Progress in Polymer Science 39 (2014) 594–626

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Advances in layered double hydroxide (LDH)-based elastomer composites

Debdipta Basu[a,b], Amit Das[a,c], Klaus Werner Stöckelhuber[a], Udo Wagenknecht[a], Gert Heinrich[a,b,*]

[a] Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany
[b] Dresden University of Technology, Institute of Materials Science, 01062 Dresden, Germany
[c] Tampere University of Technology, Department of Materials Science, 33101 Tampere, Finland

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form 15 July 2013
Accepted 22 July 2013
Available online 11 August 2013

Keywords:
Layered double hydroxide
Intercalation
Modification
Elastomer composites
Mechanical properties
Dynamic mechanical properties
Applications

ABSTRACT

This article reviews the advances in layered double hydroxide (LDH) materials and the synthesis of LDH-based elastomer composites. The potential of tuning the structure of LDH materials for desired properties and applications has attracted both academic and industrial interest in recent years. The modification of LDH materials and the use of such materials in the synthesis of composites with different elastomer matrices have been critically analyzed. Emphasis has been given to the use of Mg-Al LDHs and Zn-Al LDHs with different elastomers. The use of modified LDHs with elastomers substantially improves their mechanical, thermal and optical properties. Even "smart properties" of elastomers, such as reversible thermotropic optical characteristics, have been realized with the use of LDH-based multifunctional additives in rubber formulations. The flame retardance of some elastomer composites has also been enhanced with the use of modified LDHs. The possibility of replacing ZnO with LDH during rubber compounding has also been discussed, which would lead to drastic interventions in the well-established rubber processing technologies. LDH materials have also been reported to be biocompatible. Therefore, among the various possible applications of LDHs in different material development processes, their use in rubber technology offers the potential for environmentally friendly rubber products, even tires. Throughout this article, the structure, synthesis, properties and applications of elastomer/(LDH) composites are discussed, including suitable examples taken from the relevant literature.

Abbreviations: LDH, layered double hydroxide; XRD, X-ray diffraction; FTIR, Fourier transformation infra-red; XNBR, carboxylated nitrile butadiene rubber; ZnO, zinc oxide; EPDM, ethylene propylene norbornene diene monomer; EVA, ethylene vinyl acetate; PU, polyurethane; NBR, nitrile butadiene rubber; SSBR, solution styrene butadiene rubber; NR, natural rubber; HT, hydrotalcite; MMT, montmorillonite; DS, dodecyl sulfate; SDS, sodium dodecyl sulfate; DBS, dodecylbenzenesulfonate; SDBS, sodium dodecylbenzenesulfonate; BEHP, bis(2-ethylhexyl) hydrogen phosphate; CLDH, calcined layered double hydroxide; TGA, thermogravimetric analysis; DTG, derivative thermogravimetric; WAXS, wide angle X-ray scattering; TEM, transmission electron microscopy; PVC, poly vinyl alcohol; DMA, dynamic mechanical analysis; AFM, atomic force microscopy; TMTD, tetramethylthiuram disulfide; XZ, carboxylated nitrile butadiene rubber-zinc oxide; XZ-LDH, carboxylated nitrile butadiene rubber-layered double hydroxide; XZ-mLDH, carboxylated nitrile butadiene rubber-modified layered double hydroxide; SD, standard deviation; OLDH, organically modified layered double hydroxide; OMMT, organically modified montmorillonite; CR, chloroprene rubber; Q, silicon rubber; IIR, isobutylene isoprene rubber; TS, tensile strength; EB, elongation at break; LOI, limiting oxygen index; UV–vis, ultraviolet visible spectroscopy; OLED, organic light emitting diode; MDR, moving die rheometer; SSS, sodium styrene sulfonate; NBR-SL, nitrile butadiene rubber-sodium styrene sulfonate-modified layered double hydroxide; NBR-SDL, nitrile butadiene rubber-sodium dodecylbenzene sulfonate-modified layered double hydroxide.

* Corresponding author at: Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany. Tel.: +49 351 4658 360/361; fax: +49 351 4658 362.
E-mail address: gheinrich@ipfdd.de (G. Heinrich).

0079-6700/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.progpolymsci.2013.07.011

Contents

1. Introduction 595
2. Layered double hydroxide 597
    2.1. Structural features and synthesis of layered double hydroxide 597
    2.2. Modification of layered double hydroxide 600
    2.3. Characterization of LDH materials 601
        2.3.1. Characterization of unmodified LDH 601
        2.3.2. Characterization of modified LDH 602
    2.4. Zinc-stearate-modified LDH 606
    2.5. Potential applications of LDH materials 606
3. Elastomer-layered double hydroxide (LDH) composites 608
    3.1. Preparation of elastomer-layered double hydroxide (LDH) composites 608
    3.2. Different LDH-filled elastomer composites 608
        3.2.1. Carboxylated nitrile rubber (XNBR)/LDH composites 608
        3.2.2. Ethylene propylene diene monomer rubber (EPDM)/LDH composites 611
        3.2.3. Chloroprene rubber (CR)/LDH composites 612
        3.2.4. Inorganic silicone rubber (Q)/LDH composites 614
        3.2.5. Ethylene vinyl acetate (EVA)/LDH composites 616
        3.2.6. Poly (1-butene) (PB-1)/LDH composites 617
        3.2.7. Polyurethane-nitrile rubber (PU-NBR) blend/LDH composites 618
        3.2.8. Solution styrene butadiene rubber (SSBR) LDH composites 618
        3.2.9. Acrylonitrile butadiene rubber (NBR)/LDH composites 621
4. Conclusions 622
References 623

1. Introduction

For many decades, elastomers have been an interesting class of materials that can be designed to obtain wide ranges of properties for use in various large- and small-scale applications, such as vehicle tires, conveyor belts, gaskets and seals, hoses, rollers, cable jackets, footwear and fire-proofing materials, among others. It is well known that rubber is rarely used in commercial applications without fillers and chemical cross-linkers; silica and carbon black are currently the most commonly used fillers, and ZnO is the most common cross-linking activator for the vulcanization process. In contrast to other polymer composites, elastomers are a type of material that must be prepared in a very special way. Fig. 1 briefly describes the process for preparing an elastomeric composite. Enhancement in the mechanical properties has been the key feature observed after adding these compounds to rubbers. Enhancements in the properties of the final compound depend largely on the morphological aspects of these fillers, such as their sizes and shapes, and sometimes upon the chemical modification, e.g., the use of a silane coupling agent to modify silica. Elastomeric composites currently have a wide range of applications because of the differences in the structural features of the fillers and activators. However, materials scientists are placing continuous effort into examining elastomeric materials with different fillers and activators with improved physicochemical properties that are dimensionally more suitable. It has been recognized that particulate fillers, such as carbon black with a large specific surface area (high structure), are more effective than spherical carbon black particles in reinforcing rubbers [1]. The large interfacial surface area between the filler and polymer could offer a high degree of interaction with the hydrocarbon polymer, resulting in good abrasion and wear resistance properties. Furthermore, the stiffness of the rubber matrix increases with the use of a filler with a large surface area due to a more developed filler–filler network, and they generate strong hysteresis under dynamic operating conditions. Thus, some physical properties, e.g., the stiffness imparted by a certain mass of filler, are clearly enhanced when the filler aggregates. This effect is attributed to the 'hydrodynamic effect', which is analogous to the effect of a particulate solute on the viscosity of a solution [2–4]. The difficulty in obtaining primary particles from these conventional fillers to contribute toward the reinforcement of rubbers forced scientists to consider some different materials, preferably in a modified

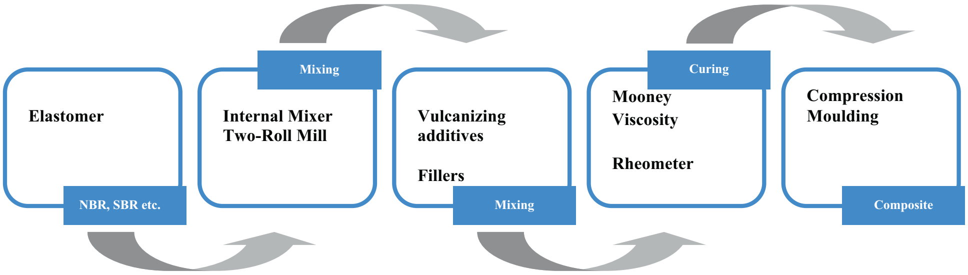

Fig. 1. A schematic flow chart illustrating the formation of a typical elastomer composite.