JOURNAL OF MATERIALS SCIENCE 22 (1987) 3417–3420

Rubber-modified polymer composites

A. G. ANDREOPOULOS
Laboratory of Special Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, 42 Patission Street, 106 82 Athens, Greece

G. C. PAPANICOLAOU
Department of Theoretical and Applied Mechanics, NTU of Athens, 5 Heroes of Polytechnion Avenue, GR-157 73 Athens, Greece

The effect of rubber modification on the mechanical properties of a polymer composite consisting of polymethyl methacrylate (PMMA) beads embedded in a PMMA matrix was studied. The synthetic rubber used, a styrene–butadiene copolymer (SBR), was dissolved after mastication into the methyl methacrylate monomer, thus ensuring that rubber dispersion takes place in the matrix phase. The results obtained show that the mechanical properties of the rubber-modified material produced by the technique described are greatly dependent on the total rubber content, since it affects the form and particle size of the dispersed phase.

1. Introduction

The use of acrylic polymers in applications which require the combination of light weight, excellent optical properties, chemical resistance and outdoors stability is very extended. However, these applications are restricted by the brittleness that the polymer presents, due to its elevated glass transition temperature (T_g) [1].

Many methods have been proposed to improve this behaviour, such as plasticization [2], internal plasticization [3–5] or rubber modification [6–8]. For the conventional plasticization, diesters of phthalic anhydride can be used (dibutyl phthalate, etc.). The plasticizer can be added to the acrylic monomer before polymerization or incorporated in the polymer by hot mixing. In both cases a transparent, more or less flexible material results, but the possibility of the plasticizer migrating restricts the servicability of the plasticized materials.

The internal plasticization uses plasticizers with functional groups which can be chemically attached to the acrylic macromolecule. The copolymerization of methyl methacrylate with n-butyl acrylate or diallyl phthalate are typical examples.

The third method, i.e. incorporation of rubber particles into the polymer, seems to be the most interesting because it improves the mechanical behaviour of the material while retaining its optical clarity. The rubber particles can absorb energy by their deformation in the face of a propagating crack and redistribute the stresses to the surrounding matrix, thus dissipating the energy that causes the crack to propagate.

Many factors affect the efficiency of a given type of rubber for improving the impact properties of an acrylic. The chemical nature of the rubber is of primary importance, because in cases where it is too compatible with the matrix, dissolution and dispersion on a molecular scale results. This leads to little or no reinforcement, since the rubber particles become smaller than the radius of the tip of a stress-induced propagating crack [9]. On the other hand, if the rubber is highly incompatible, good adhesion between rubber and matrix cannot be obtained. For example, polybutadiene rubber adheres poorly to a styrene–acrylonitrile copolymer, while a nitrile rubber adheres well to the above copolymer.

The impact strength increases with increasing rubber content, but other properties such as tensile strength and modulus, creep and weather resistance tend to lower values.

The rubber particle size is also an important factor for the efficiency of the modification. If the particle size distribution is wide, i.e. 1 to 20 μm, the large particles tend to reduce the tensile strength and to give a poorer surface finish when compared with a narrow particle size distribution (1 to 5 μm).

Another critical parameter for impact properties is the degree of rubber adhesion to the matrix. Without sufficient adhesion, the energy of a propagating crack can tear a rubber particle and the crack will effectively bypass the particle. A grafting process is commonly used to adhere rubber to the matrix, offering the possibility of using rubbers which are only moderately compatible with the plastic matrix, since the chemical bonding ensures adhesion.

Finally, the molecular weight of the polymer which comprises the matrix is of primary interest. This parameter has to attain medium to high values in order to give good impact properties.

Some factors are also critical for the modification of the optical properties of a rubber-modified material. The dominant parameter for such changes is the refractive index of the continuous and dispersed phase. The effects of semi-compatible polyblending on the optical properties are generally undesirable, leading to transluscent to opaque products. One way to

0022–2461/87 $03.00 + .12

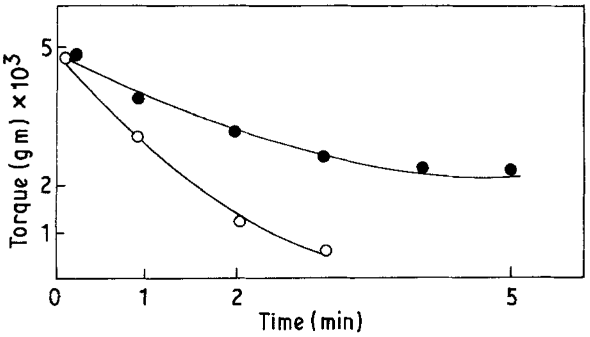

Figure 1 The torque as a function of mastication time. (●) SBR, (○) SBR + 2 p.h.r. MBT.

overcome this problem is to match the refractive index of the matrix to that of the rubber.

Another method to produce transparency is to make the particle size of the rubber phase smaller than the wavelength of visible light (less than 400 nm).

Finally, an additional factor affecting optical properties is related to the uniformity of composition of the polymer material, especially in the case of incorporation of the rubber during polymerization.

2. Experimental procedure

2.1. Materials

A two-component acrylic resin was used for the production of the polymer matrix. The first component is granular acrylic resin, containing an excess of free catalyst (benzoyl peroxide). The second component is essentially methyl methacrylate (MMA) monomer. The two components are mixed in the weight ratio powder : liquid = 2.5 : 1, producing a dough which can be readily polymerized with the application of temperatures above 75° C. The acrylic granules used were DP 300 (ICI Ltd), a polymer with a molecular weight suitable for a quick cure. The MMA was freshly distilled to remove inhibitors or other additives normally present in the monomer. The rubber used as impact modifier was a styrene–butadiene copolymer containing 23.5% styrene structural units (SBR 1507, Shell Chemicals Ltd).

2.2. Specimen preparation and tests

The specimens were prepared after mixing and curing polymer powder and monomer liquid containing different amounts of rubber. Since the viscosity of the solution is of great importance, leading to a more or less efficient wetting of the acrylic granules, the rubber was at first masticated. The mastication leads to chain scission, thus reducing the molecular weight and allowing greater amounts of rubber to be dissolved, retaining simultaneously a low viscosity. The mastication was based on the thermomechanical stressing of rubber which took place in a Brabender Plasticorder working at 140° C, 30 r.p.m. for 5 min. In order to eliminate the free radicals produced a peptizer was added, mercaptobenzothiazole (MBT), to a concentration of 2 p.h.r. (parts per hundred of resin). The mastication process was followed by observing the torque value variations which are related to the melt viscosity and the molecular weight. The curing of the dough was carried out in a heated-plate hydraulic press at 100° C for 20 min. The specimens produced were rectangular sheets and plates of 3 or 13 mm thickness for tensile and compression or impact tests, respectively.

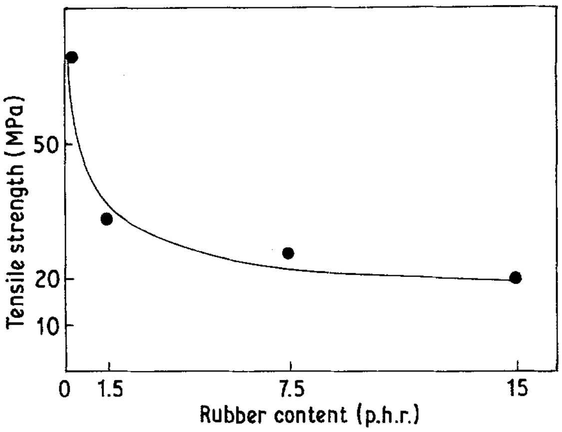

Figure 2 Tensile strength variation with rubber content.

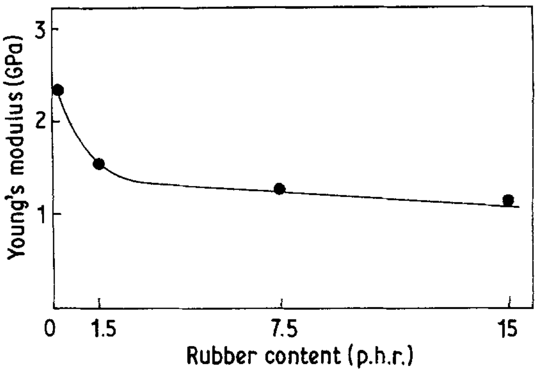

Figure 3 The Young's modulus as a function of rubber content (GPa).

The ASTM D638 and D695 designations were followed for tensile and compression strength, respectively, using an Instron universal testing machine. For the impact tests, the ASTM D256 designation was followed by testing notched bars, according to the Izod method, in a Zwick impact machine.

Scanning electron microscopy was also used to give a picture of the material structure.

3. Results

The torque value, as a function of time, is shown in Fig. 1. It is evident that the torque reaches an equilibrium value after a few minutes. This equilibrium corresponds to equivalent rates of degradation and recombination of free radicals. The presence of peptizer reduces the equilibrium time and leads to lower torque values, i.e. lower molecular weight.

The variation of ultimate tensile strength and modulus of elasticity with the rubber content are presented in Figs 2 and 3. As the curves indicate, there is a decrease in both strength and modulus with increasing rubber content. This effect is clear for relatively low rubber concentrations, then showing a more or less steady behaviour.

The compression measurements are plotted against rubber content in Fig. 4. As the curves indicate, there is at first an increase in elastic modulus and compression

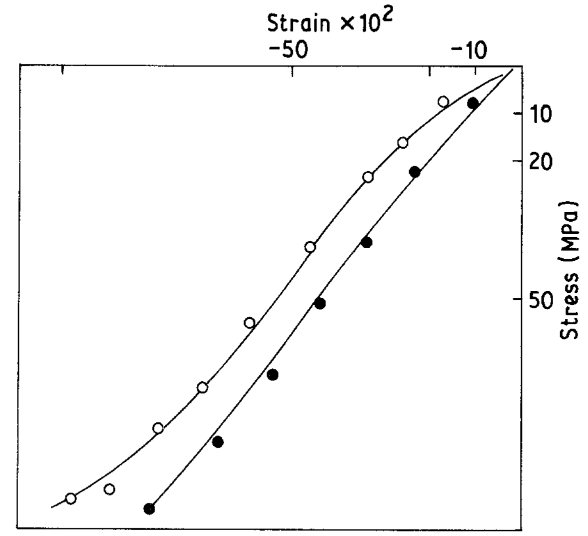

Figure 4 Compressive stress–strain curves of the modified specimens. (●) 1.5 p.h.r. SBR; (○) PMMA, 7.5 and 15 p.h.r. SBR (MPa).

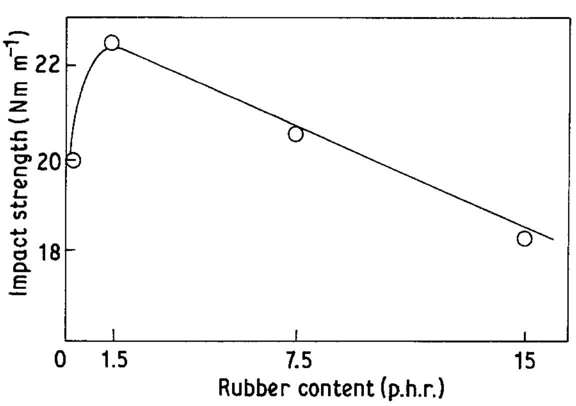

Figure 5 Impact strength as a function of rubber content (Nm m^{-1}).

strength, followed by a decrease as the rubber concentration increases. The curves for 7.5 and 15 p.h.r. rubber concentration are essentially the same as the curve corresponding to the unmodified polymer.

The impact measurements are shown in Fig. 5. An increase is evident for low rubber concentrations, but on increasing the rubber content the impact energy decreases and finally reaches values lower than the strength of the unmodified material.

Finally, the structure of the rubber-modified material for 7.5 p.h.r. rubber content is presented in Fig. 6. The PMMA phase (dark areas) is surrounded by the rubber phase. This is a result of the incorporation procedure followed, i.e. rubber dissolution and the wetting of the PMMA powder by the rubber solution.

The decrease in tensile strength and modulus of elasticity with the rubber content is also referred to by other authors. Roylance *et al.* [10] studied a terpolymer consisting of methyl methacrylate, styrene and acrylonitrile units, modified by particles of butadiene rubber in concentrations up to 13%. The decrease of tensile strength and elasticity modulus with rubber content seems to be rather linear. Similar results were presented by Dickie [11], at least concerning the moduli of elasticity of rubber-modified, glass-reinforced PMMA, but the decrease seems again to follow a rather linear model.

The impact and compression properties of the material show a similar variation, i.e. an increase for relatively low rubber concentrations and then a decrease up to the initial values or less.

The same effect is reported by Silberberg and Han [12] who studied rubber-modified polystyrene. The decrease with increasing rubber content is attributed by the above authors to the improper dispersion of the higher rubber amounts.

In our case the explanation must be found in the technique of rubber incorporation, i.e. the dissolution and then wetting of the acrylic. This technique leads to a rather continuous rubber phase, provided that the total amount of dissolved rubber is sufficient to surround the wetted acrylic granules. Fig. 6 demonstrates this possibility for a relatively high rubber content (7.5 p.h.r.). On the other hand, for lower concentrations the rubber phase is restricted, thus becoming a dispersed phase, where the rubber particles obtain a given size. The above dispersion of the rubber phase is a condition for good mechanical behaviour of the modified material [9, 12], and its optimization, expressed in terms of the rubber particle size distribution, could lead to optimal mechanical results.

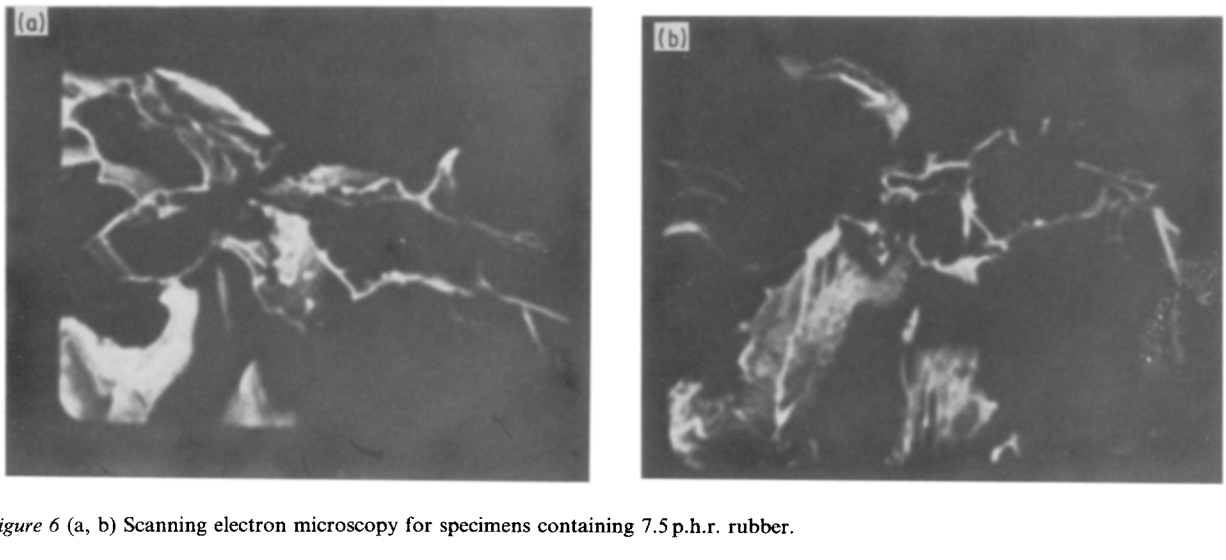

Figure 6 (a, b) Scanning electron microscopy for specimens containing 7.5 p.h.r. rubber.

References

1. J. BRANDRUP and E. H. IMMERGUT, "Polymer Handbook" (John Wiley & Sons, New York, 1975), Vol. III, p. 147.
2. A. G. ANDREOPOULOS and G. L. POLYZOIS, *J. Mater. Sci. Lett.* **3** (1984) 1029.
3. S. L. KIM, M. SKIBO, J. A. MANSON and R. W. HERTZBERG, *Polym. Eng. Sci.* **17** (1977) 194.
4. A. G. ANDREOPOULOS, *J. Mater. Sci. Lett.* **4** (1985) 293.
5. R. E. TOUHSAENT, D. A. THOMAS and L. H. SPERLING, in "Toughness and Brittleness of Plastics", edited by R. D. Deanin and A. M. Crugnola, (American Chemical Society, Washington, DC, 1976) pp. 206–233.
6. R. G. BAUER and P. S. PILLAI, *ibid.* pp. 284–291.
7. C. J. HOOLEY, D. R. MOORE, M. WHALE and M. J. WILLIAMS, *Plast. Rubb. Process. Applic.* **1** (1981) 345.
8. F. F. KOBLITZ, S. D. STEEN, P. R. KULP, R. C. GILL and J. F. GLENN, in "Toughness and Brittleness of Plastics", edited by R. D. Deanin and A. M. Crugnola, (American Chemical Society, Washington, DC, 1975) pp. 292–301.
9. B. BAUM, W. H. HOLEY, H. STISKIN, R. A. WHITE and P. B. WILLIS, *ibid.* pp. 263–283.
10. M. E. ROYLANCE, D. K. ROYLANCE and J. N. SULTAN, *ibid.* pp. 192–205.
11. R. A. DICKIE, *J. Appl. Polym. Sci.* **17** (1973) 2509.
12. J. SILBERBERG and C. D. HAN, *ibid.* **22** (1978) 599.

Received 8 December
and accepted 11 December 1986