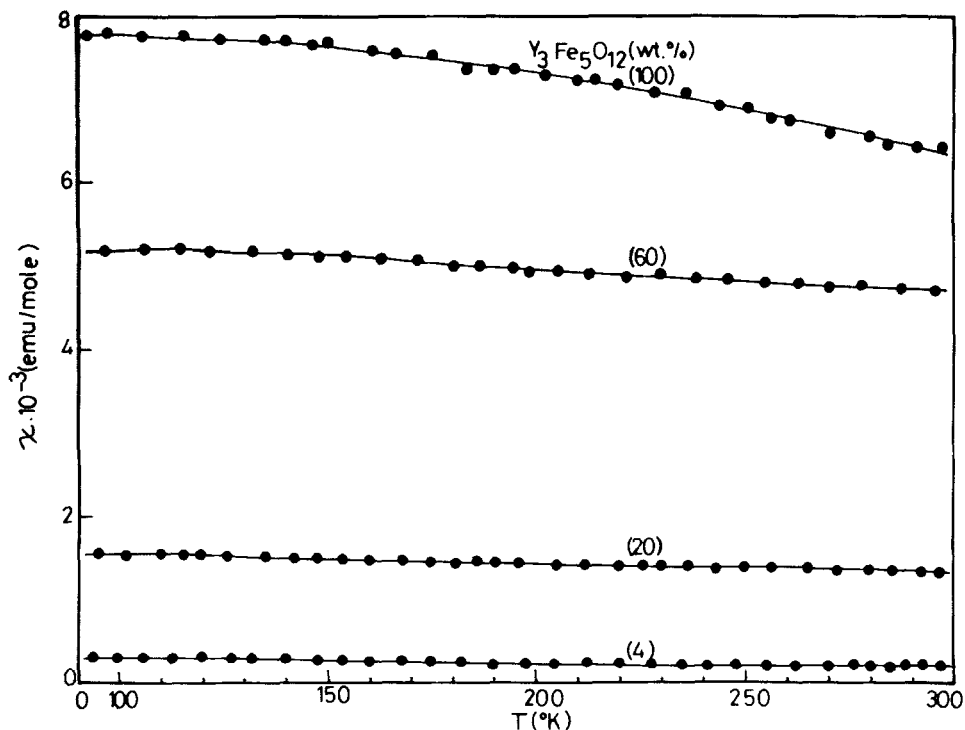


FIGURE 10 The temperature dependence of  $\chi$  for PMMA composites loaded with  $Y_3Fe_5O_{12}$  in low temperature range.

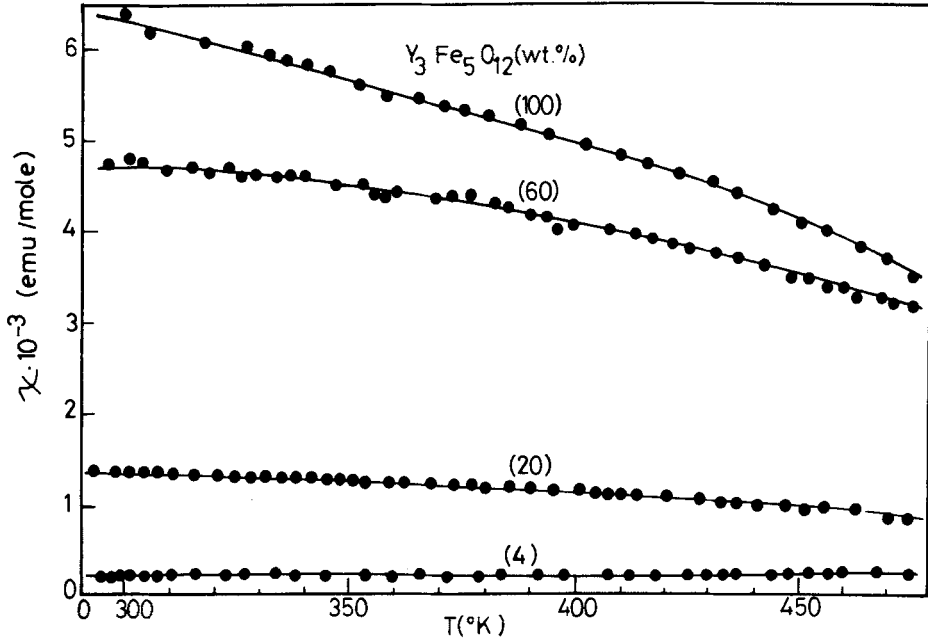


FIGURE 11 As in Figure 10, but in high temperature range.

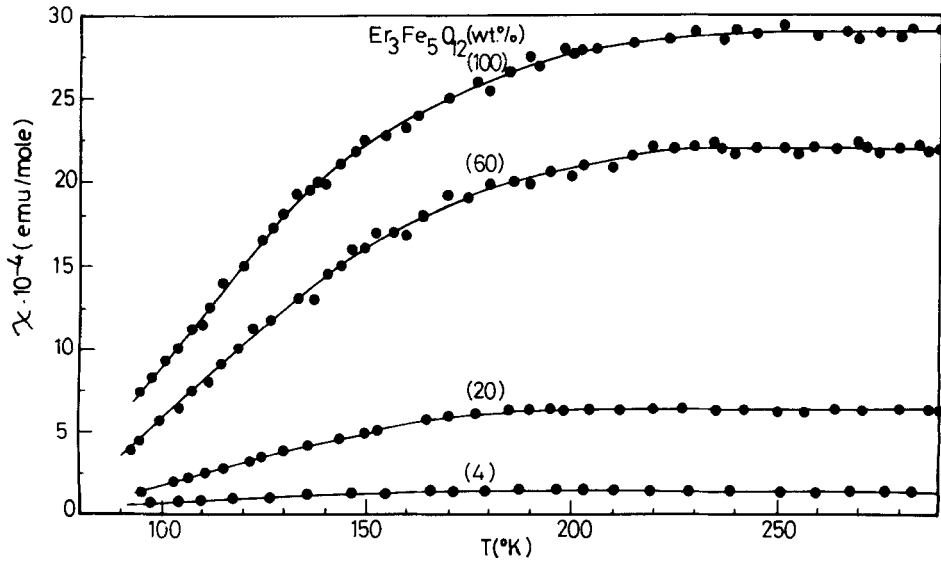


FIGURE 12 The temperature dependence of  $\chi$  for PMMA composites loaded with  $Er_3Fe_5O_{12}$  in low temperature range.

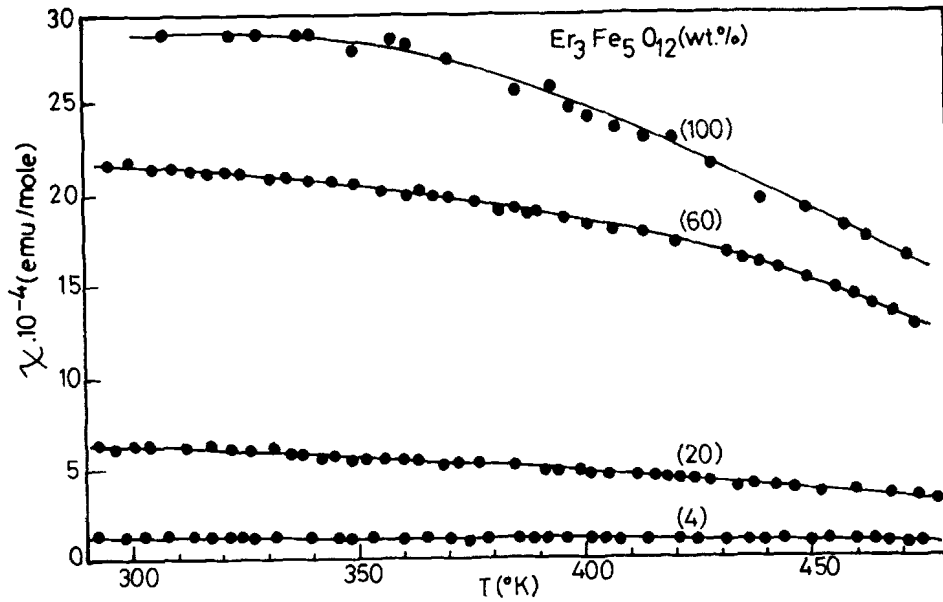


FIGURE 13 As in Figure 12, but in high temperature range.

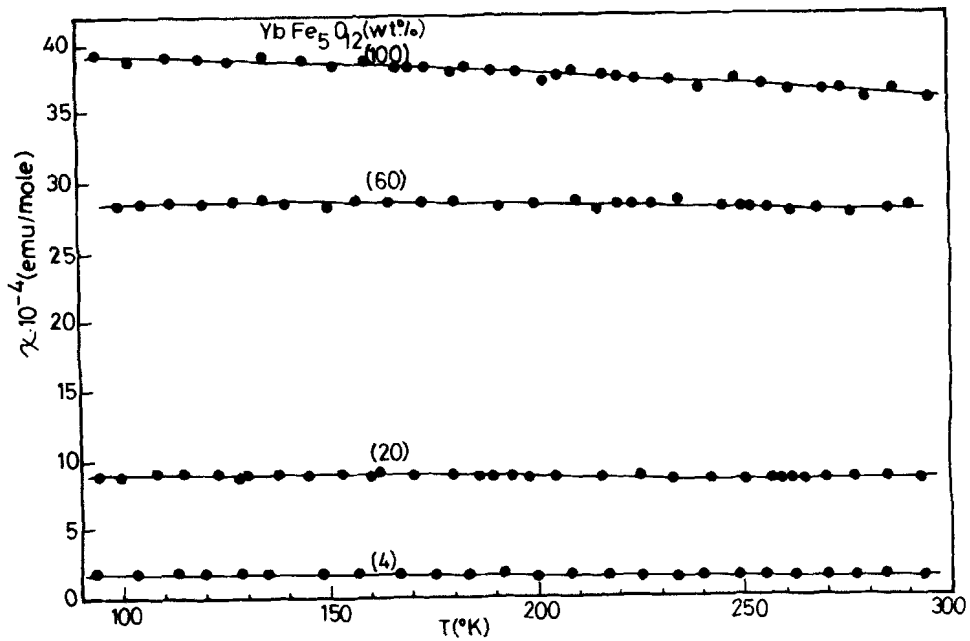


FIGURE 14 The temperature dependence of  $\chi$  for PMMA composites loaded with  $\text{YbFe}_5\text{O}_{12}$  in low temperature range.

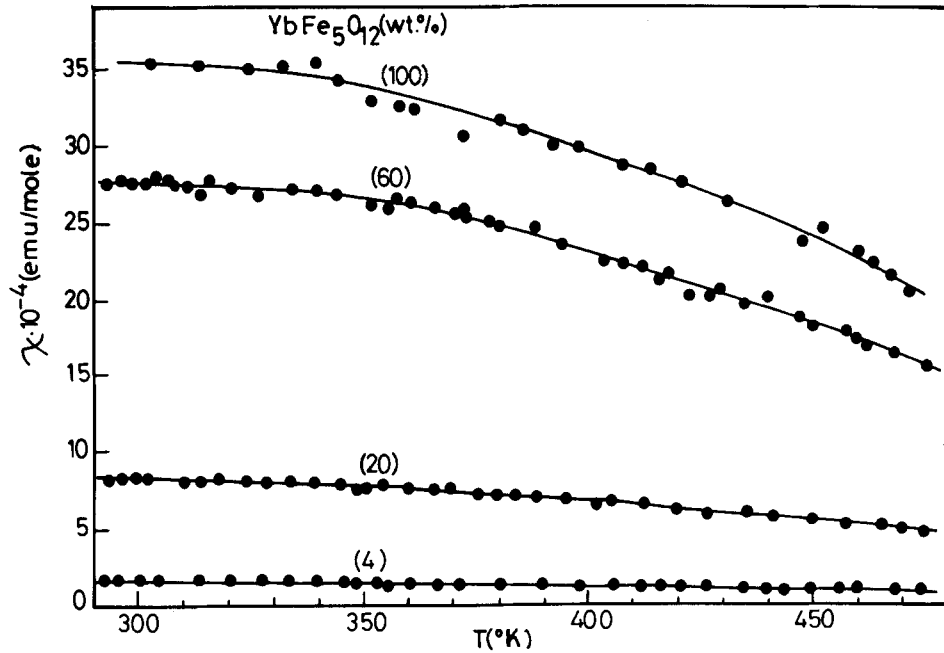


FIGURE 15 As in Figure 14, but in high temperature range.

TABLE II

Values of calculated and determined magnetic moments for PMMA composites filled with garnets

EIG wt%	$\mu_d$ (BM)	$\mu_e$ (BM)	$\mu_s$ (Bm)
100	$2.65 \pm 0.025$	$2.65 \pm 0.025$	0
60	2.05	2.31	+ 0.26
$\text{Er}_3\text{Fe}_5\text{O}_{12}$ 20	1.19	1.22	+ 0.03
4	0.54	0.53	- 0.01
100	2.93	2.93	0
60	2.27	2.58	+ 0.31
$\text{YbFe}_5\text{O}_{12}$ 20	1.33	1.36	+ 0.03
4	0.582	0.602	+ 0.02
100	3.9	3.9	0
60	3.02	3.365	+ 0.345
$\text{Y}_3\text{Fe}_5\text{O}_{12}$ 20	1.760	1.782	+ 0.022
4	0.780	0.753	- 0.027

composites. This is due to the probable formation of nonclassical polymeric segments. However PMMA can be used as a good keeper for REIG filler.

## References

1. V. K. Imshennik, I. P. Suzdalev, L. Bogner, A. Ogradink and F. J. Lius, *J. Phys. (Paris)*, **37**, Colloq. 6, C6-751, (1976).

2. J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli and H. D. Gillman, *Phys. Rev.* B12, 356 (1975).
3. J. M. D. Coey, *J. Appl. Phys.* **49**, 1646 (1978).
4. C. T. Meyer *J. Phys. (Paris)* **37**, Colloq. 6, C6-777 (1976).
5. A. Tawansi, M. D. Migahed and M. I. A. El-Hamid, *phys. D: Appl. Phys.*, **20**, 766 (1987).
6. A. Tawansi, "Magnetic properties of some alloys containing rare earths an uranium" Ph.D. Thesis, Moscow state University, (1977).
7. J. G. Powles, *J. Polym. Sci.*, **22**, 79 (1956).
8. G. B. Mikhailov, *Uszpehi Khimi*, **24**, 875 (1955).
9. J. Koppelman, *Z. Kolloid*, **175**, 97 (1961).
10. A. J. Epstein, H. Rommelmann, M. A Druy, A. J. Heeger and A. G MacDiarmid, *Solid state commun.* **38**, 683 (1981).
11. A. Strepikheyev, V. Derevitskaya and G. Slonimsky, In "A first course in polymer chemistry" Mir Publishers, Moscow (1971) 354.
12. J. J. Ritsko, E. J. Mele, A. J. Heeger, A. G. MacDiarmid and M. Ozaki, *Phys. Rev. Lett.* **44**, 1351 (1980).
13. G. B. Smith, *J. Phys. D: Appl. Phys.*, **10**, L39 (1977).
14. N. N. Tyutyulkov, O. E. Polansky, P. Schuster, S. H. Karabunarliev, and C. I. Ivanov, *Theoret. Chim. Acta* **67** 211 (1985).
15. N. N. Tyutyulkov, P. Schuster, and O. E. Polansky, *Theoret Chim. Acta* **63** 291 (1983).
16. M. M. Schieber "Nonmetallic magnetic materials" North Holland Publishing Company Amsterdam (1967).