The Study of the Relaxation Properties of Recycled Polypropylene Filled with Galvanic Waste

N Skakun¹ A Slavin¹ and M Petunova²
¹Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, Russian Federation
²A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova St. 28, Moscow, Russian Federation

E-mail: nikita_skacun@mail.ru

Abstract. The article shows the influence of the content of galvanic waste with different chemical composition on the physico-mechanical properties of thermoplastic composite material. In this study, samples of a secondary polypropylene filled with 15 wt.% galvanic waste with high content of iron and chromium were analysed. For a detailed evaluation of the mechanical behavior of filled recycled polypropylene, stress relaxation of the samples was tested in a wide temperature range from 20 to 120 degrees Celsius. According to the results of the study a generalized relaxation curve was developed in a special computer program by a parallel shift of initial curve of the stress relaxation along the axis of log(t).

1. Introduction

The main method for disposal of industrial sewage electroplating industry in Russia and abroad is a chemical treatment in which water-soluble toxic compounds are converted to insoluble precipitates (sludge) that are being sent to dumps or burial. Of particular interest are the technical solutions, excluding the disposal of electroplating waste and allowing it to them on the basis of low-toxic commercial products with sales on the market of construction materials.

The construction industry is one of the largest consumers of polymeric materials (12% of total consumption). This is not only due to the unique physico-chemical and physico-mechanical properties of polymeric materials, but also valuable architectural and construction specifications products and designs based on them [7, 5, 9, 8, 11, 12]. They are the closest ratios of the temperature of the human habitat and the ranges of their health. This saves energy consumption for the synthesis of polymers and their processing into products.

Previously it was shown that the introduction of galvanic waste of the two formulations of iron - and chromium-containing 25 wt.% in the secondary polypropylene, does not render strong influence on physical-mechanical properties of the filled material.

The properties of secondary polypropylene depend on the operating conditions of polymer products: the less they have been exposed to external influences, the more their properties close to the properties of the primary polymer. In the operation of polymer products in harsh environments the durability of recycled polypropylene is not more than 60-75% of the durability of the primary polymer. Improving the efficiency of secondary polymers is achieved through the creation on its base
of highly filled polymeric materials [5]. Therefore seemed appropriate to investigate the mechanical behavior of recycled polypropylene filled with electroplating waste.

2. Methods

In order to establish the influence of galvanic waste on the relaxation properties of filled recycled polypropylene were tested for stress relaxation in a wide range of temperatures from 20 to 110 °C, which make up the operating temperature range of polypropylene.

Externally, waste galvanic production represent dispersed powders of unsaturated brown, which were taken by averaging for wastewater treatment electroplating plants. In this work, studies were carried out recycled polypropylene filled with 15 wt.% galvanic waste averaged compositions: the first - with a high content of iron, the second - with a high content of chromium.

Waste electroplating plants before use were dried to constant weight at 80 °C for 3 h, proglivali at 700 °C for 1 h and milled in a planetary ball mill to a particle size of 10-15 µm. Dried and calcined waste galvanic production is a dispersed powders of unsaturated brown.

Filled with secondary polypropylene were obtained by the method of press molding at a pressure of 30-40 MPa and a temperature of 180-190 °C. Electroplating waste mixed with recycled polypropylene melt at a temperature of 160 to 170 °C.

Relaxation behavior of filled recycled polypropylene was investigated in conditions of static stress relaxation on device design Dubov-Regel [6] on samples of size 4x4x6 mm. at a temperature of 20-110 °C and permanent deformation (3%) when the strain rate of 0.75 mm/min. the Obtained curves (figure 1) tension relaxation was rebuilt according to module from the relaxing time which was calculated by the formula:

\[ \sigma_p = \sigma_0 \left[ 1 - \int_0^t \tau d\tau \right] \]  

(1)

where \( \sigma_p \) is the value of relaxing tension, \( \varepsilon \) is the constant deformation.

To obtain the relaxation behavior of filled polypropylene and secondary characteristics calculation approach was used to obtain cores of relaxation, based on consideration of thermodynamic functions and their changes during the relaxation process. using the model in [6] for experimentally obtained dependences of the relaxation was calculated relaxation parameters. They are shown in table 1 and 2.

To calculate the relaxation parameters of recycled polypropylene filled with electroplating waste was used the equation of Boltzmann-Volterra:

\[ \sigma = \sigma_0 \left[ 1 - \int_0^t \tau d\tau \right] \]  

(2)

where \( \sigma \) – relaxing tensione, \( \sigma_0 \) is the initial stress that develops in the end of the "instant" job strain, \( T(\tau) \) – is the kernel of the relaxation, \( \tau \) – is the current time, which runs through values from 0 to t, t is the end time.

3. Results and Discussion

Curves of stress relaxation for recycled polypropylene filled with 15 wt.% iron-containing electroplating waste, measured at various temperatures are shown in Fig. 1. Thus, the lower the temperature, the difference in position of the curves of stress relaxation more pronounced. This means that not only the initial elastic modulus, measured with the rapid job strain, but relaksiruyushaya module throughout the relaxation process for recycled polypropylene filled with always significantly higher than for primary. The reason is, as shown in [5], the formation of a more perfect spherulitic structure in the secondary polypropylene.

From table 1 and 2 shows that the correlation coefficient \( r \) in all cases when using the kernel \( T_1(\tau) \) is always higher than when using the kernel \( T_2(\tau) \). From the considered positions it means that the limiting stage of the relaxation process for filled recycled polypropylene is the rate of interaction of often and move them in nearelectrode material.
The estimated values of $\sigma_0$ for all samples when using the kernel $T_1(\tau)$ is always slightly higher than the experimental one. This is because in the process of setting the warp tension is already beginning to relax, and the estimated value obtained without considering this factor.

**Figure 1.** Curves of stress relaxation recycled polypropylene filled with 15 wt.% iron-containing electroplating waste, measured at different temperatures: 1 – 20°C, 2 – 40°C, 3 – 70°C, 4 – 110°C.

**Table 1.** The parameters of the relaxation process recycled polypropylene, filled with 15 mass% of iron-containing electroplating waste at different temperatures.

| The parameters of the kernels | Test temperature, °C |
|------------------------------|-----------------------|
|                              | 20                    | 40        | 70        | 110       |
| **The core $T_1(\tau)$**    |                       |           |           |           |
| $k$, min$^{-1}$              | 0,01                  | 0,01      | 0,01      | 0,01      |
| $\beta$                      | 0,3                   | 0,2       | 0,2       | 0,2       |
| The correlation coefficient, $r$ | 0,985               | 0,986    | 0,989    | 0,984    |
| $A\cdot10^6$, Дж град/м$^3$ | 2,779E+24             | 3,620E+24 | 6,076E+24 | 3,139E+27 |
| The initial voltage, $\sigma_0$, MPa | 24,221              | 22,158   | 15,394   | 8,811    |
| Quasi-equilibrium voltage, $\sigma_\infty$, MPa | 11,713              | 8,206    | 4,253    | -3,21    |
| **The core $T_2(\tau)$**    |                       |           |           |           |
| $a$                          | 0,05                  | 0,05      | 0,0403    | 0,0403    |
| $\gamma$                     | 0,5                   | 0,5       | 0,5       | 0,5       |
| The correlation coefficient, $r$ | 0,961               | 0,956    | 0,958    | 0,945    |
| $A\cdot10^6$, Дж град/м$^3$ | 6,814E+23             | 6,771E+23 | 1,598E+24 | 3,430E+24 |
| The initial voltage, $\sigma_0$, MPa | 17,352              | 15,546   | 9,748    | 5,135    |
| Quasi-equilibrium voltage, $\sigma_\infty$, MPa | 11,968              | 9,299    | 4,868    | 1,695    |
| **The experimental values**  |                       |           |           |           |
| $\sigma_{нач.}$, MPa         | 20,39                 | 17,69     | 12,346    | 6,998     |
| $\sigma_{180}$, MPa          | 11,354                | 8,515     | 4,434     | 1,307     |

To identify the nature of the change the start and end of relaxing modules with temperature, in Figure 2 shows the dependencies of experimental values $E_{p0}$ and $E_{p180}$ temperature. Here $E_{p0}$ – modulus of elasticity, which develops at the time of the task "instantaneous" deformation; $E_{p180}$ – relaxation modulus observed in the duration of the relaxation process 180 min.

Using the obtained curves of stress relaxation was constructed generalized relaxation curves for filled recycled polypropylene both formulations. As an example, in Fig. 3 shows curves of stress relaxation filled with 15 wt.% iron-containing electroplating waste recycled polypropylene in the coordinates "$E_p – lgt$", where $t$ is the time measured in minutes. For construction of generalized
curves, we used the unconventional technique, which consists in the following. Each relaxation curve determined at different temperatures, is first approximated using the Boltzmann equation when using the kernel $T_1(\tau)$, since this kernel has the largest correlation coefficient close to 1. Then automatically calculated curves were shifted along the axis of the $\text{lg}$ by means of specially written programs MasterCurve. The result was obtained two generalized relaxation curves of the two compounds (Figure 4).

Table 2. The parameters of the relaxation process recycled polypropylene, filled with 15 mass% of chromium electroplating waste at different temperatures.

| The parameters of the | Test temperature , °C |
|-----------------------|-----------------------|
| kernels               | 20    | 40    | 70    | 110   |
| $k, \text{min}^{-1}$  | 0,01  | 0,01  | 0,01  | 0,1   |
| $\beta$               | 0,4   | 0,2   | 0,5   | 0,3   |
| The correlation coefficient, $r$ | 0,979 | 0,991 | 0,967 | 0,973 |
| $A \cdot 10^9, \text{Дж кг град/м}^3$ | 2,953E+24 | 4,512E+24 | 6,823E+24 | 9,753E+23 |
| The initial voltage, $\sigma_0$, MPa | 21,987 | 17,52 | 12,321 | 9,63  |
| Quasi-equilibrium voltage, $\sigma_\infty$, MPa | 10,181 | 6,732 | 3,095  | 2,264 |

| The core $T_2(\tau)$ |
|-----------------------|
| $a$                   | 0,05  | 0,0403| 0,05  | 0,05  |
| $\gamma$              | 0,5   | 0,5   | 0,5   | 0,5   |
| The correlation coefficient, $r$ | 0,946 | 0,964 | 0,918 | 0,768 |
| $A \cdot 10^9, \text{Дж кг град/м}^3$ | 7,679E+23 | 1,355E+24 | 1,512E+24 | 2,819E+24 |
| The initial voltage, $\sigma_0$, MPa | 15,092 | 12,057 | 6,745  | 3,661 |
| Quasi-equilibrium voltage, $\sigma_\infty$, MPa | 10,231 | 7,325 | 3,078  | 2,084 |

| The experimental values |
|-------------------------|
| $\sigma_{\text{нв},}$, MPa | 18,22 | 15,787 | 10,298 | 6,705 |
| $\sigma_{180}$, MPa     | 9,736 | 6,904  | 2,751  | 2,069 |

The resulting curves allow us to predict the relaxation behavior of these polymers on times $10^6 – 10^{18}$ min. clearly shows that the generalized curve-filled recycled polypropylene lies significantly higher than the same curve for the primary polypropylene.

Now it is of interest to find the temperature dependence of the shift factor logat. The most commonly used equation to describe this is the equation of Williams-Landel-ferry (WLF) [6, 7]. According to this equation, the temperature dependence of the shift factor as follows:

$$
\text{lg } a_T = \frac{C_1(T - T_0)}{C_2 + (T - T_0)}
$$

(3)

where $T$ is the temperature, $T_0$ is the temperature of the casting C1 and C2 are material parameters.

Dependence of the logarithm of the shift factor (logaT) from the temperature difference $(T-T_0)$ shown in Fig. 5. A description of these dependencies using equation LWF has shown that for this case it is not satisfied. The most appropriate expression, as shown by our analysis, is a linear relationship.

Filled with secondary polypropylene is significantly tighter than the original, and this is evident not only in the ordinary definition of the modulus of elasticity, but also all over the curves of stress relaxation up to very large durations of this process. From a practical point of view, this means that the
secondary is filled with polypropylene can not only be successfully used for production of different polymeric materials, but also can be used to make more rigid structures that can withstand significant stresses, not softening and not destroyed for a long time.

![Figure 2](image)

**Figure 2** Graphic of dependence of the initial $\varepsilon_{p0}$ (a) and end $\varepsilon_{p180}$ (b) modules from the set temperature recycled polypropylene filled with 15 wt.% galvanic waste: 1 – iron, 2 – chromium.

![Figure 3](image)

**Figure 3.** A summary graph of the generalized curves of the relaxation dependency of recycled polypropylene filled with 15 wt.% galvanic waste: 1 – iron, 2 – chromium.

![Figure 4](image)

**Figure 4.** The dependence of the logarithm of the shift factor of the temperature difference $T-T_0$ for recycled polypropylene filled with 15 wt.% galvanic waste: 1 – iron, 2 – chromium.

4. **Conclusions**

Thus, the conducted researched-filled recycled polypropylene the use of galvanic waste for production of composite materials based on recycled polypropylene contributes to the increased modulus of elasticity and strength, reduce deformability of materials. Galvanic waste allow to obtain a composite building materials based on polyolefin wastes consumption with high performance properties. The optimum content of waste galvanic production, as filler in construction products from recycled polypropylene, obtained by extrusion is ~15 mass%.

**References**

[1] Hanna J. G., Siggia S. 1962 Primary and secondary hydroxyl group content of polypropylene glycols *Journal of Polymer Science Part A: Polymer Chemistry* vol. 164 pp. 297-304.

[2] Rong M. Z. et al. Structure–property relationships of irradiation grafted nano-inorganic particle

[3] Silva A. C., Mello-Castanho S. R. H. 2007 Vitrified galvanic waste chemical stability *Journal of the European Ceramic Society* vol. 2 pp. 565-570.
[4] Walawaska B., Kowalski Z. 2000 Model of technological alternatives of production of sodium chromate (VI) with the use of chromic wastes Waste Management vol. 8 pp. 711-723.

[5] Martsul V. N. et al. 2012 Some applications of galvanic manufacture waste.

[6] Tocháček J. 2004 Effect of secondary structure on physical behaviour and performance of hindered phenolic antioxidants in polypropylene Polymer degradation and stability vol. 2 pp. 385-389.

[7] Dudić D., Djoković V., Kostoski D. 2004 The high temperature secondary crystallisation of aged isotactic polypropylene Polymer testing vol. 6 pp. 621-627.

[8] Tsuchiya Y., Sumi K. 1969 Thermal decomposition products of polypropylene Journal of Polymer Science Part A: Polymer Chemistry vol. 7 pp. 1599-1607.

[9] Bockhorn H. et al. 1999 Kinetic study on the thermal degradation of polypropylene and polyethylene Journal of Analytical and Applied Pyrolysis vol. 2 pp. 93-109.

[10] Sakurada I., Nukushina Y., Ito T. 1962 Experimental determination of the elastic modulus of crystalline regions in oriented polymers Journal of Polymer Science Part A: Polymer Chemistry vol. 165 pp. 651-660.

[11] Jancar J., Dibenedetto A. T. 1994 The mechanical properties of ternary composites of polypropylene with inorganic fillers and elastomer inclusions Journal of materials science vol. 17 pp. 4651-4658.

[12] Hanna J. G., Siggia S. 1962 Primary and secondary hydroxyl group content of polypropylene glycols Journal of Polymer Science Part A: Polymer Chemistry vol. 164 pp. 297-304.

[13] Kawasumi M. et al. 1997 Preparation and mechanical properties of polypropylene–clay hybrids Macromolecules vol. 20 pp. 6333-6338.

[14] Karger-Kocsis J. (ed.). 2012 Polypropylene structure, blends and composites: Volume 3 composites. – Springer Science & Business Media.

[15] Natta G., Corradini P. 1960 Structure and properties of isotactic polypropylene Il Nuovo Cimento (1955-1965) vol. 15 pp. 40-51.

[16] Manchado M. A. L. et al. 2005 Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing Carbon vol. 7 pp. 1499-1505.

[17] Torras J. et al. 2012 Chromium recovery from exhausted baths generated in plating processes and its reuse in the tanning industry Journal of hazardous materials vol. 209 pp. 343-347.

[18] Alves L. C. et al. Environmental valuation of the galvanic solid waste generated in a chroming process.

[19] Rong M. Z. et al. 2001 Structure–property relationships of irradiation grafted nano-inorganic particle filled polypropylene composites Polymer vol. 1 pp. 167-183.